Nanoscience with Nanocrystals

Abstracts

Klosterneuburg, Austria

3-7th July 2023

NaNaX10

NANOSCIENCE WITH NANOCRYSTALS

Can we Reinvent Colloidal Synthesis of Semiconductor Quantum Dots Using Molten Inorganic Salts?

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Abstract: Many semiconductor nanomaterials used for displays, lighting, photodetectors, photocatalysts and other applications are synthesized by colloidal methods. The scope of chemical transformations accessible to colloidal chemists is determined by thermal and chemical stability of solvents and surfactants used. For example, very few traditional solvents can handle temperatures above 400 °C, while the temperatures used in CVD and MBE growth of GaAs and other important semiconductors are typically above 500 °C. We are developing comprehensive understanding for a novel class of colloidal systems, colloids in molten inorganic salts. Nanoparticles of different transition metals, semiconductors, oxides, and magnetic materials can form true colloids in molten inorganic salts. The colloidal stability of nanoparticles in molten salts could not be explained by traditional electrostatic and steric stabilization mechanisms. Our experimental and computational studies point to the importance of the long-range ion correlations in the molten salt near the nanocrystal interface.

In parallel with the fundamental exploration of new colloidal systems, molten salts expand the boundaries for solution synthesis of many nanomaterials that have been out of reach for colloidal chemists. We have used molten salts to synthesize colloidal GaAs, GaP, $In_xGa_{1-x}P$, $In_xGa_{1-x}As$, and $In_xGa_{1-x}Sb$ quantum dots, which resisted numerous synthetic attempts for over two decades. By further developing colloidal chemistry in molten salts, we hope to enable synthetic routes toward various functional nanomaterials previously considered unsynthesizable by colloidal methods.

Structural and Compositional Engineering of Superlattices Comprising Halide Perovskite Nanocubes

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Abstract: Colloidal lead halide perovskite nanocrystals (LHP NCs, NCs, A=Cs^+, FA^+, FA=formamidinium; X=Cl, Br, I) have become a research spotlight owing to their spectrally narrow (<100 meV) fluorescence, tunable over the entire visible spectral region of 400-800 nm, as well as facile colloidal synthesis. These NCs are attractive single-photon emitters and building blocks for creating controlled, aggregated states exhibiting collective luminescence phenomena. Attaining of such states through the spontaneous self-assembly into long-range ordered superlattices (SLs) is a particularly attractive avenue. The atomically flat, sharp cubic shape of LHP NCs is also of interest because the vast majority of prior work had invoked NCs of spherical shape. Long-range ordered SLs with the simple cubic packing of cubic perovskite NCs exhibit sharp red-shifted lines in their emission spectra and superfluorescence (a fast collective emission resulting from coherent multi-NCs excited states).

When $CsPbBr_3$ NCs are combined with spherical dielectric NCs, perovskite-type ABO_3 binary NC SLs form, wherein $CsPbBr_3$ nanocubes occupy B- and/or O-sites, while spherical dielectric Fe_3O_4 or $NaGdF_4$ NCs reside on A-sites. When truncated-cuboid PbS NCs are added to these systems, ternary ABO_3-phase form (PbS NCs occupy B-sites). Such ABO_3 SLs, as well as other newly obtained SL structures (binary NaCl, AlB_2- and ABO_6 types, columnar assemblies with disks, *etc.*), exhibit a high degree of orientational ordering of $CsPbBr_3$ nanocubes. These mesostructures also exhibit superfluorescence, characterized, at high excitation density, by emission pulses with ultrafast (22 ps) radiative decay and Burnham-Chiao ringing behaviour with a strongly accelerated build-up time. Combining $CsPbBr_3$ nanocubes with large and thick $NaGdF_4$ nanodisks results in the orthorhombic SL resembling CaC_2 structure with pairs of $CsPbBr_3$ NCs on one lattice site. We also implement two substrate-free methods of SL formation. Oil-in-oil templated assembly and self-assembly at the liquid–air interface result in the formation of binary supraparticles.

Controlling the Nucleation and Growth Kinetics of Spheroidal Lead Halide Perovskite Quantum Dots

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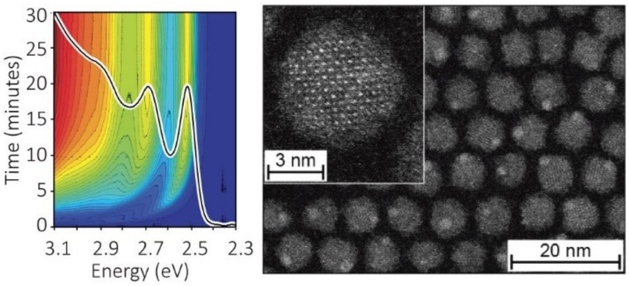
Abstract: Colloidal lead halide perovskites LHP (LHP) nanocrystals (NCs) have recently become popular light-emissive materials, of practical interest for LEDs, LCDs, lasers, as well as single photon light sources. Most studies on LHP NCs focus on relatively large cuboidal NCs exceeding 10 nm in size, pointing out the inherent challenge of producing small (sub 10 nm), stable and monodisperse LHP quantum dots (QDs). This challenge originates from the highly ionic lattice of LHPs, which makes it very challenging to control their growth on an atomic level. Consequently, the current generation of LHP QDs (especially the hybrid organic-inorganic ones) show significantly less excitonic absorption landscapes compared to conventional QDs such as CdSe. To solve this, we developed a room-temperature synthesis, in which the overall QD formation occurred on a time scale of up to 30 min, slowing down the reaction kinetics by several orders of magnitudes compared conventional LHP QD syntheses. The size of these QDs are tunable between 3 and 13 nm range and exhibited a rhombicuboctahedral (spheroidal) shape. These $CsPbBr_3$, $CsPbCl_3$, $CsPb(Cl:Br)_3$, $FAPbBr_3$ and $MAPbBr_3$ QDs exhibited up to four well-resolved excitonic transitions, even for mixed Cl:Br compositions, finally bringing them on par with the highly excitonic absorption landscapes of CdSe and PbS QDs. This growth method also allowed for the first *in-situ* study into the illusive reaction mechanism of LHP QDs using absorption spectroscopy and small angle X-ray diffraction, demonstrating the effective separation of the nucleation and growth stages due to the self-limiting formation of an $Cs[PbBr_3]$ intermediate.



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Nanocrystalline $CuCr_2Se_4$: Synthesis Mechanism, Electrochemical/Cation Doping, and Magneto-optical Properties

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Abstract: Spinels (AB_2X_4) are a unique class of materials that exhibit a range of magnetic, optical, and magnetooptical properties tunable through choice of A and B site cations.[1] While many of the oxides have been synthesized at the nanoscale, research into nanocrystalline chalcogenide spinels is lacking. Amongst these the copper chromium chalcogenides are of particular interest for their high Curie temperatures (>350K) and large magneto-optical Kerr effects.[2] Only a handful of reported syntheses for these materials exist, with conflicting magnetic properties (e.g. superparamagnetic vs. ferromagnetic), minimal mechanistic understanding, and no optical data.[3–6] Here, we delve deeper into the synthesis of this material. Copper precursor identity and oxidation state play a key role in the rate of reaction and formation of binary (Cu_2Se) and ternary ($CuCrSe_2$) intermediates. Furthermore, Cu_2Se nanocrystals can be used as “seed” precursors for preparation of $CuCr_2Se_4$ through cation exchange, allowing finer control over size, shape, and monodispersity.

The metallic nature of $CuCr_2Se_4$ results in a plasmon resonance in the NIR that shows strong magneto-optical signal. The nanocrystalline composition maintains these properties, but with the ability to prepare thin films for absorptive measurements as opposed to the reflective measurements required for single crystals. The spinel structure also shows robustness for cation doping. Inclusion of different A-site species including Co, Zn, Cd, and Mn readily occurs modulating the carrier density and thus the position of the plasmon feature. Modulation of carrier density is also tuned through spectroelectrochemical measurements of thin films.

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Copper-Chalcogenide Based (Hetero)Nanocrystals: Emergent Nanomaterials for Optoelectronic Applications

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Abstract: Colloidal nanocrystals (NCs) of compound Cu-chalcogenides are promising alternatives to Cd- and Pb-chalcogenide NCs due to their inherently lower toxicity and wide range of compositions, allowing access to a very broad spectral window, spanning from the UV to the second Near-IR biological window.[1] Moreover, they also offer characteristics that are unmatched by Cd- and Pb-chalcogenide NCs, such as large global Stokes shifts and plasmonic properties. However, the realization of their full potential has been hampered by both their underdeveloped synthesis and the poor understanding of their optoelectronic properties. In our group, we have applied a multistage preparation strategy that allows the sequential combination of different synthesis techniques in order to achieve the targeted preparation of size, shape, and composition-controlled Cu-chalcogenide based multinary NCs and hetero-NCs with dimensions in the quantum confinement regime (*e.g.*, wurtzite $CuInS_2$ and $CuGaS_2$ NCs,[2-3] chalcopyrite $CuInS_2$ NCs,[4] ultrathin $Cu_{2-x}S$, $CuInS_2$, $CuInSe_2$, and Cu-rich covellite $CuInS_2$ nanosheets,[5-7] $CuInS_2/ZnS$ graded alloy and core/shell quantum dots,[4,8] $CuInSe_2/CuInS_2$ and $CuInS_2/ZnS$ dot core/rod shell heteronanorods, Janus-type $Cu_{2-x}S/CuInS_2$ and $Cu_{2-x}S/ZnS$ heteronanorods).[9-12] The availability of these nanomaterials makes it possible to tailor the properties of nanoscale excitons in Cu-chalcogenide based (hetero)NCs, paving the way towards their use in a number of applications (*e.g.*, luminescent solar concentrators).[13] Moreover, our work has provided novel insights on the origins of the optoelectronic properties of ternary Cu-chalcogenides.[14-18] In this talk, I will address recent developments concerning both the synthesis strategies and the understanding of the optoelectronic properties of these emergent nanomaterials.

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Unlocking the Potential of Metal Borides Nanocrystals: A Journey Through Synthesis and Surface Modification

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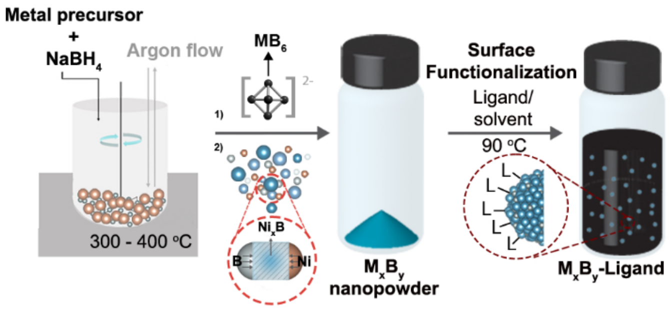
Abstract: Metal borides, a versatile class of materials used in various industrial applications such as superconductors, magnetic materials, and hot cathodes, remain under-explored at the nanoscale due to the challenges in synthesizing single-phase nanocrystals (NCs). Their small size, high surface area-to-volume ratio, and well-defined surfaces exhibit unique physical and chemical properties, making them appealing for various applications, including catalysis, energy storage, electronics, and biomedical imaging. While metal-rich borides, like Ni_3B, are mainly used in electrocatalysis, boron-rich metal borides (metal hexaborides, MB_6) are highly valued for their broad range of physical properties that vary based on the metal ion present in their structure. For example, CeB_6 and LaB_6 have low work functions, while CaB_6 and SrB_6 exhibit high potential for high-temperature thermoelectric applications. Additionally, they are known for their high hardness, making them suitable for ultra-hard protective coatings.

In this presentation, we will showcase a novel method for synthesizing boron-rich M_1B_6 (M_1=Sr, Ca, Ba, La, Ce) and metal-rich $M_{2x}B$ (M_2=Ni, Co, Fe, x=2,3)[1] NCs through solid-state synthesis at low temperatures (380-440°C), as well as a strategy for stabilizing these crystals for use in solution-based mass production processes. Our discussion will highlight the reaction mechanisms in both classes of nanomaterials, demonstrating the versatility of boron chemistry. By using specific surface modifications, including inorganic and organic ligands, we have achieved stable suspensions of these nanocrystals in both polar and non-polar solvents, with the potential for implementation in cutting-edge technologies.



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The Formation of $NaYF_4:Er^{3+},Yb^{3+}$ Nanocrystals Studied by In-Situ X-Ray Scattering: Phase Transition And Size Focusing

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Abstract: β-$NaYF_4$ nanocrystals are a popular class of optical materials.[1] They can be doped with optically active lanthanide ions and shaped into core–multi-shell geometries with controlled dopant distributions. $NaYF_4$ NCs of the cubic α-phase were first reported in 2004.[2] A synthesis procedure for NCs of the hexagonal β-phase followed in 2006.[3] The latter procedure did not use molecular precursors but small α- $NaYF_4$ precursor particles for the nucleation and growth of β-$NaYF_4$ NCs. Despite considerable efforts, the synthesis mechanism is not yet clear.

In this presentation, I will show our efforts to follow the synthesis of β- $NaYF_4$ nanocrystals from α- $NaYF_4$ precursor particles using in-situ small-angle and wide-angle X-ray scattering and ex-situ electron microscopy (Figure 1A). We observe an evolution from a monomodal particle size distribution to bimodal, and eventually back to monomodal. The final size distribution is narrower in absolute numbers than the initial distribution. These peculiar growth dynamics happen in large part before the α-to-β phase transformation (Figure 1B). We propose that the splitting of the size distribution is caused by variations in the reactivity of α-$NaYF_4$ precursor particles, potentially due to inter-particle differences in stoichiometry.[5] Rate equation modeling confirms that a continuous distribution of reactivities can result in the observed particle growth dynamics.

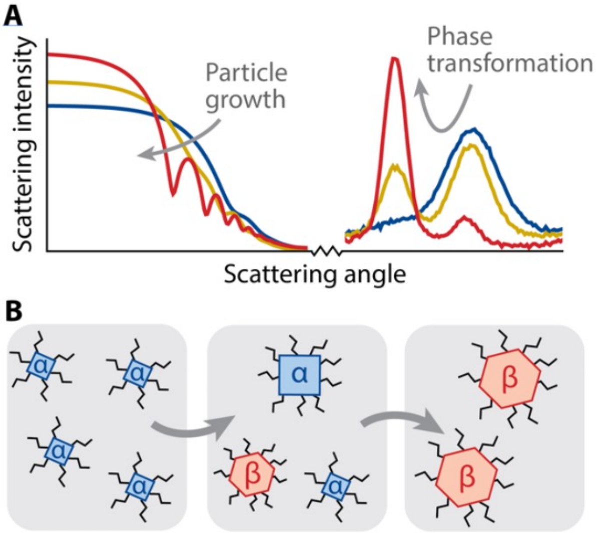

Figure 1. A In-situ X-ray scattering as a function of reaction time reveals particle growth small angles) and phase transformation (large angles). B. α-phase particles develop a bimodal size distribution before they transform into β-phase.

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Cation Exchange With Metallic Radioisotopes : A Novel Method for Radiolabeling With High Specific Activity for Therapeutic Applications

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Abstract: The cation exchange (CE) reaction is used to substitute the existing ions in a nanocrystalline structure with a different metal ion. This technique has proven to be highly efficient, especially when converting metal chalcogenide nanocrystals. In this work, we exploit CE reactions to load chalcopyrite NCs ($CuFeS_2$) with Cu-64 radioisotope. This optimized CE protocol requires one simple step, to mix the water-soluble NCs with a ^{64}Cu solution, in presence of vitamin C, thereby obtaining $^{64}Cu:CuFeS_2$ in very high yields that do not require further purification. This unique approach of CE reaction to load radioisotope into nanocrystals leaves us with an unprecedentedly high specific activity in the range of 2-100 TBq/g. In addition, the $CuFeS_2$ are promising heat mediators for photo-thermal therapy, and the radiolabeled $^{64}Cu:CuFeS_2$ NCs still retain these PTT properties after the partial-CE reaction. The synergic toxicity of photo-ablation and ^{64}Cu mediated radiotherapy ionization is here used to eliminate the glioblastoma and epidermoid carcinoma tumor cells. Further, the dual therapy is evaluated on xenograft mice models bearing epidermoid carcinoma tumor, resulting in elimination of solid tumor in mice. As an advancement of the CE approach to radiolabel NC, we applied the same protocol to insert pure β^- emitter, ^{90}Y, in $NaLnF_4$ (Ln = Gd, Lu) as well. The radioloading was successful and the resultant NCs were able to eliminate the cancer cells in even lower radiation dosage, owing to the β^- emission from ^{90}Y.

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Zirconium And Hafnium Oxide Nanocrystals And Oxo Clusters

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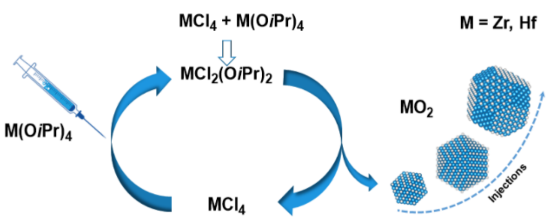
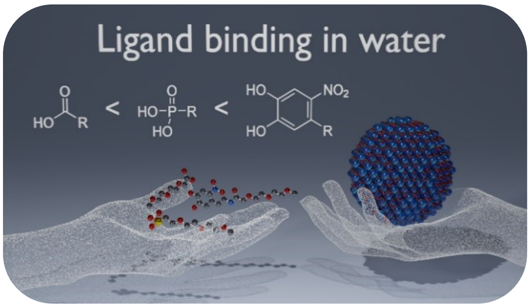
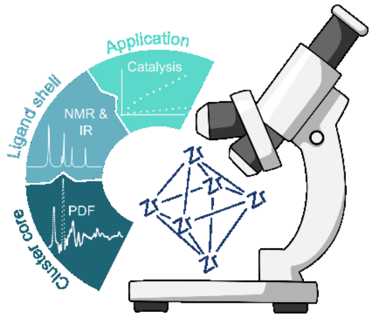
Abstract: Colloidal nanocrystals are usually hybrid inorganic-organic objects. They have an inorganic, crystalline core which is capped by a layer of organic surfactants. Metal oxide nanocrystals find application in solar cells, batteries, bio-imaging, etc. On the other hand, oxo clusters are building blocks in metal organic frameworks (MOFs) with exciting catalytic properties.

First, we introduce surfactant-assisted synthesis of colloidal nanocrystals and the (undesired) chemistry that can occur with solvents and ligands. Second, we elaborate on the precursor chemistry during the synthesis of zirconium and hafnium oxide nanocrystals. After establishing an E1 elimination mechanism, we focus on the crystallization mechanism and find that an amorphous phase precedes the crystalline nanoparticles. Third, we develop a comprehensive picture of the surface chemistry of these metal oxide nanocrystals. We establish ligand exchange rules in both nonaqueous and aqueous media. As such, we find the optimal binding moiety for physiological conditions; nitrodopamine derivatives. Tailoring the surface chemistry allows to use hafnium oxide nanocrystals as contrast agent in Computed Tomography (CT) imaging. We will discuss both *in vivo* and *ex vivo* applications of such contrast agents. Finally, we take the oxo clusters out of the MOF and consider it an atomically precise nanocrystal. Using the same ligands as for nanocrystals, the clusters are endowed with the same solubility properties and become useful catalysts. The cluster-catalyzed reaction has a five times higher rate than the nanocrystal-catalyzed reaction. To analyze the soluble clusters, we use X-ray total scattering and Pair Distribution Function analysis.

We thus present here a comprehensive overview of oxide nanochemistry, focusing on group 4 metals.







High-Efficient Colloidal Inp Core-Shell Quantum Dots: Synthesis, Surface Chemistry, And Their Applications

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Abstract: Semiconductor colloidal quantum dots (CQDs) have gained significant attention for their tunable electronic and optical properties, cost-effective production, high efficiency, and stability. Indium phosphide (InP) quantum dots, in particular, have been widely explored for next-generation display technologies due to their low toxicity and tunable emission range from visible to near-infrared. However, achieving high quantum yield and narrow size distributions, crucial for realizing high color pure emissions, has been a challenge in the current synthesis methods for InP-based QDs.

To address this, our group has focused on precisely controlling the reaction kinetics of InP QDs through a two-step growth process and engineering the shell coating to reduce interfacial defects, resulting in InP QDs with the narrowest size distribution and high photoluminescence yield quantum yield (PLQY). In this talk, I will present the significant synthetic progress we have made in InP core-shell QDs based on surface chemistry and interfacial engineering. By optimizing synthesis conditions, we have successfully achieved a bright green and red emission with very high quantum yield and narrow emission linewidth of more than 90% and less than 33 nm, respectively, in the as-synthesized InP QDs core-multishell.

Finally, I will discuss the current challenges and opportunities in the development of InP QLED applications, including achieving high-performance devices.

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Towards Applications of Carbene stabilized Gold Nanoparticles

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Abstract: In the quest to develop highly stable nanoparticles, N-heterocyclic carbenes (NHC) have emerged as an alternative to thiol-based ligands for stabilizing metal nanoparticles (NPs), as the metal-NHC bond is usually much stronger than the corresponding metal-thiol bond. This should result in more stable NPs which are less susceptible to ligand exchange reactions. Over the last decade an increasing number of NHC-stabilized NPs have been reported and significant effort was made in utilizing these compounds, such as for bioimaging, sensing and also heterogeneous catalysis.[1]

We will give an account on our efforts to develop carbene-stabilized gold nanoparticles. Firstly, we will discuss NHC-stabilized AuNPs where the NHC is derived from the natural chiral pool.[2, 3] For this, L and D- histidine was converted into its imidazolium salt using methyl iodine. Subsequently, the imidazolium salt is converted to its corresponding organometallic gold chloride complex, which can be reduced to histidine-2-ylidene stabilized AuNPs. Due to the chiral nature of histidine, dichroic effects can be detected in circular dichroism spectroscopy. Further water-soluble and pH-responsive histidine-2-ylidene stabilized AuNPs can be obtained through a free unprotected C-terminus of the employed histidine.[4] Subsequently we will also report on the synthesis of hyper-crosslinked polymers containing benzimidazolium as NHC precursors to stabilize AuNPs and their application if flow catalysis.[5] Finally this talk will also touch on the first examples of protic acyclic diamino carbene stabilized AuNPs (ADCAuNPs).[6]

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$CuInS_2$ Nanocrystals for Solar-Driven Oxidation of Redox Mediators

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Abstract: Copper indium sulfide quantum dots (CIS-QDs) are ternary semiconducting nanocrystals which have been studied in the last twenty years as an alternative to cadmium or lead-based QDs. One of their greatest advantages is their tunability: the synthetic strategy, the Cu-to-In ratio, the dimension of the nanocrystal are just some of the methods by which CIS-QDs' properties can be adjusted to meet the required qualities.[1] Therefore, CIS-QDs may be employed in many different areas, ranging from photocatalysis to bioimaging.[2,3]

Our research aims to employ CIS-QDs as anodic material in photoelectrochemical cells for the oxidation of redox mediators. We developed a sustainable approach for the functionalization of FTO-TiO_2 photoanodes with CIS-QDs which allowed high yield, mild conditions and low waste of reagents. The inclusion of CIS-QDs on TiO_2-based photoanodes increases the absorption of the photoanode in the visible spectrum, allowing charge separation under solar illumination.

CIS-QDs were attached to the FTO-TiO_2 photoanodes and a shell of CdS was deposited by SILAR to improve the electrode performances. The functionalized electrodes (TiO_2@CIS@CdS) were included in a photoelectrochemical cell and tested in ascorbate, sodium sulfide and TEMPOL aqueous solution. Both sodium sulfide and ascorbate are oxidized by the electrode, with photocurrent densities as high as 3 mA/cm^2. TEMPOL could not be oxidized, either for thermodynamic reasons or for an unfavorable interaction between TEMPOL and the photoanode. In future studies, we would like to test TiO_2@CIS@CdS photoanodes with different molecules, to get a deeper understanding of the oxidizing power and interfacial properties of the deposited CIS-QDs.

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Colloidal Nanocrystals of Heavy Pnictogen Chalcohalides

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Abstract: Chalcohalide semiconductors are attracting a fast-growing interest for energy conversion purposes.[1] These materials may indeed combine promising optoelectronic properties with a high chemical stability, thus representing a potentially valid alternative to metal chalcogenides and halides. Nevertheless, synthetic protocols to prepare mixed anion semiconductor nanomaterials are lacking.

It is here presented a colloidal method to synthetize phase pure nanocrystals (NCs) of heavy pnictogen chalcohalides. Such a method relies on the hot-co-injection of both the chalcogen (E = S, Se) and the halogen (X = Cl, Br, I) precursors to a solution of heavy pnictogen metal (M = Sb, Bi) complexes.

With this method, we prepared colloidal NCs of the orthorhombic MEX phase.[2] The colloidal MEX NCs display composition-dependent band gap spanning the visible spectral range with high absorption coefficients and are chemically stable at ambient conditions. The solution processing of these NCs yield robust solid films generating stable photoelectrochemical current densities.

With this method, we prepared colloidal NCs of the hexagonal $Bi_{13}S_{18}X_2$ phase.[3] These colloidal NCs show a mixed valence character related to the presence of subvalent Bi atoms, which results in an anomalously narrow band gap extending the NC optical absorption to the near infrared spectral range.

With such a method, we also prepared quaternary chalcohalide semiconductor NCs.[4] As distinct from ternary chalcohalide semiconductor NCs that commonly show an indirect band gap, the quaternary $AgBiSCl_2$ NCs feature a direct band gap, further supporting the potential relevance of the chalcohalide semiconductor NCs to light harvesting purposes.

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Lead-Halide Epitaxial Heterostructures: From Serendipity Tto Rational Design

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Abstract: Colloidal epitaxial heterostructures are nanoparticles made of two crystalline materials connected at an interface. These architectures profitably combine the properties of their components, and can express unique ones stemming from their interactions. Historically, heterostructures have produced major breakthroughs in the field of colloidal nanomaterials, with core/shell quantum dots being the most renown examples. Indeed, heterostructures are often grown from isostructural materials like CdSe/CdS, where the only requirements are similar lattice parameters. However, the increasing number of heterostructures reported between non-isostructural materials points to the limits of this design strategy. In this talk, we will take the serendipitous discovery of heterostructures between lead halide perovskites ($CsPbX_3$) and lead sulfohalides ($Pb_4S_3X_2$) as a case study.[1,2] We will first identify empirical criteria behind the formation of these heterostructures by comparing them with other interfaces formed by lead halides.[3] Then, we will take advantage of such criteria to master the synthesis of two competing nanomaterials ($Pb_4S_3Cl_2$ vs $Pb_3S_2Cl_2$) by exploiting heterostructures as phase-selective reaction intermediates.[4] This approach is inspired to the retrosynthetic strategies typical of organic chemistry, and provides advanced control over the product of colloidal syntheses. Finally, we will introduce possible strategies to predict the formation of colloidal heterostructures at large, with the goal of making their design, synthesis, and ultimately their widely appealing properties more accessible.

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Anisotropic Lead Halide Perovskite Nanocrystals for Light-Emitting Applications

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Abstract: In recent years, lead halide perovskite nanocrystals (NCs) have attracted much interest due to their outstanding optoelectronic properties, including facile band gap tunability, high exciton binding energies, and ultrafast radiative recombination. While green and near-infrared perovskite emitters are well established, blue-emitting $CsPbCl_3$ NCs suffer from insufficient stability and low photoluminescence quantum yields.

Herein, we present anisotropic $CsPbBr_3$ NCs as a promising alternative for light-emitting applications.[1,2] Quasi-1D and quasi-2D NCs are prepared at room temperature following a wet synthesis approach. As a result of size-dependent quantum confinement effects, anisotropic $CsPbBr_3$ NCs with 2-8 monolayer (ML) thickness exhibit a tunable photoluminescence (PL) between 430 to 510 nm. We implement a data-efficient machine-learning algorithm to optimize synthesis parameters and enhance the quality of resulting perovskite NCs. Not only are their PL profiles significantly narrower, but for the first time, we synthesized monodisperse 7ML and 8ML perovskite NCs.[3] Furthermore, we successfully studied the synthesis with 10 ms time resolution by combining in situ small-angle X-ray scattering (SAXS) and PL spectroscopy. We find that, contrary to commonly assumed mechanisms, the formation of anisotropic perovskite NCs proceeds via growth of intermediate perovskite clusters in well-ordered superlattices. Interestingly, both 2D nanoplatelets and 1D nanorods were obtained from the same synthesis approach by varying the antisolvent. Lastly, $CsPbBr_3$ nanorods exhibit isotropic growth after synthesis when prepared under Cs-rich reaction conditions. This process results in a gradual PL redshift but can be easily terminated by adding an enhancement solution, thus allowing for nm-precise tuning of blue-green emission.

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Chiral Perovskite Nanoplatelets Exhibiting Circularly Polarized Luminescence Through Ligand Optimization

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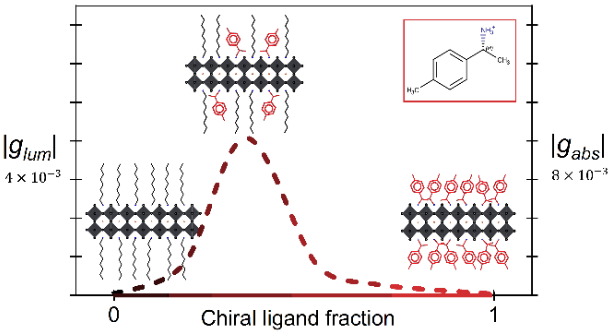
Abstract: Chiral halide perovskite nanocrystals have many applications in next-generation optoelectronic devices due to their interaction with circularly polarized light. Through the careful selection of chiral organic surface ligands, control over the circular dichroism (CD) and circularly polarized luminescence (CPL) of these materials can be achieved. However, while recent developments of CD-active perovskites have seen significant advances, effective CPL remains a challenge. Here, we synthesize colloidal perovskite nanoplatelets exhibiting room temperature CPL with dissymmetry factors up to $g_{lum}=4.3\times10^{-3}$ and $g_{abs}=8.4\times10^{-3}$. Methylammonium lead bromide nanoplatelets are synthesized with a mixture of chiral dimethyl benzyl ammonium ligands and achiral octylammonium ligands, the precise ratio of which is shown to be critical to achieving high *g*-factors. We investigate the competitive binding of these surface ligands using ^{1}H NMR, and use an equilibrium model to demonstrate the ligand affinity. The magnitude of CPL and CD is quantitatively shown to exhibit a linear correlation, such that $g_{lum}=0.4\times g_{abs}$. Lastly, by screening several amines with close structures, we show that subtle differences in ligand structure have significant impact on the resulting CD signal of the nanoplatelets. Our findings provide new insights for the effective design of perovskites exhibiting CPL and can facilitate the development of high-performance devices based on circularly polarized luminescence.



Magnitude of polarized absorption and emission depends on fraction of chiral ligands on nanoplatelet surface.

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Characterization of $CuInS_2$ Quantum Dots by SAXS/WAXS Methods

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Abstract: In the quest for quantum dots with green formulation, Cu-based materials turn out to be potential candidates.[1-2]

Our group has combined reciprocal space X-ray total scattering techniques in the wide- (WAXS) and small-angle regions (SAXS) to achieve a characterization of size, morphology, and defects in $CuInS_2$ as a promising alternative to more well-known quantum dots (QDs), that possess favorable photophysical properties combined with low toxicity.

We have optimized a colloidal synthesis approach to obtain QDs with selected size and morphology. This can be achieved by tuning the reaction conditions, such as – reaction temperature, ratio of precursor's concentration.[4] $CuInS_2$ can be synthesized following high-temperature colloidal pathways using octadecene as solvent, oleic acid (OA) as capping agent, and dodecane thiol (DDT) as both sulfur source and capping agent. By changing the ratio of two precursors, the photophysical properties of the samples can be tuned.

The purification protocol was specially designed to enable the size selection of the QDs by exploiting their dispersibility in different solvents by fractional separation and centrifugation. The process was closely monitored by a combination of laboratory X-ray diffraction and absorption/emission spectroscopies.

Finally, a thorough structural and microstructural characterization of the QDs was carried out by SAXS/WAXS reciprocal space total scattering methods[4-5], based on the Debye Scattering Equation (DSE).[6]

The results of this study may serve as an important reference point to further the understanding of the correlation between the structural and functional properties of this important class of materials.

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Synthesis of III-V Quantum Dots Using Indium Monohalides and Aminopnictogen Precursors

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Abstract: III-V semiconductor QDs such as InP and InAs hold great promises for use in displays, LEDs, biological imaging, photocatalysis, and photodetectors. They are widely considered a safer alternative to toxic cadmium- and lead-based QDs.[1] Significant progress has been made during the past decade in their synthesis using aminopnictogen $E(NR^2)_3$ compounds (with E = P, As and R= Me, Et) as non-pyrophoric group V precursors. However, it is still highly challenging to achieve narrow emission line widths and a broad QD size range with these approaches.

We present a novel synthetic scheme relying on the co-reduction of aminophosphines via two different pathways by replacing indium trihalides, routinely used as the In precursors, with indium monohalides. This method gives access to tetrahedral InP QDs whose sizes can be tuned from around 3 to 10 nm. Narrow emission line widths down to 110 meV at 730 nm and photoluminescence quantum yields up to 80% are obtained.[2] Finally, the extension of this approach to InAs QDs is also discussed.

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Towards Understanding the Chemistry of Tin Halide Perovskite Nanocrystals

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Abstract: Tin halide perovskites are deemed to be as a more sustainable alternative to the lead-halide perovskites. However, a clear understanding and control of their mercurial chemistry remains slender as compared to the Pb counterparts in bulk as well as in nano owing to their inability to provide a stable Sn(II) oxidation state to maintain pristine crystal structure phase in ambient conditions. In this work, I will discuss the physical and chemical parameters which can help us to achieve a stable, tunable and monodisperse $CsSnX_3$ perovskite nanocrystals with defined optical features. Pertaining to the formation energies of nanostructures, the interplay of the 2D Ruddlesden-Popper ($L_2Cs_{n-1}Sn_nX_{3n+1}$) phases with 3D $CsSnX_3$ nanocrystals is apparent with respect to ligand combinations (ammonium, carboxylate, phosphinate), precursor ratios and temperature when SnX_2 salt is used as a precursor. X-ray diffraction and scattering studies conjoined with optical spectroscopy and electron microscopy helps us in acquiring the useful insights into directing the chemistry of Sn-halide perovskites at nanoscale. This research work showcases the insistent necessity for the development of mechanistic understanding to design efficient synthetic routes in order to achieve high-quality tin-halide perovskite nanocrystals.

Colloidal Supercrystal growth studied in-situ by SAXS

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Abstract: Chemical synthesised colloidal nanocrystals (NCs) offer the opportunity for realising novel materials with tailored functionalities.[1] Especially an inner core/shell structure of the semiconducting NCs leads to an increased photoluminescence (PL) output,[1,2] but also, the NCs' shape determines their optical[2,3] or magnetic performance. The NC's shape can also significantly influence the super-crystal structure of colloidal supercrystals SCs,[1] where NCs act as building blocks to form 3D nanocrystal solids with designed properties.[1] To what extent these properties are enhanced depends on the specific ordering of the NCs within the superstructure.[4]

Recently, we used faceted semiconducting PbTe/PbS NCs as building blocks, which are synthesised by the Ibáñez-Group at ISTA and can be used for thermoelectric applications.[1,5] The supercrystals' structure was investigated during growth by time resolved SAXS measurements at lab and synchrotron (ELETTRA) sources. We tried to reveal the impact of the NCs&apos shape on the superstructure and thus to understand not only the positional ordering of the NCs, but also their orientation ordering within the supercrystals. We determined the atomic crystal structure (with XRD/WAXS) of the NCs within the supercrystals and demonstrated the connection between crystal structure and superstructure via the NCs' shape. Finally, we try to relate the *micrometer sized shape* of the SCs investigated by optical microscopy to their internal supercrystal structure.

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Anion-Assisted Yb^{3+} Doping of 2D Organic-Inorganic Perovskite Nanoplatelets Resulting in Near-Infrared Emission

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Abstract: Currently, lead halide perovskite nanocrystals are in a focus in terms of design of materials with attractive optical properties. Photoluminescence of perovskite nanocrystals can be tuned by several means: changing their dimension, anion exchange, and different doping strategies where lead ions are replaced with various metal ions (so-called B-site doping). Recently, it has been shown that the B-site doping can be more effective with the assistance of simultaneous anion exchange, since it leads to the effective surface passivation and greater implementation of metal ions.[1–3] However, the approaches of anion driven cation exchange for nanoplatelets and nanowires are still under-developed because of the usage of polar solutions as precursors of metal halides, what leads to high possibility of rearrangement of the brittle structure of 2D nanocrystals.[4] Moreover, Yb^{3+} doping usually requires high temperature and occurs during nanocrystal formation.[5] Herein, we report a non-destructive doping strategy of organic-inorganic $FAPbBr_3$ nanoplatelets (FA: formamidinium cation) with Yb^{3+} cations, which allows us to shift their photoluminescence into the near-infrared (NIR) spectral range. Perovskite nanoplatelets with a thickness of 2 monolayers were synthesized by the ligand-assisted reprecipitation (LARP) method and treated with $YbCl_3$ to achieve the NIR emission, whose emerging band was studied by means of steady-state and time-resolved spectroscopy. The preservation of the 2D shape of perovskite nanoplatelets during anion assisted Yb^{3+} doping was confirmed by TEM. The obtained results open new ways towards fabrication of perovskite nanocrystals with controlled dimensions and attractive optical properties.

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Exciton-Phonon Coupling and Charge-Carrier Localization in ZnCdSe/CdS Dot-in-Rod Nanostructures

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Abstract: The properties of heteronanostructures are determined by their band-alignment. A type-I band alignment is beneficial high fluorescence quantum yields,[1-3] while a type-II band alignment is ideal for catalytic applications.[4-6] The corresponding excitonic properties can be revealed by performingtime- and energy-resolved photoluminescence (PL) spectroscopy. Investigating individual nanoparticles circumvents inhomogenous broadening effects of the characterized properties. Carrying out the measurements at low temperatures around 10 K reduces the linewidths of the emission spectra and allows to resolve spectral diffusion, as well as additional emission lines originating for example from exciton-phonon coupling. Here, we report on a study with a set of heteronanostructures consisting of $Zn_{1-x}Cd_xSe$ cores embedded in rod-shaped CdS shells. With increasing x, these samples change their conduction and valence band alignments across the heterointerface from type-I to type-II, which in turn changes the localization of photoexcited excitions. We analyze the exciton-phonon coupling strength by determining the intensity of the LO-phonon-replica of core and shell in low-temperature single-nanoparticle PL spectra. By comparing our spectroscopical results with quantum mechanical calculations within the effective mass approximation, which are performed by using COMSOL Multiphysics, we find that the exciton-phonon coupling is a good measure for the localization of excitons within the heteronanostructures.

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Two Biexciton Types Coexisting in Coupled Quantum Dot Molecules

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Abstract: Extensive research of colloidal quantum dots (CQDs) gave rise to the development of nano-chemistry as a method to fuse two CQDs to form coupled QD molecules (CQDMs).[1] While QDs are often described as "artificial atoms" due to their discrete electronic states, CQDMs are analogous to artificial molecules, manifesting hybridization of the electron wave-function, as evidenced by a red shifted spectrum. The joining of two light emitting centers and the increase in the volume stabilize charged- and multi-excitons, relative to such states in the parent QDs.[2] The unique structure of the CQDMs can accommodate new types of excitonic states and different relaxation pathways. An interesting example is biexcitons (BXs), as they have two possible configurations in the CQDMs: localized BX, with two excitons in one QD, and segregated BX, with one exciton in each QD.

In this study, we aim to characterize the two types of BX in CQDMs and compare their properties to BXs in the parent monomer QDs. Recently, Heralded spectroscopy, a direct approach to probe the BX events was introduced, and resolved the ambiguity of previous indirect methods.[3] Heralded spectroscopy is based on an array of avalanche photodiodes at the output of a grating spectrometer, which enables the post-selection of BX events in a time-resolved-spectrally-resolved manner. Herein, we use Heralded spectroscopy to explore the BX events in CQDMs. We find evidence to the coexistence of the two BX configurations in a model system of CdSe/CdS core/shell CQDMs, according to their different BX binding energies and BX lifetimes. We support our findings with theoretical analysis.

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Quantum Wells for Recording Cell Membrane Potential

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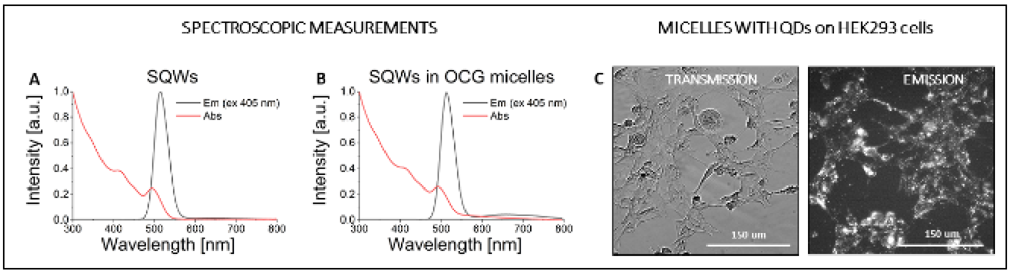
Abstract: Studying the brain and understanding its complexity has been one of the greatest scientific challenges of our time. One of the limitations to achieve a better understanding of neuronal activity is the lack of tools for accurate mapping of neuronal circuits. Inorganic voltage nanosensors, in particular quantum dots (QDs), show great potential for non-invasive recording of electrical activity with high spatial resolution and fast temporal response in neuronal systems.[1] The transmembrane electric fields, which are characteristic of neuronal spiking, can modulate electronic structure of QDs and lead to changes in the intensity and position of emission wavelength (Quantum Confinement Stark Effect),[2] providing a means to report voltage dynamics with millisecond precision. Since electric fields outside the lipid bilayer of the cellular membrane decay exponentially due to Debye screening, a precise transmembrane targeting of QDs is mandatory that remains a long-lasting challenge holding back the successful use of this material in neuroscience.[3]

In this presentation, we share our research on the use of spherical quantum wells (SQWs) composed of CdS/CdSe/CdS for measuring changes in membrane potential of self-spiking HEK. A focus is put on phase transfer of nanocrystals from non-aqueous to aqueous medium through their encapsulation within octyl glucoside micelles to increase their integration into the lipid bilayer without compromising optical properties.



Spectra of absorption and emission of (A) CdS/CdSe/CdS SQWs in organic solvent and (B) SQWs encapsulated in OCG micelles, dispersed in water; (C) Transmission and emission image from optical microscope of HEK293 cells with SQWs on the surface.

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Exploring The Photoluminescence of Gold Nanoclusters And Ag_2S Nanoparticles to Boost Their SWIR Emission

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Abstract: Current challenges and objectives for non-invasive optical bioimaging are deep tissue penetration, high detection sensitivity, high spatial and temporal resolution, and fast data acquisition. A promising spectral window to tackle these challenges is the short-wave infrared (SWIR) ranging from 900 nm to 1700 nm where scattering, absorption, and autofluorescence of biological components are strongly reduced compared to the visible/NIR. At present, the best performing SWIR contrast agents are based on nanomaterials containing toxic heavy-metal ions like cadmium or lead, which raises great concerns for biological applications. Promising heavy-metal free nanoscale candidates are gold nanoclusters (AuNCs) and Ag_2S nanoparticles (NPs). The photoluminescence (PL) of both types of nanomaterials is very sensitive to their size, composition of their surface ligand shell, and element composition,[1,2] which provides an elegant handle to fine-tune their absorption and emission features and boost thereby the size of the signals recorded in bioimaging studies.

Aiming for the development of SWIR contrast agents with optimum performance, we dived deeper into the photophysical processes occurring in these nanomaterials, thereby exploring in depth how the environment, surface ligand composition, and the incorporation of transition metals influence the optical properties of AuNCs and Ag_2S NPs. We observed a strong enhancement of the SWIR emission of AuNCs upon exposure to different local environments (in solution, polymer, and in the solid state). Addition of metal ions such as Zn^{2+} to Ag_2S based NPs led to a strong PL enhancement, yielding PL quantum yields of about 10% and thus making them highly suitable for non-invasive deep imaging of vascular networks and 3D fluid flow mapping.

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Nanoengineering of low-dimensional porous silica with multi-hydrophilic block copolymer

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Abstract: Porous silica nanoparticles have become highly relevant materials in the fields of nanomedicine for their potential in targeted drug delivery strategies. Their synthesis through micelle soft-templating enables precise control over pore sizes, accessibility and tailored nanotextures. Recent progress in the field has led to the formation of new low-dimensional structures from single micelle systems.[1,2] In this context, polyion complex micelles (PICs), which are obtained through the complexation of a multi-hydrophilic block copolymer with a micellization partner, are emerging as a novel structure directing agent in alternative to traditional surfactant micelles.[3] They offer a versatile platform to modulate the structure of porous materials by adjusting each block individually.

Through the combination of silica sol-gel chemistry and PICs, we introduce a new route for the synthesis of hybrid mesoporous silica nanostructures with controlled size and shape. While most previous studies have focused on double-hydrophilic block copolymers, we used for the first time a triple-hydrophilic block copolymer (Fig. 1a), which remarkably led to the formation of 0D mesoporous nanoparticles around individual micelles and hence without 3D periodicity (Fig. 1b). The cage-type structure of these nanoparticles was resolved by single particle 3D reconstruction from TEM images (inset Fig. 1b). Varying the synthesis condition further led to the formation of first-of-its-kind 1D mesoporous nanostructures (Fig. 1c). To shed light on the formation mechanism of these low-dimensional structures, we performed in-situ SAXS measurements, revealing a change in form factor with micelle concentration and during their concerted self-assembly with silica species (Fig. 1d,e).

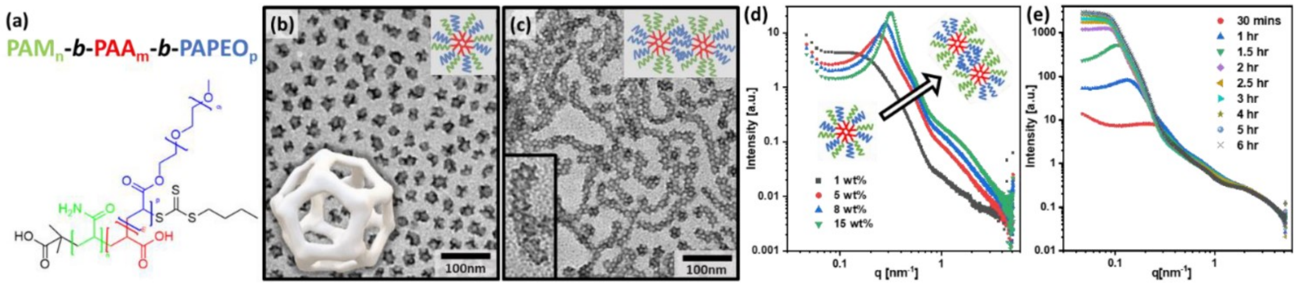

Figure 1. (a) structure of the triple-hydrophilic block copolymer. TEM images of (b) 0D nanoparticles (bottom left: 3D reconstruction) and (c) 1D nanostructures; (d) SAXS profiles of varying PIC micelles concentration; (e) in-situ time resolved SAXS measurement of 1D silica nanostructures synthesis.

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Scalable Synthesis of Hard Ferromagnetic ε-Fe_2O_3 Nanoparticles For 6G Applications

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Abstract: Ferrites showing natural ferromagnetic resonances (NFMR) in millimeter wave frequencies, particularly in 95-220 GHz are interesting because of their potential applications in self-biased non-reciprocal devices for the next generations wireless communication (6G and beyond).[1,2] ε-Fe_2O_3 is an orthorhombic iron oxide phase with a sizeable magnetization (M_S ~ 100 emu/cm^3) and a strong uniaxial magnetic anisotropy[3] reflected in an enormous coercivity (H_C ~ 20 kOe) at room temperature[4] and NFMR at around 180 GHz.[5] The resonance frequency can be controlled by substitution of Fe^{3+} with other trivalent metals which is interesting for the above mentioned application.[5] To be successfully used in self-biased non-reciprocal devices such as circulators, ε-Fe_2O_3 nanoparticles have to retain their remanent magnetization state. We have studied the relaxation of ε-Fe_2O_3 nanoparticles as a function of their size, finding that relaxation effects are largely supressed for particles above 25 nm. The current state of art allows preparing larger particle sizes but using techniques that are not compatible with a large scale production maintaining a sustainable approach.[6] In this contribution, we will discuss our newly developed method to obtain in one batch large amounts of ε-Fe_2O_3 particles which are not affected by relaxation processes, overcoming an important limitation for its application in 6G devices.

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Dual Cationic Ligand Passivated Stable Double Perovskite Nanocrystals For Optoelectronic And Photocatalysis Application

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Abstract: The doping and compositional engineering of Cs_2AInCl_6 (A = Ag, Na) double perovskite nanocrystals (DP NCs) are under spotlight due to their enhanced self-trapped excitons (STEs) emission properties and dopant-induced extended light harvesting abilities for a wide range of applications including optoelectronic devices and photocatalysis.[1,2] However, desorption of surface capping ligands during isolation and purification results in the loss of colloidal, photophysical and structural stabilities and thus limits their application in optoelectronic devices. Moreover, easy reduction of a silver ions by oleylamine leads to low photoluminescence quantum yield (PLQY) and poor stability of silver based DP NCs.[3]

In this talk, I will present the colloidal synthesis and purification of highly emissive and stable Bi and Sb-doped Cs_2AInCl_6 (A = Ag, Na) DP NCs by using a combination of strongly coordinating silver-trioctylphosphine (Ag-TOP) complex along with additional TOP ligand. The Ag-TOP complex efficiently prevent the reduction of silver ions into metallic silver.[4] While TOP facilitate the nucleophilic reaction with chloride source such as benzoyl chloride during nucleation and growth stage and forms benzoyl trioctylphosphonium chloride intermediate that serve as both halide source and surface capping ligand.[5] The antisolvent washed DP NCs shows high colloidal, structural and photophysical stability due to the tight binding of dual cationic ligand of benzoyl trioctylphosphonium and oleylammonium cations together with oleate anion to the surface of DP NCs. Moreover, I will explore our recent results on Fe^{3+} doped $Cs_2Ag_xNa_{1-x}InCl_6$ DP NCs, including synthesis, surface chemistry, optical properties and their application in photocatalytic CO_2 reduction.

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Local light-controlled precipitation and dissolution of $CaCO_3$

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Abstract: Light-activated processes enable high spatial and temporal control over the production and modification of materials. For this reason, stereolithography technology frequently relies on photochemical processes, usually involving organic resins,[1] in some cases modified with inorganic fillers.[2] In our work, we demonstrate, for the first time, that light activation can be used to control the precipitation and the dissolution directly of inorganic materials. This is possible by using a photoactive molecule that, when irradiated, triggers an event that induces the material formation/modification. We first applied this principle to the precipitation and dissolution of $CaCO_3$. $CaCO_3$ crystallization was obtained by using Ketoprofen, which releases CO_2 under irradiation,[3] and $CaCO_3$ dissolution by using Diphenyliodonium ion, which induces a decrease of pH when irradiated. These photo-induced processes allow to obtain $CaCO_3$ precipitation and dissolution just in the illuminated area of the precursor's solution, with high precision , making this technique suitable for application in photolithography. The photo-precipitation method was also investigated for other inorganic materials, such as calcium phosphate, for dentistry application. Our "photo-precipitation/photo-dissolution" principle provides a simple method to obtain local control on the formation of inorganic structures, laying the foundations to a new class of materials for several applications.

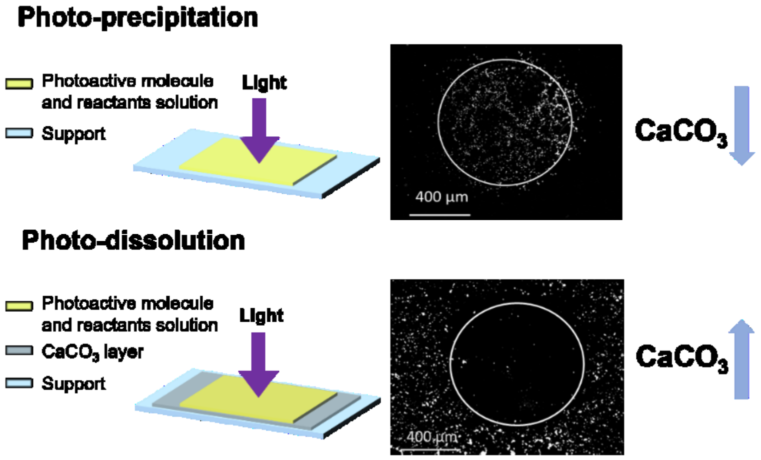

Photo-precipitation/Photo-dissolution of CaCO3: irradiation setup and optical microscope images

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Role of Water in Self-Assembly of Colloidal CdSe Nanoplatelets

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Abstract: CdSe nanoplatelets (NPL) have aroused a growing interest over the past few years thanks to their ultrathin thickness that can be controlled to the atomic layer.[1] Excitons quantum confinement imposed by this thickness leads to an intense fluorescence with a narrow spectral width and a large spectral overlap. Thus, inter-NPL ultrafast FRET can occur when NPLs in stacks and can reach distances of 500 nm[2] when happening in micrometer-long nanoplatelet threads.[3] Such assemblies are promising objects to present novel collective photophysical properties involving hundreds of emitters but are difficult to synthesize because mechanisms to explain their formation remains unclear.

In this work we explored the experimental conditions to obtain long stacks with high yield through the slow evaporation of a dispersion of NPL in presence of oleic acid. We tuned the evaporation rate, the concentration in oleic acid and the relative humidity of the atmosphere during evaporation. We found that water captured from atmosphere by oleic acid during evaporation is essential to obtain long threads. Understanding this effect is a step forward to synthesize new long threads made of NPLs with higher quantum yield or smaller ligands leading to new opto-electronics properties.

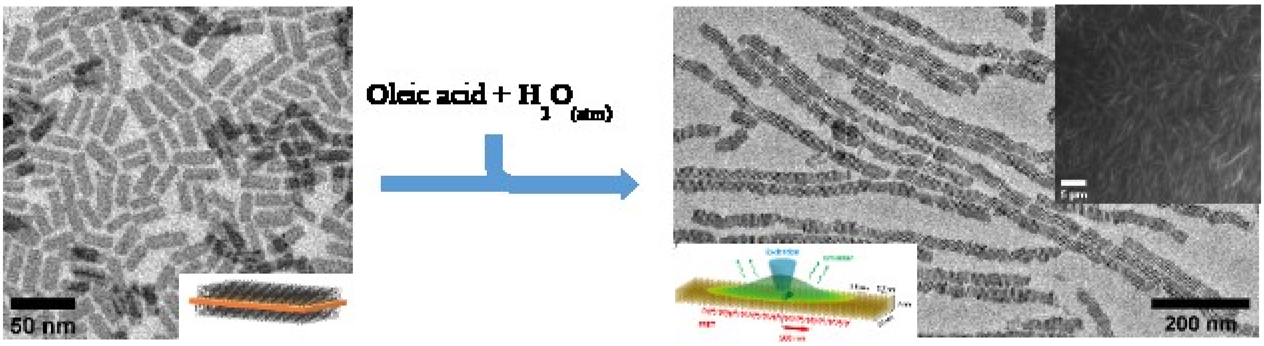

Figure 1. TEM pictures and scheme of NPLs prior and after hexane drying at a controlled relative humidity in presence of oleic acid. Top right inset show epifluorescence picture of thread solution.

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Photoluminescence Quantum Yields of Luminescent Nanocrystals and Particles in the UV/vis/NIR/SWIR in Dispersion and the Solid State

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Abstract: The rational design of functional luminescent materials such as semiconductor quantum dots and lanthanide-based upconversion nanoparticles, all photophysical and mechanistic studies, and the comparison of different emitters require accurate and quantitative photoluminescence measurements. Particularly the reliable determination of the key performance parameter photoluminescence quantum yield (Φ_f), the number of emitted per absorbed photons, and the brightness are of special importance for luminescence applications in the life and material sciences and nano(bio)photonics.[1] In this context, examples for absolute measurements of the photoluminescence quantum yields of UV/vis/NIR/SWIR emissive semiconductor quantum dots and rods, made from different materials, and spectrally shifting lanthanide upconversion nanocrystals with different surface chemistries in transparent matrices are presented including excitation wavelength and power density dependent studies utilizing integration sphere spectroscopy.[2,3] In addition, procedures for the absolute determination of the photoluminescence quantum yields of scattering dispersions of larger size quantum rods and differently sized inorganic particles have been developed as well as procedures for the characterization of solid luminescent nanomaterials such as different perovskites and YAG:Cer converter materials.[4] Thereby, challenges and pitfalls of Φ_f measurements in different wavelength regions including the SWIR and material-specific effects related to certain emitter classes are addressed, achievable uncertainties are quantified, and relative and absolute measurements of photoluminescence quantum yield measurements are compared to underline limitations of the former approach. Finally, a set of novel UV/vis/NIR quantum yield standards is presented including their certification with a complete uncertainty budget.[5]

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Polarimetric Measurements of The Bright Triplet Emission of Single Cesium Lead Halide Perovskite Quantum Dots at Cryogenic Temperature

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Abstract: Cesium lead halide perovskite quantum dots (QDs) have recently emerged as promising platform for quantum light sources. Indeed, they exhibit exceptional photoluminescence properties thanks to the emission from a bright triplet exciton state.[1] The energetic fine structure splitting, in the order of a few millielectronvolts, can be revealed by performing single QD spectroscopy at cryogenic temperature. In particular, depending on the QD orientation and on the observation direction, up to three orthogonal emitting dipoles can be spectrally detected, each of them with a high degree of linear polarization. To measure the polarization of the exciton fine structure, typically a rotating linear polarizer was used. However, this method cannot provide a complete characterization of the polarization state of the emitted light, and the polarization properties of the small, non-linearly polarized fraction of the emission were unclear. That is why in this work we are investigating the polarization properties of individual cesium lead halide perovskite QDs by more advanced polarimetric techniques that allow to measure the complete Stokes polarization vector at cryogenic temperature for each emission line. For these measurements it is crucial to perform a careful calibration of the optical path with respect to residual, unwanted birefringent phase shifts that are often occurring from optical coatings. Moreover, these measurements require colloidal QDs with very low intermittent emission fluctuations. In my presentation I will report the results of the polarimetry of single perovskite QDs, shedding light on the non-linearly polarized emission fraction and the nature of their peculiar emission properties.

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First Principles Study of HgTe Nanocrystals: Understanding Its Atomic, Electronic And Optical Properties

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Abstract: Mercury-telluride (HgTe) nanocrystals (NC) have, over the past decades, demonstrated great potential as building blocks for low-cost-high-performing infrared (IR) sensors covering spectrum from short-wave-infrared (SWIR) to terahertz frequencies (THz).[1-3] Despite the great progress in applied technology, fundamental mechanisms of HgTe NCs remain unveiled. These include atomic/electronic/optical structures, charge carrier transport and non-radiative recombination in HgTe NC thin films. We propose a systematic investigation into these properties based on density functional theory (DFT) calculations. Based on experimental observations,[3-5] HgTe NCs in different sizes, shapes and surface terminations are computationally constructed. By applying DFT calculations on these NC series, we show that our results not only agree well with experiments in absorption and photoluminescence (PL), but also give insights on atomic structures of NC surfaces, electronic structures and optical coupling. We further demonstrate the impact of surface termination and dopants/defects on the electronic coupling between neighboring HgTe NCs and optical coupling in intraband transitions (1s→1p above LUMO), which plays an important role on the enhanced magnitude of charge carrier mobility.[7-9] Finally, we show electron-phonon (EP) coupling of HgTe NCs and how surface termination can influence. Our study, bridging computational results and experimental observations, will be vital for guiding the optimization of next generation low-cost-high-performing NC-based IR photodetectors.

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Confocal Imaging of Unlabelled Nanoparticles in Cells and Biological Tissues

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Abstract: Noble metal nanoparticles (NPs), particularly gold (Au) and silver (Ag) NPs, have recognized relevance in chemistry, physics, and biology because of their outstanding optical, electrical, and photothermal properties. Optical properties, as localized surface plasmon resonance, are easily measurable signatures indicative of their morphology (size and shape), composition, surface chemistry, aggregation state and physical environment that can be used to identify molecular targets and chemical transformation processes.[1] Due to the growing interest in the use of metal NPs in medicine and biology, detailed cellular studies are required before their application in vivo for treatment or diagnostic purposes.[2] Herein, we present the observation of unlabelled Au NPs on Confocal Laser Scanning Microscopy (CLSM), by using the light reflectance instead of the commonly used fluorescence mode. The NPs size resolution limits for CLSM observation is studied experimentally. Theoretical calculations, of the size-dependent optical properties are also presented to support this argument. The Au NPs used were synthesized using the seeded growth citrate reduction method,[3] and the NPs sizes range from 15nm to 150nm. Full characterization of the produced NPs was also performed by Transmission Electron Microscopy (TEM), UV-Vis spectroscopy and Dynamic Light Scattering (DLS). Further, the intracellular observation of different sizes of Au NPs using the reflectance mode is also presented in cultured cells and tissue sections. This work reveals as a method to observe NPs in living systems in real-time and non-invasive way, which can be extended to other inorganic NPs.

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Surface Enhanced Raman Scattering-Based Lateral Flow Immunoassay For Multiplex Detection And Quantification of Histamine And Parvalbumin

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Abstract: Nowadays, the quality controls in the agri-food industry are increasingly rigorous. Detecting food allergens in meat or fish is very important for population's health. Point of care (PoC) devices are highly needed to detect contaminants as histamine and parvalbumin in this work. Histamine is a biogenic amine produced by bacteria that causes food poisoning when it is consumed in high concentrations, it can be found in fermented or preserved foods, such as wine, cheese or fish. Parvalbumin is a protein that can cause an allergic reaction in some individuals, considering it an allergen that can be found in certain fish species such as tuna.

Herein, we have combined indirect SERS technology with LFIA (lateral flow immunoassay) to develop an ultrasensitive test for PoC applications.[1,2] SERS-based LFIA will allow us to overcome some drawbacks of traditional colorimetric LFIA such as low sensitivity and/or limit of detection/quantification. This test has been designed to specifically detect and quantify histamine and parvalbumin in canned tuna fish. Thus core-shell Au@Ag nanoparticles (Au@Ag NPs) codified with Rhodamine B Isothiocyanate (RBITC) and Malachite Green Isothiocyanate (MGI), as Raman reporter molecules, and bioconjugated with antibodies against both contaminants have been obtained. Next, the performance of the SERS-LFIA for histamine and parvalbumin detection has been evaluated obtaining calibration curves for each analyte. The results revealed that our SERS-LFIA meets a successful range of quantification considering the legal concentrations of both allergens and improves the limit of detection up to 1.18 x 10^{-4} and 1.91 x10^{-3} mg/mL for histamine and parvalbumin respectively.

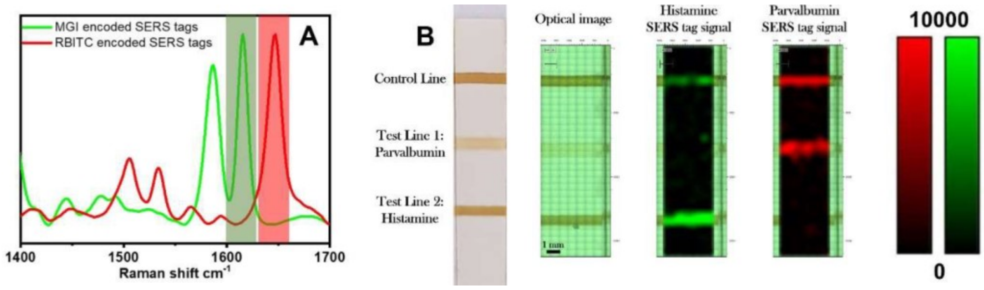

Figure 1. A) SERS analysis of the SERS tags encoded with Malachite green isothiocyanate (green spectra) and Rhodamine B isothiocyanate (red spectra). B) From left to right, LFIA strip after running, Raman optical image, SERS mapping for histamine (codified with MGI), where only control and histamine lines have SERS intensity, and parvalbumin (codified with RBITC), where only control and parvalbumin lines have SERS intensity.

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Nanoparticle-Based Gel Structures For Photoelectrochemical Applications

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Abstract: Controlled destabilization of a ligand-stabilized nanocrystal solution with an oxidizing agent can be used to build up a macroscopic highly porous self-supporting nanocrystal network with good accessibility to the surface. These networks provide charge carrier delocalization beyond a single nanocrystal building block which extends the charge carrier lifetimes and increases the probability of photocatalytic reactions. With the advances in colloid chemistry made in the last decades various ligand-stabilized nanocrystals with specific physicochemical properties can be synthesized. Combining properties of tailor-made nanocrystals and nanoparticles-based gel structures leads to novel materials with optimized photocatalytic properties. In this study, nanocrystal-based hydrogels are presented which exhibit a higher hydrogen production rate compared to their ligand-stabilized nanocrystal solutions. The gel synthesis through controlled destabilization by ligand oxidation preserves the high surface-to-volume ratio, ensures the accessible surface area and facilitates photocatalytic hydrogen production without a co-catalyst. Especially with such self-supporting networks of nanocrystals, the problem of colloidal (in)stability in photocatalysis is circumvented. The advantageous properties of the nanocrystal-based gel structures are revealed using photocatalytic measurements, X-ray photoelectron spectroscopy and photoelectrochemical measurements.

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Outperforming Catalytic Activity of Au_xPt_{1-X} Nanostructures by a Chlorine-Assisted Synthesis in Hydrogen Evolution Reaction

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Abstract: Despite the highest activity of Pt-based electrocatalysts for hydrogen evolution reaction (HER),[1] its scarcity and elevated cost calls for a rational use and for the development of nanocatalysts outperforming commercial Pt/C.[2] Herein, we present the synthesis of Au_xPt_{1-x} nanocrystals by a chlorine-mediated microwave (MW)-assisted route. The addition of chlorine ions does control the final structure of the nanocomposite leading to a Au-Pt core-shell structure with enhanced electrocatalytic activity for HER. Particularly, AuPt structures with a Pt loading of 6.86% display overpotentials of 24 and 51 mV at 10 and 100 mA cm^{-2} respectively, as well as a Tafel slope of 13 mV dec^{-1}. Those values are far lower compared to the samples produced without chlorine (32 and 81 mV at 10 and 100 mA cm^{-2} respectively, Tafel slope 26 mV dec^{-1}) and benchmark Pt/C (31, 72 mV at 10, 100 mA cm^{-2} respectively, Tafel slope 30 mV dec^{-1}). Interestingly, mass activity for that NCs were 13.7 A $mg^{-1}{}_{Pt}$ which is 3 and 7 times higher compared to that of samples produced without chlorine (4.4 A $mg^{-1}{}_{Pt}$) or commercial Pt/C (2.0 A $mg^{-1}{}_{Pt}$) respectively. The high catalytic activity of the AuPt core-shell structure may result from the combination of a high exposure of Pt atoms and electron transfer between the Au core and the Pt shell. Finally, the MW-assisted synthesis developed to produce this AuPt nanostructures alloyed electrocatalysts allows for a mass production (500 mg per synthesis) in rather short time (ca. 15 min).

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Fast And Selective Reduction of Nitroarenes Under Visible Light With an Earth-Abundant Plasmonic Photocatalyst

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Abstract: Reduction of nitroaromatics to the corresponding amines is a key process in the fine and bulk chemicals industry to produce polymers, pharmaceuticals, agrochemicals and dyes. However, their effective and selective reduction requires high temperatures, pressurized hydrogen and involves noble metal-based catalysts.[1-4] Here we report on an earth-abundant, plasmonic nano-photocatalyst, with an excellent reaction rate towards the selective hydrogenation of nitroaromatics. With solar light as the only energy input, the chalcopyrite catalyst operates through the combined action of hot-holes and photothermal effects. Ultrafast laser transient absorption and light-induced electron paramagnetic resonance spectroscopies unveiled the energy matching of the hot holes in the valence band of the catalyst with the frontier orbitals of the hydrogen and electron donor, via a transient coordination intermediate. Consequently, the reusable and sustainable copper-iron-sulfide ($CuFeS_2$) catalyst delivers previously unattainable turn-over-frequencies, even in large-scale reactions, while the cost-normalized production rate stands an order of magnitude above the state-of-the-art.

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Precursor Chemistry-Dependent Efficiency of Anion Exchange Reactions in Perovskite Nanocrystals

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Abstract: In perovskite nanocrystals, anion exchange reactions are very broadly utilized to tune the compositions, which finally results in effective modifications of electronic structures and thus emission colors. Anion exchange reactions can be simply implemented by introducing halide source and/or precursors to host perovskite nanocrystals. For example, all inorganic $CsPbBr_3$ nanocrystals can be rapidly transformed to $CsPbI_3$ nanocrystals when iodide anionic precursor source is introduced. In such anion exchange reactions, the most widely utilized halide source is the mixture of oleylamine and iodine. Although anion exchange reaction itself has been investigated by many researchers,[1] understanding on the effect of halide precursor source in anion exchange reactions is lacking.

In this study, we show the effect of halide precursor source in anion exchange reaction of all inorganic perovskite nanocrystals. We reveal, for the first time, that the efficiency of anion exchange reaction strongly depends on halide precursor chemistry. We propose the mechanism how halide precursors affect anion exchange reactions in perovskite nanocrystals. Finally, we develop the strategy to improve the efficiency of anion exchange reaction by boosting the reaction occurred in halide precursor source solutions.[2]

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980 nm Light Activated SWIR-Emitting Gold Nano-Probes For Bio-Imaging

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Abstract: Non-invasive photoluminescence imaging (PLI) has emerged as a powerful technique with clinical translation for diagnosis where it enables monitoring the progression of diseases such as cancer and helps surgeons during the tumor resection.[1] Seminal work from Dai and Bawendi's teams[2, 3] have demonstrated the benefit of shifting to shortwave infrared region SWIR (900-1700 nm) that allows to obtain detailed information with higher resolution up to few microns at higher depth down to few millimeters[2] compared to the first near-infrared window (700-900nm). Since then, several inorganic materials such Quantum dots or lanthanide-doped nanoparticles have been designed to strongly emit in the SWIR providing high resolution of the vascular networks. However, such nanoprobes still require several chemical steps to make them biocompatible as they end up in the liver which can cause some severe toxicity.

Noble metal Nanoclusters, mainly gold, are ultrasmall nanoparticles composed of tens to hundred metal atoms stabilized by capping ligands. They exhibit bright emission tunable in the SWIR, are biocompatible with high renal clearance hence promising candidates for fluorescence bio-imaging and cellular labeling.[4] A library of functionalized atomically precise SWIR-emissive gold nanoclusters with tunable near infrared absorbance has been synthesized by wet chemistry using a monothiol ligand (6-Mercaptohexanoic acid) and a dithiol co-ligand (hexa-ethylene glycol dithiol). Physico-chemical and optical characterizations indicates that the size and rigidity of the ligand shell protecting the gold core (~1.5 nm) can lead to a striking enhancement of the absorption at 980 nm and a shift of PL to higher wavelength due to possible changes of non-radiative processes. These nanoclusters could be detected by SWIR imaging in capillaries down to 6 mm in an intralipid solution mimicking living tissues using a 980 nm laser excitation. We also demonstrated the ability to monitor these emitters by SWIR imaging in small animals with a pharmacokinetic highly depend on their size.

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Opto-Electronics Properties of (2,5dmpz)PbX$_4$ Perovskite: From Single Halide to Mix Halides

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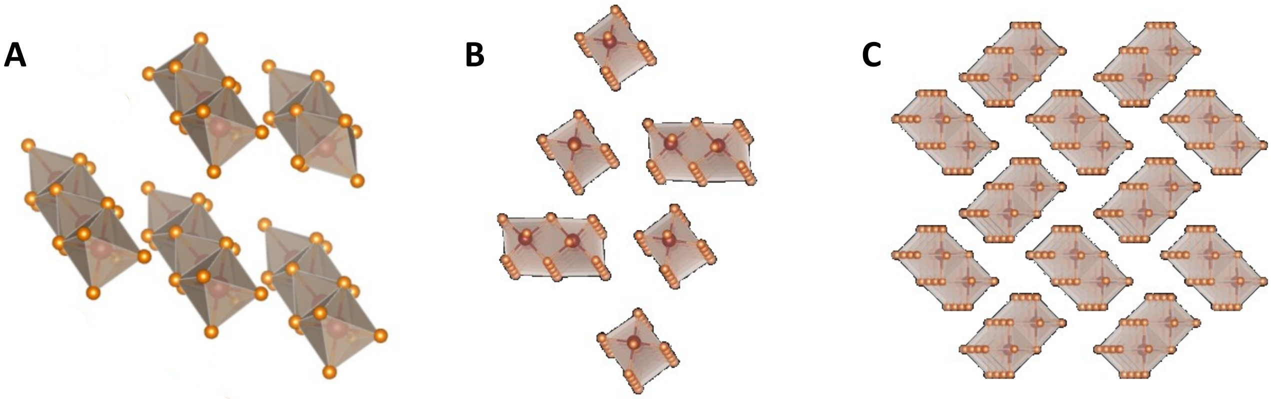
Abstract: Low-dimensionality hybrid metal-halide perovskites are a promising family of light emitters, offering highly tunable optoelectronic properties. Low-dimensionality perovskite compounds with broadband emission, associated with self-trapped excitons, can be formed in different structure types such as: face-sharing 1D chains (A), edge-sharing double chains and corner-sharing 1D chains (B), edge-sharing double 1D chains (C) which found to be the most efficient broadband emitters, to date.

(2,5dmpz) PbBr$_4$ forms 1Dl structure with edge-sharing double chains and exhibit bright, broad emission at room temperature with PLQY>40%. In this work, we study the effect of halide on the optical properties, specifically, broadband emission. We exchange the halides, mixing them, and changing the halide ratio, in order to gain control over their color rendering and bandgap. We synthesize different low-dimensionality (2,5dmpz)PbX$_4$ compounds (X = I, Br, Cl), or a mixture of halides in different ratios, through solution- and mechano-synthesis. These compounds' structural properties are studied using powder X-ray diffraction. Their optical properties were studied by diffuse reflectance, photoluminescence, time-resolved photoluminescence, temperature-dependent photoluminescence, and photoemission spectroscopy. The structural characterization has shown that moving from big to small halide maintains the same structure, with a smaller unit cell, as expected. For the same transition, the optical characterization exhibited an interesting trend, according to which, while generally, the band gap increases, a redshift of the emission (lower energy) occurs. This trend was preserved during the mixing of the halide in different ratios and is still under investigation.



Examples of low-dimensionality perovskite structure types.

2D Metal Halide Perovskites: Synthesis and Characterization

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Abstract: 2D metal halide perovskites (HPs) are recently emerging as promising materials for optoelectronic, and spintronic applications, due to their structural versatility that allows tunning of its photophysical properties. In these HPs, inorganic and organic layers are alternately stacked, creating an electronic band structure, resembling classical multiple quantum wells. The mentioned electronic band structure can be manipulated by the change of the composition either of the inorganic or the organic moieties. Furthermore, our laboratory recently demonstrated that the heterogeneity of a soft structural nature enables a motion degree of freedom, which is responsible for the breakage of inversion symmetry and the consequent formation of the Rashba effect. The last is pronounced as a split emission band at a band-edge energy with opposing circular polarization, hence beneficial for spin-related technologies.

The current work focuses on the manipulation of the electronic properties of 2D HP's single crystals via the variation of either the organic spacers or the inorganic constituent. The organic spacers will vary by using different solvents of variable polarities. Interestingly, we discovered that the polarity of the solvent regulates crystal crystallization and symmetry, as will be elaborated on at the meeting. The metal content will be altered by embedding magnetic impurities. The laboratory has implemented magnetic impurities in the past in 3D HPs, in which impurity-to-host carrier interaction has been exposed, and consequent changes in the carrier's g-factor. Similar work regarding the 2D HPs is presently in process, and some of those results will be reported at the meeting.

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Direct Observation of Charge Carrier Distribution in Contacted Nanowires Under Local Illumination

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Abstract: Kelvin probe force microscopy (KPFM) is a method of measuring the surface potential. Being based on atomic force microscopy, KPFM enables the investigation of nanostructures. Among these nanostructures are semiconductor nanowires and nanosheets. Here, we report on combining optical, electrical, and surface potential measurements in one setup to investigate the charge separation in these materials and bring insight into the properties of semiconductor-metal interfaces. Nanowires on transparent substrates are electrically contacted using lithography. This allows for optical excitation simultaneous to current and KPFM measurements.

The surface potential of semiconductors, measured by KPFM in air, is influenced by ligands and adsorbates, because a surface charge region is formed. Under Illumination, this region is filled with charge carriers, changing the surface potential. We analyze this change using KPFM, which gives insight into properties of the semiconductor, such as n- or p-type, charge carrier mobility and its surface ligands.

KPFM directly reveals how the potential drops along a contacted CdS nanowire depending on the direction of an applied bias, and the contact material. This is due to the formation of Ohmic and Schottky contacts at the semiconductor-metal interface. A Schottky contact biased in reverse impedes the current flow, and no charging is observed by KPFM. By locally illuminating the space charge region of the Schottky contact, charge carriers are spatially separated, either charging the wire, or forming a current along the nanowire. Characterizing this space charge region is necessary to tailor the properties of nanowire devices such as transistors or solar cells.

An Isotopic-Labeling Study to Investigate the Primary Source of Hydrogen in a Photocatalytic System of Pt-Tipped CdSe/CdS Dot-In-Rod Nanostructures in Alkaline Aqueous Alcohol Solution

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Abstract: Hybrid nanostructures that combine semiconductor and metal materials, such as Pt-tipped CdSe/CdS dot-in-rod stabilized by 11-mercaptoundecanoic acid (DR), exhibit promising potential as photocatalysts for generating hydrogen from alkaline aqueous alcohol solutions when exposed to light.[1] In this process, the alcohol acts as sacrificial agent because CdS cannot undergo water splitting without appropriate co-catalysts. The oxidation of alcohols releases protons that can potentially be reduced to hydrogen. However, it remains unclear which of the two reacting substances, water or alcohol, serves as the primary source of hydrogen for this system. Here, we present findings obtained by analyzing the production rates of deuterium, deuterium hydride, and hydrogen from various mixtures of isotopically labeled substances. Similar to Kandiel *et al.*, who investigated pH-neutral aqueous solutions containing TiO_2/Pt hybrid nanostructures as photocatalysts and methanol as a sacrificial agent,[2] our results confirm water as the primary source of hydrogen. Our findings provide important insights into the mechanism of this photocatalytic system and contribute to a better understanding of the roles of water and alcohol in this context.

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Organic Reactions Photocatalytically-Driven by Lead Halide Perovskite Quantum Dots

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Abstract: Photocatalysis is a cost-effective and valuable method that is used for the synthesis of important organic molecules and critical/major bond formations such as C-C, C-N and C-O bonds.[1-3] Over the last decades, a remarkable improvement was achieved in the field using purely organic, organometallic or transition metal catalysts. However, photocatalysts often comprise expensive transition metals (Ru[4], Ir[5], Au[6]), are elaborate to prepare, require air-free conditions to yield high conversions, and may be non-reusable. Thus, the design and preparation of practically usable photocatalysts remain a formidable challenge. Lead halide perovskite quantum dots (LHP-QDs) are promising candidates featuring very high absorption coefficients (~10^6 $M^{-1}cm^{-1}$), near-unity photoluminescence (PL) quantum yield (>95%) and tunable emission wavelength and high surface area.[7] These nanocrystals can act as oxidative and reductive catalysts simultaneously, their reduction and oxidation potentials can be tuned, they can be separated from the reaction mixture and regenerated similarly to bulkier heterogeneous catalysts, and their surface offers a platform for the separation of the photoexcited carriers.

Here we report on using surface-engineered LHP-QDs in dimerization reactions of benzyl bromide derivatives with high-yield and fast conversion into the desired products. Coating of the particles with various metal oxides alters the surface properties, widening the scope of reactions to conduct. The regeneration of ligand-capped particles is successfully achieved using a post-treatment method and control experiments show that these reactions are solely photocatalytic.

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Ultrafast Spin-Exchange Auger Recombination and Carrier Multiplication in Manganese-Doped Colloidal Quantum Dots

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Abstract: Manganese-doped CdSe colloidal quantum dots (CQDs) have been used in photoemission and photocatalysis thanks to their ability to generate hot carriers.[1-3] Recent studies ascribed the observed photoemission to very fast spin-exchange Auger ionization which occurred via ejection of either a 'hot' electron (single-step process) or a band-edge electron (two-step process).[2,4] In both cases, Auger re-excitation must compete with intra-band cooling which normally impedes electron ejection. However, in Mn-doped QDs, spin-exchange energy transfer is much faster than phonon-assisted cooling, which leads to highly efficient photoemission.[2,4]

Carrier multiplication (CM) occurs via impact ionization or inverse Auger recombination. During this process, the kinetic energy of a carrier relaxes via generation of additional excitons.[5] The ultrafast character of spin-exchange Auger recombination suggests that the rate of spin-exchange impact ionization can also be high, leading to highly efficient CM. To demonstrate spin-exchange CM (SE-CM), we use specially engineered Mn-doped core/shell PbSe/CdSe CQDs. In these structures, SE-CM occurs via two spin-exchange steps: (1) exciton transfer from a CdSe shell to a Mn dopant, followed by (2) spin-flip relaxation of the excited Mn ion to create two excitons in a PbSe core. The observed CM benefits from extremely fast rates of spin-exchange interactions leading to a three-fold enhancement of the CM yield versus undoped CQDs, accompanied by a considerable reduction of the electron-hole pair creation energy. These observations indicate a significant potential of spin-exchange interactions as a highly effective driver of CM for applications in advanced photoconversion.[6]

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Understanding and Engineering Catalytic Materials Using Nanocrystal Precursors

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Abstract: Catalytic processes are central to the goal of a sustainable future. A promising approach in developing catalytic materials is represented by the design of catalytic sites based on the knowledge of structure-property relationships, and in the precise synthesis of these sites at the atomic level. Colloidal nanocrystals, with tunable active sites and compositions, can help in this mission. The goal of this talk is to show how this approach can provide not only fundamental understanding of catalytic reactions, but also a way to precisely engineer reaction sites to produce efficient catalysts that are active, stable, and selective for several important transformations. Advances in the synthesis of these materials will be presented.[1] Examples of the use of these building blocks as supported systems or in combination with hybrid organic materials will be shown, both to understand trends in methane and CO_2 activation,[2-3] and in the preparation of optimized catalytic systems combining multiple active phases.[4] In all these examples, important efforts to obtain precious structure-property relationships will be highlighted, with this knowledge used to prepare more efficient and stable catalysts for reducing the emission of greenhouse gases and for the sustainable production of fuels and chemicals.

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Colloidal Nanocrystals to Advance Catalysis and Energy Technologies

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Abstract: Affordable clean energy and climate action are two of the sustainable development goals set by the United Nations to be achieved by 2030. The vast majority of energy technologies relies on nanomaterials and their progress is strongly connected to the ability of material chemists to tune their property and function-dictating features (i.e. size, composition, composition, morphology).

In this talk, I will present our recent group efforts towards the synthesis via colloidal chemistry of atomically defined nanocrystals (NCs) with properties of interest for catalysis and energy conversion.

The first part will focus on our studies on the synthesis development and formation mechanism of Cu NCs. I will illustrate how these NCs with precisely tunable shapes, sizes and interfaces serve as ideal platforms to advance our current knowledge towards improved selectivity in the electrochemical CO_2 reduction reaction. I will then share our results evidencing that these NCs can sustain their catalytic activity and selectivity at technologically relevant conditions, therefore might also offer practical solutions.

The second part will be dedicated to our colloidal atomic layer deposition (c-ALD) method to grow tunable oxide shells around different inorganic NC cores. In addition to preserve their colloidal stability, these oxide shells confer the NC with improved stability and enable further functionalization and post-processing. I will discuss the formation mechanism of the shell by sharing our insight into the surface chemistry. I will then present how we manipulated the growth process in order to incorporate an assortment of photoactive ligands as integral components of the metal oxide shell, which creates organic/inorganic hybrid structures with potential applications as photocatalysts and sensitizers for incoherent photon conversion.

Colloidal Alloy Nanocrystals for Efficient Alkyne Semihydrogenation Catalysis

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Abstract: Alloy nanocrystals (NCs) are an emerging class of heterogeneous catalysts for the selective hydrogenation of alkynes to alkenes, one of the most fundamental organic transformations with applications in both the fine chemical industry (synthesis of vitamins and natural products) as well as in the polymer industry (selective removal of acetylene to purify ethylene streams). There is a need to develop catalysts which constitute of earth-abundant and environmentally benign metals and exhibit high activity, selectivity, and durability. Here, we leverage the extend of composition- and size-control attainable in colloidal synthetic procedures to synthesize small, pristine, and compositionally tunable Ni and bimetallic Ni-X (X = Zn, Ga, In) NCs (3-4 nm in size),[1] employing an amalgamation seeded growth procedure.[2] We identify Ni_3Zn NCs as particularly active and selective alkyne semihydrogenation catalysts, operating under mild reaction conditions and low loadings. XPS measurements and DFT calculations reveal the electronic and geometric effects resulting in the high catalytic activity of Ni-Zn NCs. Ni_3Zn NCs also display good functional group tolerance, efficiently catalyzing a wide scope of alkyne substrates, which were rationally selected in an unbiased manner after mapping the chemical space of alkynes via a data science approach. The synthesis method itself could be explored in the future beyond bimetallic nanocrystals to achieve multinary NCs to search for increasingly selective and efficient semihydrogenation catalysts, whereas the reported bimetallic NCs hold great potential for other important catalytic transformations beyond alkyne semihydrogenation..

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Tailoring Anisotropies in NIR-plasmonic Semiconductor Nanocrystals

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Abstract: Doped semiconductor nanocrystals represent an emerging class of materials that host localized surface plasmon resonance (LSPR). Their wide spectral range (from visible to the entire IR regions) and post-synthetic tunability through doping promise new plasmon-assisted active optical materials and devices. Recent studies discovered various semiconductor species that perform efficient LSPR. However, the nanocrystals' structural impact on their LSPR remain poorly explored.

This presentation illustrates how multiple structural factors can be synergistically tuned to promote novel LSPR properties that are unseen from metal hosts. For instance, hexagonal cesium-doped tungsten oxide (Cs_xWO_{3-y}) nanocrystals exhibit crystalline anisotropy that causes a strong LSPR band-splitting into two distinct and intense peaks.[1] We combine this structural anisotropy effect with the well-known shape anisotropy effect of plasmonic nanoparticles to tune the multimodal LSPR bands.[2] For this, we exquisitely control the synthesis of Cs_xWO_{3-y} and achieved their variable shape aspect ratio, ranging widely from 0.2 (platelets) to 20 (rods).[3] This large structural tunability enables the spectral range of LSPR peaks to cover the entire near-infrared region and beyond (750~4000 nm). Furthermore, the LSPR response of these highly anisotropic nanocrystals can be post-synthetically and reversibly tuned by inducing LSPR coupling effects in their self-assembled structures.[4] We demonstrate how this tunable LSPR can be utilized in designing window NIR-shields for energy-saving applications.[5]

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High Entropy Alloy Nanoparticles as Oxygen Catalysts For Metal-Air Batteries

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Abstract: High entropy alloys (HEAs) are solid solutions of five or more elements with high thermodynamic and kinetic stability, that hold great promise in the field of electrocatalysis owing to their high configurational entropy, subtle distortions of the atomic arrangement and electronic density, and potentially strong synergistic effects to optimize the adsorption energies and electrical conductivity. HEAs also offer numerous degrees of freedom to fine-tune the material structural, electronic, and catalytic properties. Overall, the use of HEAs is a powerful strategy to optimize the surface adsorption properties, catalytic active centers, electronic structures, and consequently the redox catalytic activity within different electrochemical technologies. I will present our recent work on the colloidal synthesis of HEA nanoparticles, discuss their electrocatalytic properties and demonstrate their potential as oxygen catalysts at the cathode of metal-air batteries.

Designed Synthesis and Assembly of Inorganic Nanomaterials for Energy, Catalysis and QLED Applications

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Abstract: We present a synthesis of highly durable and active fuel cell electrocatalysts based on ordered intermetallic PtM (M= Fe, Co) nanoparticles for oxygen reduction reaction.[1] We report on the design and synthesis of highly active and stable Co-N_4(O) moiety incorporated in nitrogen-doped graphene (Co_1-NG(O)) that exhibits a record-high kinetic current density and mass activity with unprecedented stability (>110 h) for electrochemical H_2O_2 production.[2] Guided by computation, we report a supramolecular approach for H_2O_2 electrocatalysis that uses a combination of oxygen functional groups in a carbon nanotube (CNT) substrate and a cobalt phthalocyanine (CoPc) catalyst.[3] We synthesized various multimetallic heterostructured oxide nanomaterials and investigated their structure-property relationship in energy devices and catalysis.[4] We report on the design and synthesis of highly active TiO_2 photocatalysts incorporated with site-specific single copper atoms (Cu/TiO_2) that exhibit reversible and cooperative photoactivation process, and enhancement of photocatalytic hydrogen generation and CO_2 photoreduction activity.[5] We presented a floatable photocatalytic platform constructed from elastomer-hydrogel nanocomposites, demonstrating its superiority over conventional systems in solar hydrogen production.[6]

We demonstrated a wearable red-green-blue (RGB) colloidal quantum dot light-emitting diode (QD LED) array with high resolution using a novel intaglio transfer printing technique.[7] We reported a novel device design and fabrication method using metal-based etch-stop layers and a laser-assisted patterning for 3D foldable quantum dot light-emitting diodes (QLEDs).[8] Shape-tunable multiplexed phototransistor array was fabricated using an intrinsically stretchable and color-sensitive semiconducting nanocomposite consists of size-tuned quantum dots, blended in a semiconducting polymer within an elastomeric matrix.[9]

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Directed Design of Shaped Metal Nanoparticles Using In Situ Electrochemical Measurements

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Abstract: This talk will describe an integrated electrochemical approach to nanoparticle synthesis that has been developed in our lab to enable directed synthesis of shaped nanoparticles both in colloidal solution and on electrode surfaces. Our approach links metal nanoparticle synthesis with real-time monitoring of chemical changes in the reaction solution using a combination of colloidal particle synthesis, electrochemical particle synthesis, and electrochemical measurements. Importantly, this is one of the only available techniques for the *in situ* collection of real-time information about the chemical processes that drive metal nanoparticle growth. In addition, this approach enables bidirectional translation of syntheses between electrochemical and colloidal growth methods. This provides a pathway for the directed adaptation of the extensive library of existing shaped colloidal nanoparticle syntheses to growth on a surface—something that remains a non-trivial challenge. It also opens opportunities for using electrochemical growth of shaped nanoparticles—where reaction conditions are highly tunable using an applied current or potential—to design syntheses that go beyond the boundaries of existing chemical reduction-based synthesis conditions. In combination with open circuit measurements of the reaction between common reducing agents and metal precursor complexes, these electrochemically-designed syntheses can then be used to identify novel conditions for growth of analogous nanostructures using colloidal growth and chemical reducing agents.

Oxidation Front and Magnetic Gradient in FeO/Fe_3O_4 Core/Shell Nanoparticles Unveiled by a Multicharacterization Approach

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Abstract: FeO/Fe_3O_4 core/shell nanoparticles (NPs) are a subject of considerable current interest both due to their appealing magnetic properties (e.g., tunable exchange bias or the presence of both a Néel and a Verwey transitions) and their potential applications (e.g., magnetic hyperthermia, magnetic bioassays, microwave absorbers, anode materials for Li-ion batteries, or solar hydrogen production via water splitting). In FeO/Fe_3O_4 core/shell NPs both core and shell exhibit magnetic properties, hence, not only is the structural/morphological interface important but also the magnetic arrangement at the interface can play a crucial role in the properties and performance of the NPs. In this work we have revealed two important features to understand the magnetic properties of bimagnetic FeO/Fe_3O_4 core/shell NPs: i) the temporal evolution over four years of the oxidation front which leads to a final onion-like structure with a graded composition[1] and ii) the concomitant appearance of a graded magnetic structure[2]. We have demonstrated that the oxidation process reaches to a 'stand-by' state owing to the passivation character of the Fe_3O_4 shell and that the magnetic moment being largest at the surface decreases towards the inner part of the NP. The elucidation of these results has been addressed by a careful multicharacterization approach based on X-ray diffraction (Whole Powder Pattern Modeling-WPPM, Rietveld refinement, Pair Distribution Function-PDF), Electron Energy Loss Spectroscopy (EELS) and electron Magnetic Circular Dichroism (e-MCD) techniques. Finally, we have also unveiled that for the Fe_xO_y/ Fe_3O_4 nanoparticulated system, for small nanoparticles (9 nm) the Fe_xO_y core is highly non-stoichiometric and strained leading to the loss of its internal magnetic structure, namely, to the antiferromagnetic behaviour.

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Observation and manipulation of spin coherence in colloidal quantum dots

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Abstract: Coherent manipulation of solid-state spins is important for quantum information processing. Current solid-state spin systems either operate at very low temperatures or are difficult to scale-up. Colloidal quantum dots (QDs), by contrast, can be synthesized in large quantity in solution at low cost, yet with high finesse in size and shape control. Further, they are usually strongly quantum-confined, thus their carriers well isolated from the phonon bath, which could enable long-lived spin coherence at room temperature. We studied coherent spin dynamics in solution-grown perovskite QDs using transient magneto-optical spectroscopy. We observed ensemble-level quantum beats resulting from an exciton fine-structure gap and quantitatively controlled the gap energy using temperature-programmable lattice distortion. This unique mechanism has important implications for the application of perovskite QDs in quantum light-sources and coherent exciton control. Further, by dissociating excitons using ultrafast interfacial electron transfer, we achieved room-temperature all-optical initialization, manipulation and readout of hole spins in CsPbBr3 QDs. This represents a milestone towards a scalable and sustainable future of spin-based quantum information processing.

Colloidal Quantum Well LEDs and Lasers: A New Device Platform Using Orientation-Controlled Self-Assembly

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Abstract: Lighting and displays are integral parts of human activities and economic development. Semiconductor nanocrystals, now offering a market volume exceeding 1 Billion Euros annually, have attracted great interest in quality lighting and displays in the last decade. Such colloidal semiconductors enable enriched color conversion essential to superior lighting and displays. These colloids span different types and heterostructures of semiconductors, starting in the form of colloidal quantum dots about three decades ago and extending to the latest sub-family of nanocrystals, the colloidal quantum wells, in the last decade. In this talk, we will present most recent examples of photonic structures and device architectures using the colloidal quantum wells[1-5] for lighting and displays. Also, we will present a powerful, large-area, orientation-controlled self-assembly technique for orienting these colloidal quantum wells either all face down or all edge up.[6] We will demonstrate three-dimensional constructs of their oriented self-assemblies with monolayer precision.[7] Among their extraordinary features important to applications in lighting and displays, we will show record high efficiency from their colloidal LEDs[8] and record gain coefficients from their colloidal laser media[9] using heterostructures[2-5] and/or oriented assemblies[6, 7] of colloidal quantum wells. Given their current accelerating progress, these solution-processed quantum wells hold great promise to challenge their epitaxial thin-film counterparts in semiconductor optoelectronics in the near future.

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A Fundamental Study of Novel Infrared-Active Bismuth Tellurobromide Nanocrystals

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Abstract: Research in nanocrystals (NCs) has accelerated dramatically in recent years. Because of their excellent size-dependent optical properties, NCs have been integrated into a wide range of applications, such as photovoltaics (PV) and light-emitting diodes (LEDs). However, materials with extraordinary optical properties are desired for high-performance devices, and therefore the scientific community is constantly seeking new optoelectronic materials with ever faster and more efficient excitonic light emission. Materials with Rashba-type spin splitting are promising candidates for this search, since it has been shown that the Rashba effect can give rise to a bright ground-state exciton, leading to a remarkable enhancement of optical properties. In this work, we report a novel hot-injection synthesis of BiTeBr and BiTeCl nanoplatelets, materials known to have large Rashba splitting. We observe and explain an unusual wire-to-platelet growth pathway and make initial optical measurements of the confined excitons in the nanoplatelets.

Hafnium Oxide Nanocrystals for Contrast Enhanced Vascular Casting: From Mechanistic Insight to Application

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Abstract: Cardiovascular diseases are the leading cause of death worldwide. Vascular corrosion casting provides an in-depth understanding of cardiovascular morphology by injecting a polymer resin and subsequently removing the surrounding soft tissue via chemical maceration.[1] *In-situ* micro-computed tomography (CT) scans can provide detailed information on the vascular architecture without having to corrode the tissue, but a lack of CT contrast makes the distinction between the polymer cast and the animals' soft tissue impossible. To improve this, we introduce hafnium oxide nanocrystals (HfO_2 NCs) as contrast agents to the polymer resin. Here we communicate our insights on the HfO_2 NC synthesis, their surface chemistry and their application as CT contrast agent.

We synthesize 5 – 10 nm HfO_2 NCs starting from $HfCl_4.2THF$ in benzyl alcohol. Initially identified as a purely nonaqueous sol-gel route,[2] we find the in-situ water formation to be responsible for gelation of the reaction mixture prior to particle crystallization. Through mechanistic investigation using in-situ PDF analysis, NMR, EXAFS and rheology measurements we study this rapid precursor-to-gel conversion and subsequent nucleation and growth.

To obtain a stable and homogeneous dispersion of the NCs in the casting resin, we optimized the particle's surface chemistry. The ideal ligand is found to be a combination of a strong binding group (phosphonate), while matching the resin's polarity via its organic tail (ethylene glycol oligomers), creating highly stable nanocomposites. Finally, we perform *ex-vivo* injections of both zebrafish and mouse models with the NC-doped resin and obtain high-quality cast visualization via automatic segmentation.[3]

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Plasmonic Metal Oxide Nanocrystals

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Abstract: Ordinarily, metal oxide semiconductors are transparent owing to their wide band gaps and they offer little as optical materials beyond refractive index contrast. When doped with a few percent of aliovalent dopants, however, they become electronically conducting and doped metal oxide nanocrystals interact strongly with infrared light due to localized surface plasmon resonance (LSPR). In the prototypical material tin-doped indium oxide (ITO), we have found that the strength and spectrum of light absorption depend nontrivially on nanocrystal size and the concentration of tin dopants owing to a thin, near-surface depletion layer caused by surface trap states. The depletion layer can be minimized and the plasmonic concentration of light around the nanocrystals maximized by selectively localizing tin dopants in an outer shell region. Selective doping in either the nanocrystal core or shell also gives rise to multiple optical absorption modes with different sensitivity to changes in the surrounding refractive index suggesting opportunities for nanoscale sensors. The absorption is also highly responsive to the addition or removal of electrons, enabling optical sensing of biochemical electron transfer events. In nanocubes, made by co-doping indium oxide with tin and fluorine, distinct optical modes are associated with their faceted shapes, and the relative strength of field-enhancement around the corners is surprisingly magnified by surface depletion. Overall, this new class of plasmonic nanomaterials offers opportunities for synthetic tuning of optical properties beyond what's possible with conventional metals. Emerging applications in sensing, smart windows, and catalysis may take advantage of their unique ability to dynamically modulate and to direct energy flow from infrared light.

Anisotropic Semiconductor Nanocrystals: From Heavy-Metal-Free Compounds to Metal Halide Perovskites

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Abstract: Colloidal anisotropic semiconductor nanocrystals manifest polarized luminescence, high gain coefficient and improved charge transport, and show many advantages over isotropic spherical quantum dots in a variety of applications such as lighting and displays, lasering and catalysis. However, it is challenging to accomplish the controlled syntheses of both heavy-metal-free semiconductor nanocrystals and metal halide perovskite nanocrystals due to the narrow growth window parameters and extremely fast growth rate originated from the highly ionic nature of the materials, respectively. In this talk, I will elaborate how the size, composition and morphology of such nanocrystals can be controlled and be further self-assembled into hierarchical architectures via regulating a broad scope of factors ranging from surface energy, monomers, additives, binding ligands to temperature from a physical perspective. The optical, electronic, and catalytic properties of these intriguing materials have been interpreted based on the structure-property relationships and their super performance in optoelectronics, catalysis and latent fingermark detections have been demonstrated.

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Pathways of Evolution of Colloidal Semiconductor Magic-Size Clusters and Quantum Dots

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Abstract: Different opinions have been expressed regarding the growth relation of colloidal semiconductor magic-sized clusters (MSCs) and quantum dots (QDs), and how MSCs transform from one type to another. To have a full picture, it is important to understand the chemical reactions that are involved in the pre-nucleation stage of QDs also called the induction period (IP). First, I will present the two-pathway model (Yu) proposed for the growth relation. This model invokes important reaction intermediates, so-called precursor compounds (PCs) of MSCs. In the prenucleation stage of metal (M) and chalcogenide (E) QDs, there are two individual pathways. Metal (M) and chalcogenide (E) precursors self-assemble, followed by the M-E covalent bond formation in each assemble to result in the PC (Pathway 1). Isomerization between the PC and MSC is reversible. Pathway 2 concerns the direct M-E covalent bond formation between the M and E precursors to result in monomers, and the LaMer model of the classical nucleation theory (CNT) describes the combination of the monomers that leads to nucleation and growth of QDs. Second, I will discuss transformations among various MSCs, explaining when step-wise spectral shifts of optical absorption are observed, the transformation pathway is PC-assisted (with monomer substitution or addition). When continuous spectral shifts are seen, the mother cluster directly changes to the daughter cluster. This presentation brings a deeper understanding of the formation and transformation of MSCs and nanoplatelets (NPLs), the difference between nanochemistry and traditional organic and inorganic chemistry, and the confidence that the synthesis of colloidal nanocrystals is transforming from an empirical art to science.

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Gloveboxes – Operation, Maintenance, and Common Misunderstandings

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Abstract: In the last 60 years, gloveboxes with integrated gas purifiers have become more and more important worldwide in applications (R&D and manufacturing) of synthetic chemistry, in the pharmaceutical industry, welding processes, OLED technology, perovskite solar cells, battery technology, and 3D printing, as convenient devices to handle air sensitive compounds (e.g. hydrides, borohydrides, phosphorus halides, and metal-organic compounds), processes, and reactions.[1-4]

It is very important to refine the specifications of the gloveboxes carefully regarding the requirements of the processes being carried out inside and the demands of the users. Often, misunderstandings in choosing the right specifications, or while operating the standard gloveboxes, can result in significant consequences for the equipment itself, as well as anything which is stored or handled inside the glovebox.

While 15 to 20 years ago, the use of volatile chemicals (e.g. organic solvents) inside the glovebox (with gas purifier) was rare and very limited, or done in bare bones "purge boxes",[5, 6] today, many processes which are being carried out inside gloveboxes (with gas purifiers) can require large amounts of organic solvents. Because of this, a well-considered maintenance schedule is required to extend the lifetime of the equipment and to protect the processes and items stored in the gloveboxes.

In this talk, we highlight different examples of common issues our service team has experienced recently and, in the past, independent of the glovebox brand, and caused by misunderstandings, inefficient maintenance schedules, or an unsuitable specification of the chosen glovebox for a specific process. Furthermore, we will propose solutions to avoid these kinds of issues and to extend the lifetime of the equipment.

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Influence of Multidentate Thiol Ligands on the Photophysics of ZnAgInS Quantum Dots

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Abstract: Ternary and quaternary chalcopyrite-type quantum dots (QDs) have meanwhile attracted increasing attention due to their bright, broad, and long-lived photoluminescence (PL) in the visible and near infrared, ease of preparation, and relatively low toxicity.[1,2] Despite emerging applications, e.g., in QLEDs, photovoltaics, and bioimaging, some aspects related to the performance of these QDs are still underexplored such as the influence of the organic ligand shell on QD optical properties. As the PL of ternary and quaternary QDs is determined by defect and trap states, a systematic study of the influence of the chemical nature and denticity of the surface capping ligands could provide insights into the charge carrier recombination dynamics.

In this context, we studied the effect of different commonly utilized mercaptocarboxylic acid ligands bearing one, two, or three thiol groups on the emission characteristics of quaternary nonstoichiometric ZnAgInS (ZAIS) QDs. PL parameters assessed included the spectral position and width of the PL band, PL quantum yield, and PL decay kinetics. In addition, the colloidal stability was examined, as multidentate thiol ligands are expected to provide an improved colloidal stability of the QDs in aqueous dispersion.[3,4] Therefore, ZAIS QDs were synthesized in an organic solvent utilizing oleylamine as a stabilizing ligand, followed by phase transfer into water by addition of different amounts of mercaptopropionic acid (MPA), dihydrolipoic acid (DHLA), and 3-mercapto-2,2-bis(mercaptomethyl)propanoic acid (3MPA). Our results reveal a complex influence of the different ligands on the PL characteristics of the resulting water-dispersible ZAIS QDs. Thiol capping and phase transfer resulted in a loss in PL by at least a factor of 2. The ligand-induced PL quenching observed particularly for ligands bearing two or three thiol groups was attributed to the facilitated formation of surface-bound disulfides.

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Synthesis, Optimization and Characterization of Polymer-Perovskite Nanocrystal Composites

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Abstract: With an ever-growing demand for more efficient and sustainable semiconductor materials, halide perovskite nanocrystals (NCs) have experienced an impressive amount of attention due to their extraordinary optoelectronic properties. Tunable emission wavelengths throughout the visible range, near-unity quantum yields (QYs), ultra-fast radiative decay rates, and facile and low-cost solution-based syntheses render this material class extremely promising for various applications ranging from light-emitting diodes over solar cells to field-effect-transistors and even photocatalysis. Unfortunately, their instability towards high temperatures, light exposure, and moisture delays commercialization.

Thus, we have established a facile, room-temperature synthesis of perovskite NCs based on a library of different block copolymers (BCPs), e.g., polystyrene-b-poly(2-vinylpyridine) (PS-b-P_2VP), that drastically improves their stability towards external, degrading influences while retaining very high QYs.[1,2] The BCPs form reverse core-shell micelles, in which the P_2VP constitutes a polar core and directs the crystallization of the perovskite NC inside the micelle. While it could be argued that the non-conductive PS shell of the micelles might impede the NCs' optoelectronic properties, we could demonstrate Förster resonance energy transfer (FRET) between micelle-encapsulated perovskite NCs of different compositions as well as with anisotropically quantum-confined $CsPbBr_3$ nanocrystals in thin films.[1,3] Furthermore, significant enhancement of photoluminescence QY to near unity and tunability of the emission wavelength of the hybrid system through post-synthetic modification can be achieved. This system was ultimately implemented in a proof-of-concept OLED downconverter device, demonstrating the applicability of highly stable micelle-encapsulated perovskite NCs.[2] Currently, "single-micelle-spectroscopy" at low temperatures (down to 9K) is employed to elucidate the excitonic fine-structure of the encapsulated nanocrystals to further the understanding of their basic properties and thus further improve the optoelectronic properties of this promising hybrid system.

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Effect of a Redox-Mediating Ligand Shell on Photocatalysis by CdS Quantum Dots

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Abstract: Semiconductor quantum dots (QDs) are efficient photoredox catalysts due to their high extinction coefficients and easily tunable band edge potentials. Despite the majority of the surface being covered by ligands, our understanding of the effect of the ligand shell on photocatalysis is limited to steric effects. We hypothesize that we can increase the activity of QD photocatalysts by designing a ligand shell with targeted electronic properties, namely redox-mediating ligands. Herein, we functionalize our QDs with hole-mediating ferrocene (Fc) derivative ligands and perform a reaction where the slow step is hole transfer from QD to substrate. Surprisingly, we find that a hole-shuttling Fc inhibits catalysis, but that dynamically bound Fc ligands can promote catalysis by surface exchange and creation of a more permeable ligand shell. Despite poor catalytic behavior, a hole-shuttling Fc confers much greater stability to the catalyst by preventing a build-up of destructive holes. Conversely, we find that trapping the electron on a ligand dramatically increases the rate of reaction. These results have major implications for understanding the rate-limiting processes in charge transfer from QDs and the role of the ligand shell in modulating it.

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Light Harvesting Studies with Indium Phosphide Quantum Dots

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Abstract: Indium phosphide quantum dots (InP QDs) have emerged as a practical alternative to traditional Cd and other toxic metal based QDs because of their environmentally benign nature.[1] Our group is interested in replicating the fantastic light harvesting properties of traditional QDs in InP QDs, as well as demonstrating advanced properties. With this in mind, we have developed water-stable and highly luminescent InP QDs emitting from the pure-blue to red region of the spectrum, by fine-tuning the kinetics of the core as well the shell growth (Fig. 1a). In one study, the superior photostability of InP QDs over organic dyes was used for the photoregulation of electron and energy transfer processes, this led to the creation of high-contrast multicolor luminescent patterns from a single QD nanohybrid film (Fig. 1b).[2] In another set of studies, the surface of the InP QDs was appropriately functionalized to achieve Förster resonance energy transfer (FRET) process. In one example, ~60% efficient FRET process was demonstrated in all-QD based donor–acceptor system comprising of electrostatically bounded [-] InP/ZnS QD:::[+] CuInS2/ZnS donor:::acceptor complex (Fig. 1c).[3] In another example, we have expanded the range of solar spectrum in FRET studies by developing highly luminescent pure-blue emitting InP/ZnS QD, with an absolute quantum yield of ~50 % and a colour purity of ~80 % (CIE 0.16,0.15) in water.[4] Installing a favourable electrostatic interaction turned out to be crucial in achieving an efficient FRET process (~75%) from blue-emitting InP/ZnS QDs to rhodamine B dye (Rh B). Thus, the demonstration of interaction driven FRET in environmentally friendly InP QDs is fundamentally intriguing, and can have far reaching applications in the areas of biophysics as well as light harvesting devices.

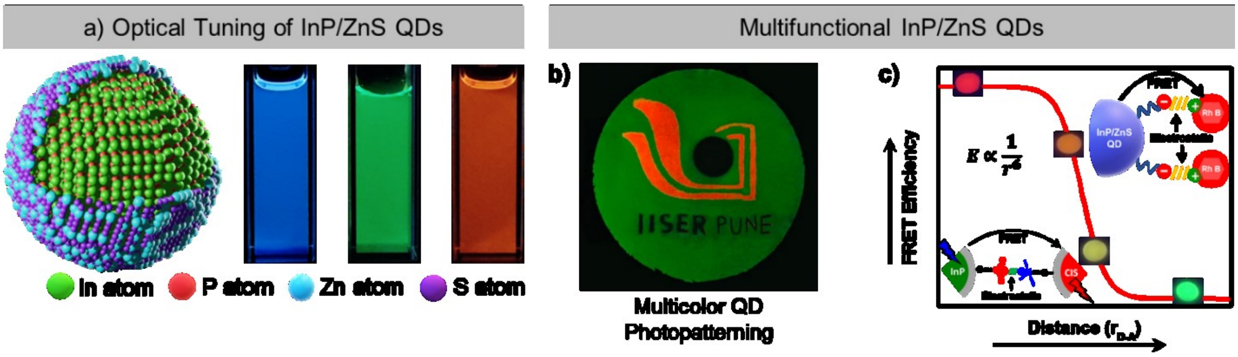

Fig. 1. (a) Optical tuneability, (b) high-contrast multicolor luminescent patterning, and (c) electrostatically driven FRET in InP QDs based hybrid systems.

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Quantum Confined Stark Effect of Spontaneous Local Charges on Cdse/Cds/Zns Colloidal Quantum Dots

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Abstract: Colloidal quantum dots (QDs) exhibit unique optical properties such as a tunable emission color, sharp emission peaks, high luminescence efficiency with a high photostability. This makes them ideal for their use in nanocrystal displays as a source of monochromatic red, green and blue light. Local charges on the QD surface, which develop spontaneously under working conditions, can significantly affect their performance. They cause, for example, spectral diffusion.1 In this work, we study the effect of fluctuating local charges on single CdSe/CdS/ZnS colloidal QDs at room temperature with high time and spectral resolution using time correlated single photon counting (TCSPC) in combination with an electron multiplying CCD (EMCCD). We identify moments of strong surface charges from the resulting slower QD emission with a redshifted and broadened spectrum.2 These changes to the QD emission properties, termed the Quantum Confined Stark Effect (QCSE), are caused by the polarization of the exciton wavefunction by a spontaneous local charge.2 Surface charges appear to have no significant influence on the biexciton emission efficiency. Yet, they introduce a fast component in the photoluminescence decay and a slightly reduced total intensity. These changes in the emission dynamics indicate changes in the excited-state decay pathways. We study the origin of these observations by varying the frequency and power of the laser pulses.

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Colloidal Control of Branching in α-MnS nanocrystals and the Related Magneto-optical Properties

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Abstract: During the colloidal syntheses of metal chalcogenides, various branched nanostructures (BNS) of nanoflowers[1], tetrapods[2], octopod[3], nanourchin[4] morphologies are observed. These BNS possess large surface-to-volume ratio, exposed edges, and geometrical uniqueness that allow capturing photons from a wide range of angles and impart long exciton lifetime for efficient charge transport for optoelectronic, catalysis, and sensor-based applications.[2] It is, thus, significant to decipher their formation mechanism to tailor-make them to study their magneto-optical properties for dedicated applications.

The fundamental pathway to branching and assembly in metal chalcogenides was found such that a during the synthesis, a fast and burst nucleation of magic clusters partially passivated by ligands and (in some cases) having surface moieties of relics from precursor molecules (like acetates) due to partial ligand exchange. These clusters undergo selective adhesion at their naked surfaces to reduce the surface energy and eventually assemble into various morphologies units.[5]

Manganese(II) sulfide (MnS) (VIIB-VIA group) has gathered attention for being a non-toxic P-type semiconductor with a wide bandgap range (Eg ~ 2.7 – 3.7 eV) and promising potential applications in catalysts, supercapacitors, blue/green light emitters, and buffer layer in solar cells.[6] The α-MnS polymorph in its bulk form is para-magnetic (PM) at room temperature and antiferromagnetic (AFM) below its Neel temperature (154 K).[6] However, the magnetic properties of the bulk can be modulated by shrinking the crystals to the nanometric scale and playing with various branched morphologies. Our work deals with colloidally synthesizing various branched morphologies of α-MnS, elucidating the underlying formation mechanism, and studying their morphology-dependent magneto-optical properties.

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Dipolar ligands tune plasmonic properties of ITO NCs

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Abstract: Surface modification through dipolar molecular layers is a well-studied strategy to tune the electronic band structure alignment in semiconductor films and colloidal quantum dots. 1-3 Nevertheless, the influence of surface modification on plasmonic nanocrystals (NCs) and their properties remains largely unknown. In this work, we functionalize tin-doped indium oxide (ITO) nanocrystals via ligand exchange with a series of cinnamic acids with different electron withdrawing and donating dipolar characters. The electronic properties of the modified-ITO NCs are investigated via ultraviolet photoemission spectroscopy, which results in the withdrawing (donating) ligands producing an increase (decrease) in work function, that agrees with reported literature on quantum dots and semiconductor films. The plasmonic properties are studied by extinction measurements of the modified-ITO NCs and analyzed using the heterogeneous ensemble Drude approximation model, which extracts quantitative optoelectronic parameters such as free electron concentration and electron-accessible volume fraction.4 Our results demonstrate that using this type of surface modification induces an anticorrelated trend between the parameters of interest mentioned above, which is not achievable by synthetic methods.4,5 Furthermore, this trend can be reproduced with simulations that can identify that the changes happening in the plasmonic properties are tied to shifts in the band bending at the material's surface. This study shows that using a surface modification approach with ITO NCs produces a new post-synthetic tunability handle of the plasmonic properties that cannot be achieved via previously studied synthetic methods, which could be useful to optimizing the performance of these materials in optoelectronic applications, sensing, and catalysis.

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Bench Stable Phosphorus Precursors to Indium Phosphide Quantum Dots

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Abstract: Quantum dots are semiconductor nanoparticles with size-tuneable emission, currently employed commercially in high-end displays.[1] Indium phosphide has emerged as a popular alternative to cadmium chalcogenide quantum dots (CdSe, CdTe), due to its comparatively lower toxicity. However, a historic challenge of indium phosphide quantum dots is overcoming the need for highly pyrophoric and hazardous precursors for their preparation (e.g. $P(SiMe_3)_3$).

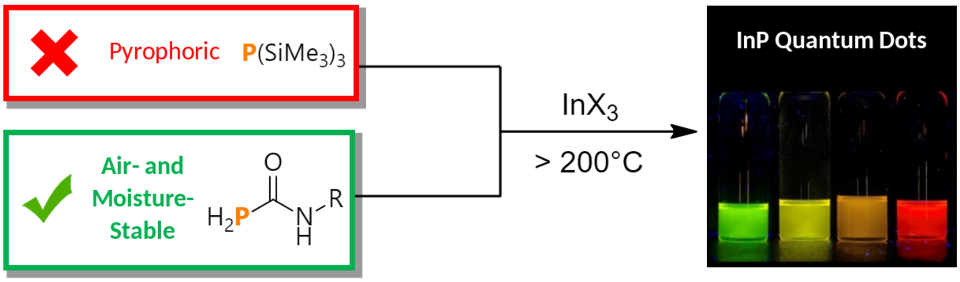

Figure 1. Phosphorus precursors to indium phosphide quantum dots.

We recently reported the synthesis of air- and moisture-stable primary phosphinecarboxamides,[2a–c] which are easily derived from primary amines and isolated on the gram-scale. Of these, the protic phosphinecarboxamide ($H_2PC(O)NH_2$) has been used as a phosphorus source in chemical vapor deposition of zinc phosphide thin films.[3] Inspired by this, we have now found that phosphinecarboxamides are viable phosphorus sources in the preparation of indium phosphide quantum dots. We reveal that they act as a 'masked' PH_3 source, supplying reactive phosphorus species in solution upon heating. By preparing a variety of phosphinecarboxamides, with bespoke side-chain functionality, we have investigated their role in quantum dot formation. This talk will present our development of primary phosphinecarboxamides as an unprecedented class of bench stable phosphorus precursors for the preparation of indium phosphide quantum dots.

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Line Broadening in NMR Spectroscopy of Colloidal CaS Nanocrystals

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Abstract: Alkaline-earth chalcogenides (AECs) are composed of a IIa metal (Mg, Ca, Sr) and S or Se (X), feature large bandgaps positioned in the UV and are commonly used as hosts for emissive ions. AEC nanocrystals could therefore be used as UV emitters, or scatter-free emitters based on lanthanide ions. Moreover, while most AEC crystallize in the rocksalt structure, MgX can also be grown as zinc blende crystals with lattice parameters that come close to those of commonly examined and used IIb-VI chalcogenides or III-V pnictides, such as CdSe and InP. Hence, AECs could extend the range of materials to form core/shell heterostructures out of these compounds. However, such implementations of AECs are hampered by the limited knowledge of the colloidal synthesis and the surface chemistry of these compounds. NMR and infrared spectroscopy revealed that ~12 nm large CaS nanocubes, synthesized with calciumoleate and diphenylthiourea in an amine mix,[1] are terminated by a densily packed oleate ligand shell. This dense shell is represented by broad NMR resonances and spectral hole burning demonstrates that very fast T_2 relaxation lies at the basis of this homogeneous broadening due to lack in local rotational mobility of the individual ligands. Addition of extra carboxylic acid induces a reorganization of this dense packing at the NC surface. Apart from providing detailed insight in the surface chemistry of CaS NCs, this work shows that known approaches and concepts to analyze and rationalize the interaction between colloidal nanocrystals and surface-active ligands can be extended to other colloidal systems.

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Synthesis of Strong Coupled Au@Ag@mSiO$_2$ Nanorattles and J-Aggregates as Ultra-Efficient SERS-Tags

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Abstract: trong-coupling regime between excitons and photonic cavities have been extensively used in energy collection, catalysis, or optical communication applications.[1,2] However, minor work has been focused on the exploitation of the strong coupling phenomenon for Surface-enhanced Raman Scattering spectroscopy (SERS).[3,4] In this work, we explore the performance of strong-coupled hybrid nanoparticles (NPs) composed of plasmonic NPs and J-aggregates as SERS nanoprobes with enhanced colloidal stability. Reported plexcitonic NPs often present limited colloidal stability. In order to overcome this issue, we have developed a plexcitonic NP via the encapsulation of J-aggregates inside a nanorattle comprising an Au@Ag nanorod inside of a mesoporous silica capsule (Au@Ag@mSiO$_2$ nanorattles) (Figure 1). The strong coupling response has been analysed by UV-vis-NIR absorption spectroscopy (Figure 1). Since the J-aggregates can act as Raman reporters, we evaluate the performance of the J-aggregate doped Au@Ag@mSiO$_2$ nanorattles for SERS study. The results have shown that these strongly coupled SERS-tags could improve the limit of detection by around two orders of magnitude in comparison to traditional SERS-tags. Besides, these results are in agreement with electromagnetic simulations. Finally, the high efficiency of the strongly coupled SERS-tags has been also demonstrated via SERSTEM analysis.[5]

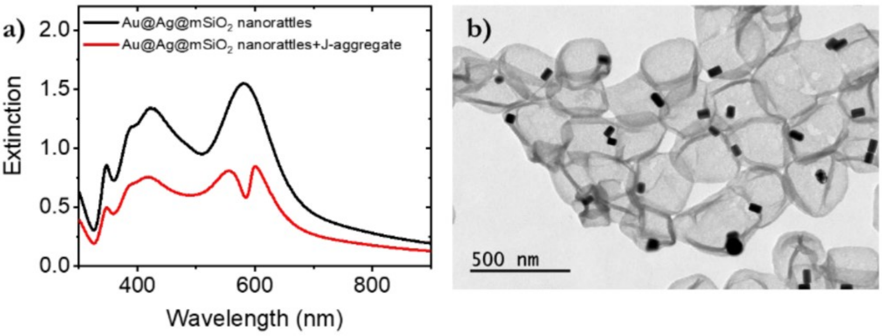

Figure 1.a) Extinction spectra of the Au@Ag@mSiO$_2$ nanorattles (black) and Au@Ag@mSiO$_2$-J-aggregate hybrids (red). b) TEM image of the Au@Ag@mSiO$_2$ hybrids.

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Morphological Tuning of Carbonate-Silica Biomorphs Using Bovine Serum Albumin

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Abstract: Micrometric and nanometric control over morphology and texture of inorganic crystalline materials it's a hot trend of the current research.[1] About that, "carbonate-silica biomorphs" are self-assembled microstructures composed by nanocrystals of carbonate (aragonite, strontianite and witherite), that growth in a highly oriented fashion in a silica matrix, displaying a biomimetic and non-crystallographic shape, as worms, sheets, and helixes, which resembles the one of living organisms.[2] Currently, the mineralization of a selected morphology is still challenging, since a lot of different shapes appear in a single reaction batch, without a control over the number, the dimension, and the forms of the micro-assemblies. In this study, we report that bovine serum albumin (BSA) demonstrated to have a big control over the precipitation process of witherite-silica biomorphs: the presence of the protein in solution inhibited the mineralization of classical carbonate-silica biomorphs morphologies, whereas the selective synthesis of new anisotropic microstructures, with a jellyfish-like shape (Figure 1), was observed at water-air interface. A high-resolution morphological evaluation and chemical characterization was performed by SEM-EDS analysis. Also, a mapping of the complex, but well-organized, distribution of the protein content was obtained through scanning fluorescence confocal microscopy analysis of biomorphs grown in presence of BSA labelled with a fluorescent molecule (Rhodamine B). This study demonstrated that proteins could act as promising additives to tune the morphology of aggregates based on nanocrystals, promoting a different organization of the crystals in the space.

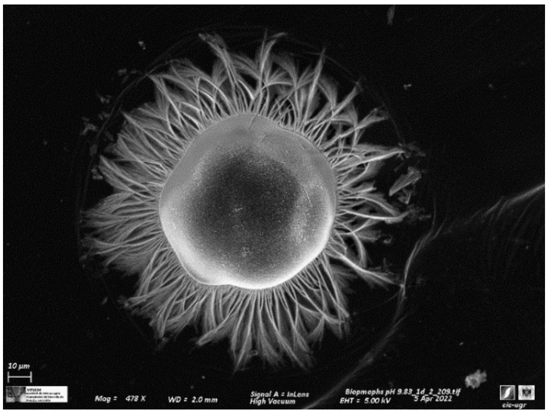

Figure 1. SEM picture of jellyfish-like biomorphs

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Exploring the Bifunctionality of Capping Agents in the Formation of Bimetallic Nanocrystals

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Abstract: Colloidal synthesis of multi-metallic nanocrystals (NCs) is inherently challenging due to the increasing complexity encountered, when expanding the synthetic landscape to reach morphologically and structurally engineered NCs. These multi-dimensional synthetic challenges both relates to the increasing number of potential chemical interactions and byproducts, the varying chemical properties of the metal ion precursors, and to the additives often introduced to promote morphological control such as capping agents.[1,2] Although capping agents are commonly believed to provide size and shape control through preferential adsorption on the NC surfaces during nucleation and growth, changes in the ligand environment of the metal ion precursors resulting from interactions with the capping agents have also been found to influence the final NCs.[3-6] Consequently, capping agents provide a bifunctional way of not only tuning the NC morphologies, but also the resulting structures by impacting the early formation kinetics before metal nuclei formation. To benefit from this bifunctional role, extensive studies are required to provide insights into how the competition between several functional groups and the different metal ions comes into play and reflects in the resulting size, shape and structure of multi-metallic NCs. Through a one-pot synthesis, we provide new insights into the influence of capping agents on the formation of bimetallic AuCu, AuPd and PdCu NCs by combining *in situ* X-ray total scattering with microscopy and spectroscopy. Ultimately, it is directly shown how system-specific side reactions and the local metal ion coordination environment can be used to selectively tune the formation kinetics and thereby tailor bimetallic NCs.

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Removal of Starting Ligand Shell Reduces Cation Impurities And Improves Luminescence of $CuInSe_2/CuInS_2$ Nanorods Produced by Cation Exchange

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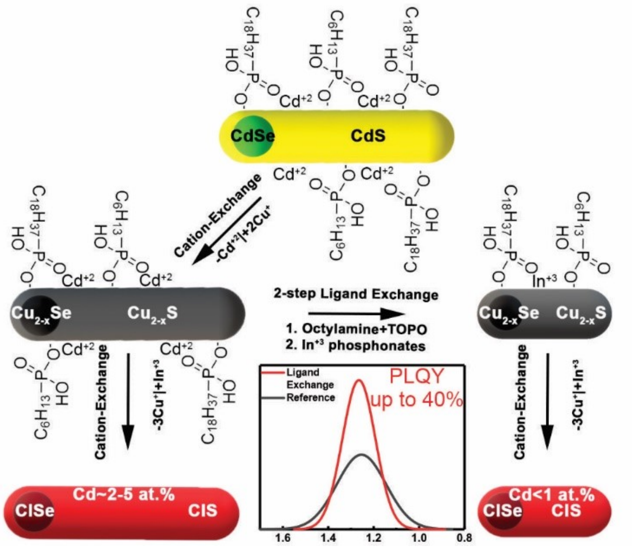
Abstract: Cation-exchange procedures involving a metal-to-copper intermediate exchange step are considered an efficient tool when it comes to preparing chalcogenide nanocrystals of a certain crystal structure and shape, which are not accessible by direct synthetic means. While highly conductive ionic character of Cu-based chalcogenides allows for rather facile and complete exchange of copper for the desired metal, cation-containing Z-type ligands inherited from starting material may cause contamination of the final product. Here we examined the influence of ligand shell of the intermediate copper chalcogenides on composition and optical properties of $CuInSe_2/CuInS_2$ nanorods produced from Cd-ones. Cadmium phosphonates were identified in the ligand shell of the $Cu_{2-x}Se/Cu_{2-x}S$ nanorods, which are the main source of Cd (~5 at.%) in the composition of $CuInSe_2/CuInS_2$ after the final cation-exchange step. Ligand exchange with octylamine and trioctylphosphine oxide results in removal of phosphonates and reduces Cd content below 1%, while subsequent Z-type ligand recovery with indium-phosphonates enhances the PLQY from 20-30% up to 34-40%, rendering them the brightest anisotropic ternary near-infrared luminophores.



Computational Design of Surface Capping Ligands for Colloidal Lead Halide Perovskite Nanocrystals

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Abstract: Versatile surface functionalization of highly ionic surfaces, ubiquitous among inorganic nanomaterials, remains a formidable challenge in view of inherently non-covalent surface bonding. Colloidal lead halide perovskite nanocrystals (NCs), which are of interest for classical and quantum light generation,[1,2] are a prominent example.[3] One of the reasons is a limited atomistic understanding of the NC-ligand-solvent interface. We would like to present how classical molecular dynamics simulations can be used in combination with experimental techniques to aid in understanding surface chemistry of ionic nanomaterials and to guide experimental discovery of new better capping ligands. In particular, we will present the first structural investigation of perovskite NC surfaces capped with zwitterionic phospholipid molecules. Combined computational and experimental evidence suggests that the phospholipid ligands bind to the surface of the NCs with both head-groups by displacing native ions of the perovskite. The ligand head-group affinity to the surface is primarily governed by a geometric fitness of its cationic and anionic moieties into the surface lattice sites. As a result, stable and colloidally robust nanocrystals of inherently labile hybrid perovskites – $FAPbX_3$ and $MAPbX_3$ (X – Cl, Br, I) – can be obtained for the first time with a lattice-matched phosphoethanolamine head-group. Stable surface passivation enables excellent optical performance of the NCs. As an example, alkylphospholipid-capped $FAPbBr_3$ NCs display stable emission with a near-unity photoluminescence quantum yield in a broad concentration range, as well as in thick films. Ligand tail engineering, on the other hand, allows diverse surface functionalization of the NCs, broadening the scope of their potential applications.

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Thin Film Plasmonic Supercrystals

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Abstract: Supercrystals of gold nanoparticles (AuNP) with diameters > 20 nm exhibit interesting optical properties. The periodic arrangement of the AuNP within the supercrystals leads to new well-defined collective plasmon-polariton modes and with tailored geometries even deep strong light-matter coupling at room temperature is possible.[1] To observe and study these phenomena a precise control of supercrystal geometry is crucial. The synthesis of such quasicrystalline supercrystals with large domain sizes will be explained and discussed.[2,3] The supercrystals with a well-defined layered structure are studied with transmission electron microscopy, small-angle X-ray scattering and X-ray cross-correlation analysis.[4] The enhanced near-fields in the supercrystals can be utilized, for instance, for surface-enhanced spectroscopies.[5] The tunable geometry of the supercrystals directly translates to tailored optical properties and in the future new materials and structures can be explored.

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Interconversion of CdSe Magic-Sized Clusters of Different Morphologies

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Abstract: Colloidal semiconductor nanocrystals, or quantum dots (QDs), show promise as next-generation emitters for their size-dependent optoelectronic properties and solution processability.[1] However, even high-quality QD ensembles display heterogeneity at the atomic level,[2] making widespread integration of QDs into these applications challenging. Magic-sized clusters (MSCs) – kinetically stable intermediates of a single size along the QD reaction potential energy surface – present an intriguing opportunity to design identical emitters with atomic precision. Over the past decade, two classes of CdSe MSCs have been disclosed: one class is cation-rich with a zincblende crystal structure, while the other is stoichiometric with a hypothesized "wurtzite-like" lattice. While single crystal XRD structures have been published of both cation-rich and stoichiometric MSCs in recent years,[3,4] many fundamental questions relating to their synthesis, structural differences, and conversion mechanisms remain. Here, we demonstrate that both cation-rich and stoichiometric CdSe MSCs can be synthesized from identical reagents and can be interconverted through the addition of either excess Cd or Se precursor. The structural and compositional differences between these two families can then be easily contrasted using a combination of ^{1}H-NMR spectroscopy, XRD, ICP-OES, and transient absorption spectroscopy, demonstrating that the stoichiometric cluster indeed has a wurtzite-like crystal structure. Then, the trajectory that the clusters follow in their conversion into larger nanocrystals is shown to be distinct and dependent on stoichiometry. This work not only helps simplify the complex picture of the CdSe nanocrystal landscape, but also provides a method to tune QD properties through atomically precise synthesis.

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Electric Field Induced Color Switching in Colloidal Quantum Dot Molecules at Room Temperature

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Abstract: Colloidal semiconductor quantum dots are robust emitters implemented in numerous prototype and commercial optoelectronic devices.[1–3] However, active fluorescence color tuning, achieved so far by electric-field induced Stark effect, has been limited to a small spectral range, and accompanied by intensity reduction due to the electron-hole charge separation effect.[4,5] Utilizing quantum dot molecules that manifest two coupled emission centers,[6] we present a novel electric-field induced instantaneous color switching effect. Reversible emission color switching without intensity loss is achieved on a single particle level, as corroborated by correlated electron microscopy imaging. Simulations establish that this is due to the electron wavefunction toggling between the two centers dictated by the electric-field and affected by the coupling strength. The quantum dot molecules manifesting two coupled emission centers may be tailored to emit distinct colors, opening the path for sensitive field sensing and color switchable devices such as a novel pixel design for displays or an electric field color tunable single photon source.

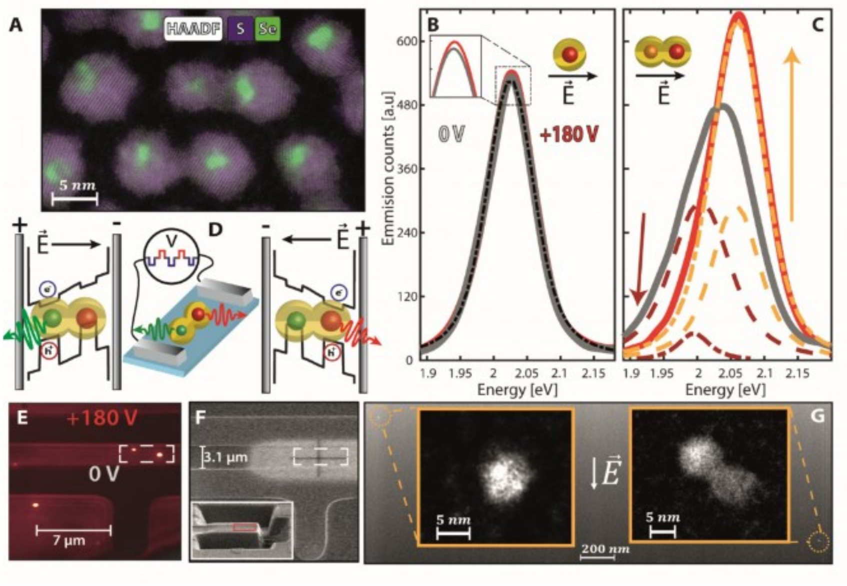

Figure 1. Optical and STEM measurements of CQDs with electric field modulation.
a, Typical dimer sample HAADF and elemental analysis from Energy-dispersive X-ray spectroscopy (EDS) of Selenium (green) and Sulfur (purple), showing the core/shell structure. (full elemental analysis in Supplementary Fig S1). Dimer-CQDM to mono-QD percentage in the sample is roughly 85%/15%. b-c, Photoluminescence emission energy spectra from a 2-minute measurement for each particle, with (red) and without (gray) an E-field. The mono-QD PL is fitted by a single Voigt function with a FWHM of 87±3 meV, while the CQDM can only be properly fit by 2 separate Voigt peaks (dashed, red peak = 2005±6 /FWHM=100±10 meV, green peak = 2057±3 /FWHM=88±5 meV, for grey line). d, Schematic mechanism of a color switching CQDM device, the CQDM is exited and generates single photons from both color centers of the system (center). When an external electric field is applied, excitons

are pushed to the QD opposing the field direction. e, Optical widefield PL image showing the exited CQDs from B-C (white dashed rectangle) between two electrodes. The outer electrodes are also designed with ruler marks to later correlate optical with electron microscopy structural measurements. f, SEM image of the same area as in E. The desired area is coated with a protective layer and then cut out of the device (insight), to produce a lamella which is put on an electron microscope grid. g, HAADF image of the area of interest shown in E-F, (dashed white rectangle). Two NCs are shown in close up- correlated with the right part of the optical image in (b), showing a single CQD (left) and a fused CQDM (right). The direction of the E-field is also shown in white.

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A Nanocrystalline ZnO-Wood Composite Obtained by CVD

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Abstract: Wood is a renewable and CO_2-storing material with excellent mechanical properties. To further promote its more widespread use, however, it is necessary to enable wood with new functions, such as electrical conductivity. This is especially interesting in view of "green electronics" applications. Piezoelectric,[1] triboelectric,[2] electroluminescent[3] and electrically conductive[3] wood materials have already been the subject of studies in our group. Regarding electrical conductivity, it is noteworthy that for wood this has mainly been achieved at the surface level. Achieving bulk electrical conductivity is challenging due to the complex hierarchical wood structure.

Here, we used an atomic layer deposition (ALD) approach to deposit a 100 nm thick homogeneous ZnO coating inside delignified spruce. ALD allowed us to not only reach the entire bulk open porosity, but also to accurately control the layer thickness of the ZnO layer inside the wood matrix. Using X-ray diffraction, the crystallite size was estimated to be well below 10 nm. The resulting composite not only is conductive, but also shows pronounced photoconductivity. Upon prolonged irradiation with UV light, the conductivity of the material increased by three orders of magnitude and decreased very slowly once the irradiation was stopped. Removing the wood matrix by thermal degradation resulted in a detailed ZnO replica of the wood scaffold.

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A Single 2D Particle For Bicolor Down Conversion

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Abstract: Two-dimensional nanoplatelets (NPLs) of II-VI semiconductors present the narrowest optical features among nanocrystals, explaining their increasing interest in optoelectronics applications, especially inside displays. In this domain, a major challenge is to generate white light. In the state-of-the-art Quantum Liquid Crystal Displays, it is obtained through the use of blue light-emitting diodes that pump a blend of red and green down-converters to finally obtain white. Despite being widely used today, this method suffers from a major drawback as the optical properties of those two different emitters need to be resistant to their integration into the device. Using a unique particle with two emissions would thus drastically reduce the incorporation and compatibility issues.

While a myriad of studies has been carried out to modulate the emission wavelength of II-VI NPLs, a few have been focusing on the elaboration of bi-emitting nanocrystals from those 2D materials. Starting from the classic CdSe 4.5 ML that emits in the green, the chemist can use various strategies to generate a second red emission thanks to the versatility of those objects. For example, one can dope the material using metallic cations[1] or create core-crown heterostructures.[2] In particular, by engineering the band alignment of the crown, type II interfaces can be obtained inducing a second red-shifted emission.[3] In this work, we present a clever way to obtain bi-emitting nanocrystals through the band engineering of II-VI NPLs.[4]

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Tuning the optical properties of cadmium chalcogenide nanoplatelets via changing their surface and core composition

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Abstract: Cadmium chalcogenide nanoplatelets (NPLs) exhibit superior properties if compared with nanocrystals of other dimensionalities. They arise from the strong confinement in only one direction and the ability to control NPLs' thickness with the precision down to one monolayer resulting in narrow absorption and emission lines. Over the years, it became possible to prepare NPLs with various compositions, thicknesses and absorption and photoluminescence bands lying across the whole UV−visible range. However, the ability to control NPLs' thickness in only integer increments prevents continuous tailoring of their optical features with the precision achieved for other nanocrystals.

In this presentation several strategies for the manipulation of NPLs' optical properties will be discussed. Firstly, the exchange of native carboxylates with other ligands (i.e., thiols or phosphonates) was shown to significant shift the position of optical bands for up to 240 meV. With the help of X-ray diffraction such shifts were shown to be connected with the distortion of crystalline lattice of the core. However, while extending the optical range covered by NPLs, ligand exchange is still not enough to afford continuous tunability. Another more powerful and flexible approach consist in the modification of nanocrystal composition through the synthesis of alloyed NPLs. Recently, we presented a new approach to the synthesis of alloyed NPLs by employing highly reactive stearoyl chalcogenides as sulfur and selenium sources. Unlike previous procedures for the synthesis of similar NPLs, our method enables straightforward and precise tuning of the NPLs composition and hence the position of their absorbance and photoluminescence bands.

Combining Plasmonic Single-Domain Supercrystal And Microfluidics For Highly Sensitive And Selective SERS Detection

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Abstract: Surface-enhanced Raman scattering (SERS) substrates have the potential for a wide range of applications in sensing and detection due to their ability to enhance the Raman signal of molecules mainly due to the presence of strong electromagnetic fields generated after the plasmon excitation. Moreover, this effect could be more intense in the case of plasmonic supercrystals due to antenna effects. However, developing SERS substrates faces several challenges such as achieving homogeneous and reproducible enhancement, these need to be overcome to develop reliable and reproducible substrates for use in real-world applications.

Herein, we demonstrate how the employment of microfluidic platforms allows to generate gold plasmonic supercrystals through the slow pervaporation of the solvent of a colloidal dispersion of gold nanooctahedra (**Figure 1A-B**). The characterization of the formed supercrystals reveals a single-domain supercrystal with dimensions of 1.7×0.3 mm^2, and that all the obtained supercrystals present the same orientation. Furthermore, the integration of a plasmonic supercrystal inside a microfluidic platform guarantees the infiltration of any analyte, even without affinity for gold surface, within the plasmonic supercrystals and therefore its ultrasensitive detection. The study of the sensing capabilities of these platforms showed a highly uniform and intense SERS activity, being both key parameters to achieve quantitative and ultrasensitive analysis (**Figure 1C-E**). In fact, a limit of detection of 10^{-19}M was achieved for crystal violet. Also, the possibility of combining the capabilities of our SERS sensor with the chromatographic properties of silica nanoparticles to develop a sensor device with charge selectivity was investigated (**Figure 1D**).

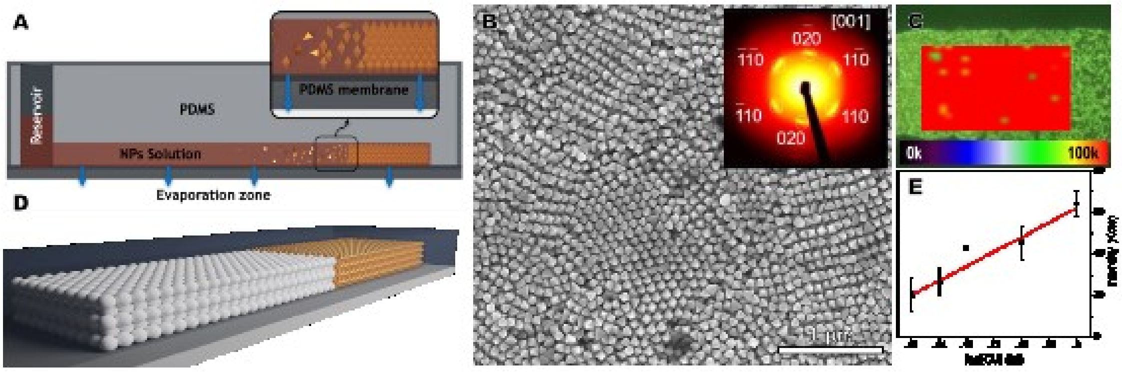

Figure 1. (A) Schematic illustration of self-assembly of gold octahedra nanoparticles inside microfluidic platform induced by pervaporation. (B) Scanning Electron Microscopy (SEM) image of the supercrystal. Inset corresponds with 2D-SAXS images with the indexation of the strongest Bragg peaks. (C) SERS intensity map obtained at 1617 cm-1 in the presence of 10-7 M of crystal violet. (D) Schematic representation of the final SERS Sensor modified with a silica supercrystal for chromatographic separation. (E) SERS intensity obtained for different concentrations of crystal violet (10-9 - 10-15 M).

Ultrathin Colloidal QDs Optoelectronic Devices For Ultrafast Photodetection And Light-Emitting Diodes

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Abstract: Colloidal quantum dots (QDs) are considered as a rising candidate for new-generation electronics, due to their unique properties, such as tunable bandgap, narrow emission bandwidth, and cost-effective solution processing. However, ultrafast response and super bending resistance are still two obstacles which prohibit the application of colloidal QDs in real-time diagnosis, high-speed communication, and wearable devices.

Here, we design ultrathin structure for colloidal QDs photodetector, which shows the record 2.8 ns response time for ultrafast photodetection in PbS QDs system, record super stability under 100,000 repetitive bending cycles in flexible QDs devices, and the internal quantum efficiency of 100% at short-wave infrared (SWIR) region. We also get 50 ns response time of light-emitting diode (LED) by applying this structure, this is the fastest LED at SWIR region.

Moreover, formation of high-quality PN junction and inhibition of capacitance effect in ultra-thin devices are also proposed in this work. This work demonstrates the ultra-high performance in ultra-thin devices, and shows this structure has the bright future in ultra-fast and ultra-bending resistance colloidal QDs optoelectronics.

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Cooperative dynamics of DNA Grafted Magnetic Nanoparticles: Implication In Magnetic Biosensing And Functionalization of DNA origami

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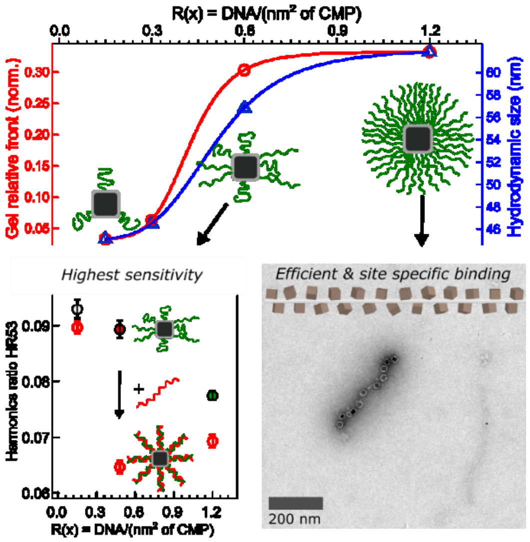
Abstract: Magnetic nanoparticles (MNPs) enable unique capabilities for biosensing, actuation, and functionalization of DNA nanostructures, yet how DNA grafting density affects their dynamics and accessibility remains poorly understood. Here, we demonstrate clickable magnetic nanoparticles (CMPs) offering copper-free click chemistry conjugation as a highly versatile nanoplatform to tune the grafting density of ssDNA over a broad range. We show that magnetic relaxation, hydrodynamic, and electrophoretic dynamics of CMP-DNA conjugates change in a cooperative manner in response to ssDNA grafting, which can be described by a Hill equation. Whereas at low grafting density the ssDNA strands are coiled on CMPs and minimally influences the dynamics of CMPs, at high grafting density they form dense polymer brushes and cooperatively change the dynamics of CMPs. Exploiting our CMPs as nanomarkers for magnetic-based biosensing, we find that CMP-DNA conjugates at the ssDNA grafting density corresponding to the midpoint of the Hill equation reveal the largest magnetic signal change upon hybridization to the target sequence. We propose that the ssDNA strands are in a mixture of coiled and brushed states at the intermediate grafting density. This configuration leads to high accessibility to the complementary sequences and the largest change in magnetic relaxation dynamics of particles upon duplexing with the target. In addition, we demonstrate coupling of our CMP-DNA conjugates to six- (6 HB) and 24-helix-bundle (24 HB) DNA origami structures. We find that high ssDNA grafting density favors binding to DNA origami structures with high efficiency and site specificity.



Remote Activation of a Prodrug Converting Enzyme By Magnetic Heating

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Abstract: In this study, we have synthesized nanohybrids that allow for remote activation of a therapeutic enzyme for its use in Directed Enzyme Prodrug Therapy (DEPT). By using biomimetic silica as an entrapment matrix, magnetic nanoparticles (MNPs) were co-encapsulated with horseradish peroxidase (HRP) to form nanosized hybrids (nHs) for targeted tumor therapy. The MNPs respond to alternating magnetic fields (AMFs), becoming local hotspots, which triggers an increase in the bioconversion rate of HRP matching the activity displayed at its optimal temperature without altering the temperature of the reaction media. HRP converts indole-3-acetic acid (3IAA) into tumor cytotoxic peroxylated radicals. This demonstrates for the first time that nanoactuation is possible for an enzyme not directly attached to the MNPs.

We also identified the spatial location of each nH's component and found that the silica matrix played a critical insulating role in introducing remote control over HRP. In vitro assays using a human pancreatic cancer cell line (MIA PaCa-2) showed that only upon exposure to AMFs and in the presence of 3IAA, the therapeutic enzyme triggered cell death. Additionally, in vivo experiments demonstrated higher reductions in tumor volume growth in animals treated with the therapeutic enzyme in the presence of the prodrug and exposed to AMFs.

This work demonstrates the feasibility of developing a spatiotemporally controlled strategy for targeted tumor therapy using thermophilic enzymes, which can overcome the unwanted activation of mesophilic ones, currently the preferred choice for this therapy. Overall, these nanohybrids represent a promising approach for targeted and controlled tumor therapy.

Synthesis of InAs Colloidal Nanocrystals Using a Pre-Activated Arsenic Precursor

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Abstract: Indium arsenide (InAs) colloidal nanocrystals (NCs) are attractive materials for optoelectronic devices due to their large absorption coefficient and wide bandgap tunability, which ranges from the visible to the short-wave infrared region.[1] As the size uniformity and tunability are crucial for various applications, there is a need for a development of arsenic precursors having appropriate reactivity. Precursors with too high reactivity can result in quick depletion of the monomer and inhibition of NC growth,[2] and precursors with low reactivity often requires an additional activation source during NCs synthesis.[3]

Here, we propose a pre-activated arsenic precursor with moderate reactivity made from the reaction between amino-arsine and a reducing agent. The activation of As can be controlled by selecting a reducing agent with proper reactivity and heating temperature. Since activation can be achieved only through heating, the pre-activated arsenic precursor is easy to handle and store at room temperature. Consequently, this pre-activated arsenic precursor can be used directly in InAs NC synthesis under various reaction conditions and process methods, such as hot injection, heating up, and continuous injection. We anticipate that this precursor will enable the widely tunable, large-scale synthesis of InAs NCs.

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Aptamer-modified Prussian blue nanoparticles as means to Improve Nanozyme Activities

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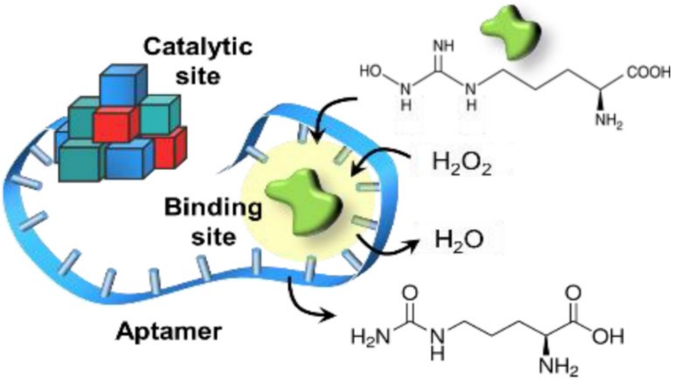
Abstract: Nanomaterials mimicking natural enzymes, nanozymes, posse several distinct advantages over natural enzymes as well as other reported artificial enzymes, such as higher operational stability and sensitivity to environmental conditions. As a result, there has been a significant interest in using them for diverse applications. However, different from natural enzymes, nanozymes do not have an active site composed of a binding pocket and a catalytic unit that cooperatively lead to superior catalytic activities.

Aptamers are sequence-specific nucleic acids exhibiting selective binding properties towards low molecular weight substrates and macromolecules to which a catalytic unit can be tether. In this work the covalent linkage of aptamer binding sites to nanozymes, "aptananozymes", is introduced as a versatile method to improve the selectivity and catalytic activity of nanozymes by concentrating the reaction substrates at the catalytic nanozyme core, thereby emulating the binding and catalytic active-site functions of native enzymes. The concept was exemplified with the synthesis of Prussian blue (PB) nanozymes, functionalized with the L-hydroxy arginine binding aptamer for the H_2O_2-mediated oxidation of N-hydroxy-L-arginine to L-citrulline. The aptananozymes reveal enhanced catalytic activities as compared to the separated catalyst and respective aptamer constituents.



Schematic model of the catalytic "aptananozymes"

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Synthesis of Air-Stable and Full Color-Emitting ZnSeTe/ZnSe/ZnS Quantum Dot by Utilizing Simple Surface Chemistry

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Abstract: Next-generation high-performance displays will be made using quantum dots with adjustable band gaps because of their superior optical properties and ease of processing in solutions. However, high-performance QLEDs with heavy metal-free QDs are urgently needed for more eco-friendly display technology. Sufficient lifetime and EQE that are extremely near to the theoretical maximum were attained in red and green InP-based LEDs.[1,2] Since it is difficult to cover the blue region with InP QDs, however, an alternative is required. Although ZnSeTe semiconductor QDs recently obtained extremely high photoluminescence quantum yield (PL QY) and EQE, the well-known extremely toxic hydrofluoric acid (HF)-based synthesis of ZnSeTe/ZnSe/ZnS QDs makes it difficult to commercialize.[3] In addition, PL QY in ZnSe/ZnSe/ZnSe/ZnS QDs is rapidly reduced under ambient conditions despite the existence of double shells due to fast oxidation, which could be caused by facile desorption of the surface ligands.

We developed a non-toxic synthetic method that fully eliminated toxic HF to synthesize ZnSeTe/ZnSe/ZnS heterostructure QDs appropriate for QLED applications. Instead of HF, excessive metal halides were introduced, and PL QY was shown to be substantially greater. Also importantly, we first demonstrate highly stable ZnSeTe/ZnSe/ZnS QDs in both solution and solid state through a very simple surface chemistry including ligand exchange that enables stronger surface binding via thiolate functional groups. Finally, by synthesizing these stable QDs with a broad color spectrum extended from green to red, a new possibility for full-color QD display materials was demonstrated.[4]

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Size- and Shape-Tuned InAs Synthesis From Aminoarsine Precursors

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Abstract: Colloidal InAs quantum dots (QDs) recently stand out as an infrared-active material for next-generation optoelectronic applications in the near-infrared (NIR) and short-wave infrared (SWIR) wavelength. However, despite the significant development of their implication for optoelectronic devices, the creation of a well-defined InAs QDs of various sizes and shapes remains challenging.

One state-of-the-art synthetic method uses acid-free and non-hazardous materials to create oxidation-free and halide-amine co-passivated surfaces, resulting in tetrahedral-shaped III-V QDs.[1] The size and shape of colloidal semiconductor QDs are known to play a significant role in their optoelectronic properties, with surface properties contributing as well.[2] However, previous attempts to synthesize tetrahedral-shaped InAs QDs have resulted in unclear shapes, facet heterogeneity, and surface defects, hindering comprehensive understanding of their electronic structure and surface properties.[3]

To address these issues, we have synthesized tetrahedral InAs QDs in sizes up to the first excitonic absorption feature of 1500 nm, achieving fine edges in various sizes through modified synthetic methods using aminoarsine precursors.[4] We have also studied the reaction parameters for size control and polydispersity, as well as the shape evolution. By carefully selecting and purifying QDs of various sizes, we have studied their size-dependent electronic transitions through surface passivation, which could lead to further development of their surface chemistry.

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Investigating the Temperature-Induced Structural Evolution in Cu_xAu_{1-x}-PbS Metal-Semiconductor Core-Shell Nanoparticles

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Abstract: Nanoparticles can be used as tunable precursors capable of evolving into bulk materials with specific structural features under proper reaction conditions. In this approach, the characteristics of the nanoparticles can determine the processes that occur, such as sintering solid-state reactions, melting, etc., during the transformation into bulk materials, determining the final structure and composition. Using nanoparticles as precursors have yielded unique nanocomposites with record performances in, e.g., thermoelectrics;[1-2] however, the full potential of the approach requires a better understanding of the transformation nanoparticles undergo under reaction conditions. Especially considering there is still much unknown due to the fact that when nanoscale systems are subjected to external stimuli, such as temperature, their behavior can vary substantially from that of bulk systems. Hence correlation between nanoparticle properties and final solid characteristics cannot be established, making the approach based on pure serendipity. In this study, we shed some light on this problem by focusing on a particular material system and studying the temperature-induced transformation by *in situ* high-resolution transmission electron microscopy. In particular, we investigate core-shell NPs in which the core is constituted by Au or Au-Cu alloys and the shell is PbS. The work presented here focuses on comprehending the structural evolution of these metal-semiconductor core-shell structures when heated and understanding the core-composition-induced differences. While this system refers to a very particular combination of materials of interest in thermoelectrics, it establishes a proof of concept on the unique diffusion mechanism that can be tailored at the nanoscale when a high degree of control is obtained at the nanoparticle level.

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Ligand-mediated Formation of 3D Organized Assemblies of Nanocrystals

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Abstract: Colloidal nanocrystals self-assembled into 2D or 3D superlattices can present collective phenomena, with prospects to be exploited among others in electronics, catalysis, and optics. Such assemblies have been produced mostly by destabilization of the colloid by controlled solvent evaporation or nonsolvent addition. Herein we propose a new approach to prepare 3D organized assemblies, supercrystals, of different types of nanocrystals through the interaction between the nanocrystals and the precursors present in the solution. We tracked the formation of these assemblies during the reaction and gained insight into the mechanism by performing *in situ* small-angle x-ray scattering (SAXS) measurements. Our experiments reveal that an excess of metal-oleate forces the nanocrystals to assemble into high-quality supercrystals rapidly. We show that the assembly can happen directly during the synthesis of the nanocrystals. Additionally, we show that this approach can be generalized to different kinds of nanocrystals, such as PbSe, PbTe, PbTe@PbS, and Au.

Atomic Structure and Trap States in Single CdSe Colloidal Nanoplatelets by Low-Temperature Scanning Tunneling Microscopy

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Abstract: CdSe nanoplatelets (NPLs) contain many surface traps caused by crystal defects and unsuccessful passivation between organic ligands and surface atoms. Trap states provide pathways for non-radiative Auger recombination that is harmful to NPL-based optoelectronic devices.[1] On the other hand, trap states also play a positive role in improving the on/off switching ratio in resistive random access memories[2] and field-effect transistors for data storage.[3] Therefore, it is necessary to intensively study trap states in single NPLs at the nanoscale. Here, we use low-temperature scanning tunneling microscopy (LT-STM) and spectroscopy (LT-STS) to study the morphological and electronic properties of single CdSe (4.5 ML) NPLs. We provide the 3D-STM images of single CdSe NPLs that showed their long edges are truncated, and most surface traps concentrate near the NPL edges. The STS measurements on individual NPLs provide in detail the electronic band structure of the NPLs, especially the position of hole and electron trap states with respect to the Fermi level. The STM measurements allows for investigating the current fluctuations over time through individual trap states.

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Energy Transfer in Magic-Sized $(CdSe)_{13}$ Clusters Doped with Single Mn^{2+} Impurites and Mn^{2+} Pairs

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Abstract: $(CdSe)_{13}$ magic-sized clusters (MSCs) represent a material class at the boundary between molecules and quantum dots. Due to strong quantum confinement, the electron-hole exchange interaction is significantly enhanced in these clusters, resulting in the emergence of a pronounced excitonic fine structure. Chemical synthesis allows the replacement of single atoms of the host crystal by individual Mn^{2+} ions. These individual dopants strongly change the optical properties of the clusters, as their ligand-field states reside within the band gap of the host semiconductor. Since the incorporation is limited to two atoms per cluster, this material class enables the differentiation of the energy transfer from exciton fine structure states to single Mn^{2+} dopants or to coupled Mn^{2+}-Mn^{2+} pairs, respectively. A comparison of photoluminescence excitation (PLE) data and absorption measurements indicates a pronounced difference in the energy transfer efficiency from the individual exciton fine structure states to the Mn^{2+} dopants. Probing the Mn^{2+} luminescence in MSCs as function of excitation energy for various dopant concentrations, we demonstrate a distinctly different energy transfer mechanism to a single Mn^{2+} ion and to Mn^{2+} ion pairs, respectively, which can be attributed to a change of the selection rules for Mn^{2+} pairs. Furthermore, the PLE data exhibit higher ligand field states that exhibit specific fingerprints for single Mn^{2+} ions and Mn^{2+} pairs. These different fingerprints can be explained by considering spin ladder formation of the ground- and excited states due to the Mn-Mn coupling.

Combined Optical and Atomic Force Microscopic Investigation of Type-I CdSe/CdS Dot-in-Rod Particles with Metal Tips

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Abstract: In order to become independent of fossil fuels in the near future, scientists are focusing on the production of hydrogen, which can be obtained by splitting water through illumination with semiconductor-metal-hybrid nanostructures as photocatalysts. Here, understanding and controlling the charge-transfer processes within such nanostructures is crucial for further development.[1]

We investigate hybrid nanostructures consisting of a CdSe-core/CdS-shell dot-in-rod nanoparticle with a metal tip attached. Optical characterization is performed by time-resolved single-particle photoluminescence (PL) spectroscopy. Thereby, the attachment of the metal tip can be correlated with the decrease in quantum yield (QY) and PL lifetime of the semiconductor, giving detailed information on charge-carrier separation.[2]

We present an all-in-one setup that combines PL spectroscopy to kelvin probe force microscopy (KPFM) with simultaneous local illumination of the nanostructure. KPFM is based on an atomic force microscope (AFM) with a conductive cantilever and provides information about the local surface potential by measuring the contact potential difference (CPD) between the sample and the AFM tip. This requires a transparent substrate with a back-gate on which markers can be generated using electron beam- or optical-lithography. The combination of optical and KPFM techniques allows the study of energy-band profiles and the generation of charge-carriers and their concentrations.

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Electrospinning And Electrospray as Versatile Tools For Improving Encapsulation Processes

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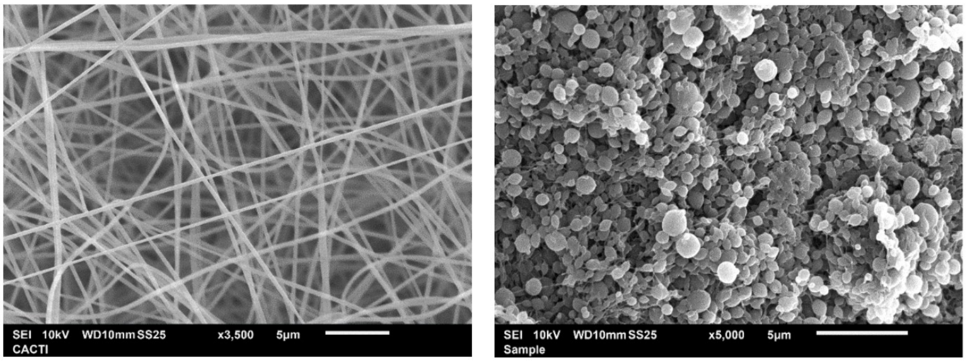
Abstract: Nowadays, electrospinning and electrospray are considered one of the versatile techniques for the manufacture of nanofibers and polymeric nanospheres, respectively. Both techniques are based on the application of a strong electric field on a polymer solution, injecting a charge of a certain polarity onto the needle that dispenses it and accelerating it towards the collector with the opposite polarity. The property that characterizes these two types of structures is their porosity, which can change according to the parameters applied in its production.[1]

Using the same setting, with only the modification of two parameters, structures with different properties are obtained. The use of polymers with a lower molecular weight and the application of a higher electric field will lead to obtaining polymeric nanospheres. However, the combination of polymers with a higher molecular weight and a weaker electric field will result in the assembly of nanofibers that will form a membrane.

The systematic study of these parameters allows us to take advantage of the high capacities of these systems with the aim of creating a versatile tool for optimizing catalytic and encapsulation processes, which can be used in applications such as drug delivery and therapy.[2]



SEM images of nanofibers (left) and nanospheres (right) formed by polyvinyl alcohol (PVA)

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Telluride Quantum Dots and Molecular Inks for Phase Change Memory Applications

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Abstract: A structural change between amorphous and crystalline phase provides a basis for reliable and modular photonic and electronic devices, such as non-volatile memory, beam steerers, solid-state reflective displays or mid-IR antennas. The most studied phase change materials fall within the pseudobinary tie line of GeTe and Sb_2Te_3. Aside from Sb, doping GeTe with other p-block and transitional metals has been shown to improve power efficiency, induce faster crystallization, and enhance phase-contrast during switching. Furthermore, recent theoretical studies have proposed dozens of new phase change materials with improved properties enabling multibit data storage, sub-nm crystallization, and a number of more earth abundant compositions. Testing these materials experimentally requires high-throughput synthesis and device fabrication.

Wet chemistry has shown great versatility for the synthesis of inorganic nanomaterials followed by cost-effective liquid-based device fabrication methods. Here, we leverage the benefits of liquid-based synthesis to access phase-change memory materials in the form of colloidally-stable nanoparticles or molecular inks. We report several approaches, which enable all phase change materials to be prepared in the liquid. For example, our amide-promoted synthesis unlocks a wide library of ternary M-Ge-Te colloids (where M is e.g., Sn, Bi, Pb, Co, Ag, Sb or Cu). Nanoscale amalgamation reaction allows reaching the non-equilibrium Sb-rich bimetallic compositions. Finally, thiol-amide co-solvent method brings ternary M-Sb-Te materials to the liquid phase, including prototypical Ge-Sb-Te as well as highly performing Sc-Sb-Te phase-change materials.

Our solution-based engineering approach offers a generalizable platform for materials development and their rational choice through the studies of structure and dynamics of liquid-borne phase change nanomaterials. We report some outstanding characteristics, such as high reflectivity contrast between amorphous and crystalline phases or composition dependent crystallization temperature offset compared to the bulk. Using solution-based deposition, we realize nonvolatile reflective images, electro-optical devices, and nonvolatile electrical devices, offering a proof-of-concept for liquid-borne phase-change applications. Finally, ternary telluride nanomaterials, reported here, are of high demand beyond the phase-change applications, including thermoelectrics, IR-photodetectors, ferroelectrics, and energy harvesting applications.

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Ligand on Nanocrystal Surfaces, a Solution NMR Perspective

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Abstract: Surfaces are an integral part of colloidal nanocrystals (NCs). Hence, understanding the binding and packing to NC surfaces of organic ligands, which are often used to stabilize NC colloids, is an essential aspect of the formation of NCs with desired chemical or physical properties. Since NCs lack a unique structure, not a single analytical technique can provide a complete description of the chemistry of NC surfaces. Even so, solution 1H nuclear magnetic resonance spectroscopy stands out as a unique method to study the organic ligand shell for its capability to distinguish between surface bound species and surface inactive residues from NC synthesis and purification.

In this presentation, we discuss the surprisingly detailed picture solution NMR can provide of the NC surface chemistry, with an emphasis on ligand shell heterogeneity. In a first part, we show how ligand displacement reactions indicate the presence of different binding sites at the NC surface, as characterized by a widely different binding energy. In the case of CdSe NCs in particular, weak and strong binding of ligands could be related to edge-localized and facet-localized sites, respectively. Interestingly, such a diverse set of binding sites leads to bunching of ligands on specific facets, while other facets remain nearly uncovered; a point in line with the frustrated exchange of linear versus branched ligands.

In a second part, we focus on the resonance shape as a source of information on ligand packing. Two examples that illustrate this point are the relation between linewidth and ligand solvation, where better solvated ligands yield more narrow resonances, and the possibility to identify different parts of the inhomogeneously broadened resonance with ligands bound on different locations at the NC surface by means of spectral hole burning. Interestingly, such results question the limits of NC size and ligand packing density at which the current bound-ligand paradigm - modest inhomogeneous broadening - will break down. Building on this question, we outline directions for further research.

Band Gap Engineering in Zn/CdSe - CdS Dot-Rods: Transition From Type-II to Type-I Structures by Gradual Cation Exchange

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Abstract: The adjustment of the energetic band alignment in semiconductor dot-in-rod heterostructures (DRs) is crucial for their electronic and optical properties. While in type-I CdSe/CdS DRs the photogenerated electrons and holes are mainly localized in the CdSe-core, a strong charge separation is expected for type-II ZnSe/CdS DRs, where the electron is more strongly localized on the elongated CdS-shell. Here we show that the first step in a typical synthesis of ZnSe/CdS DRs is a partial cation exchange of Zn- vs. Cd-cations, which effectively reduces the type-II band offset of the conduction bands. Moreover, we show that an initial injection of Cd-precursors followed by a delayed addition of S-precursors during CdS-shell growth allows to adjust the degree of cation exchange within the core, to effectively tune the band-offset between core- and shell material.

We will show that this band gap engineering in Zn/CdSe-CdS DRs can change the fluorescence lifetime at room temperature from 150 ns for zero delay between Cd- and S-injection, to 60 ns for 1 min delay, while the lifetime of pure CdSe/CdS-DRs is 30 ns. The low-temperature PL-dynamics of the various samples can be explained by different decay channels due to a change in the electronic level structure. Finally, the fluorescence spectra of individual Type-I/II DRs at 10 K show a systematic change of electron-phonon coupling upon different degrees of cation exchange. All the data is explained based on self-consistent COMSOL-simulations to calculate the expected degree of charge carrier localization in the core- and shell-region of the DRs.

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Quasi-Reversible Photoinduced Displacement Of Aromatic Ligands From Semiconductor Nanocrystals

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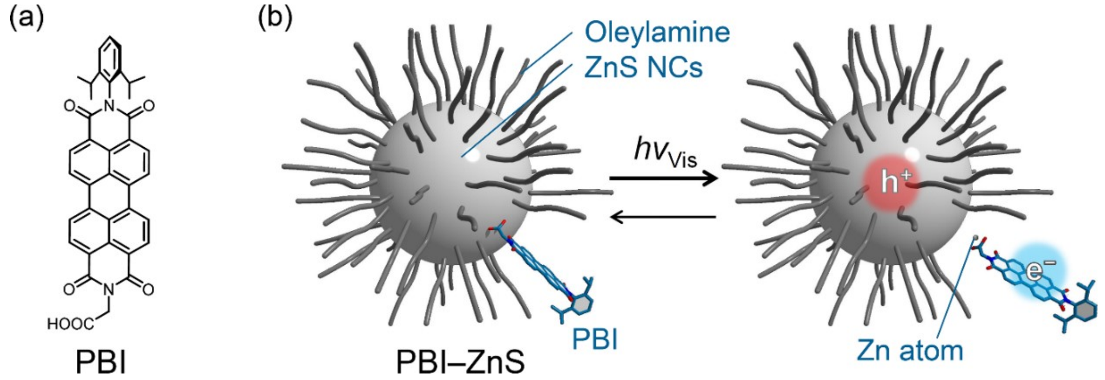
Abstract: Organic-inorganic nanohybrids using semiconductor nanocrystals (NCs) coordinated with aromatic organic molecules have been widely studied in the fields of optoelectronic materials, such as solar cells, photocatalysis, and photon upconversion. In these materials, coordination bonds of ligand molecules are usually assumed to be stable during optical processes. However, this assumption is not always valid. In this study, we demonstrate that the coordination bonds between ligand molecules and NCs by carboxyl groups are displaced quasi-reversibly by light irradiation using zinc sulfide (ZnS) NCs coordinated with perylenebisimide (PBI) as a model system.[1] Time-resolved spectroscopy over a wide range of time from tens-of femtosecond to second timescales and density functional theory calculations show that the photoinduced ligand displacement is driven by ultrafast hole transfer from PBI to ZnS NCs, and that the dissociated radical anion of PBI survives over the second timescale. Photoinduced ligand displacements are important to be considered in various organic-inorganic nanohybrids and offer a new possibility of NCs covered by non-photoresponsive organic ligands for advanced photofunctional materials.



(a) Molecular structure of PBI and (b) schematic of the quasi-reversible photoinduced displacement of PBI coordinated to the surface of ZnS NCs. It is noted that PBI is supposed to be bound to the surface of ZnS NCs as a carboxyl anion, and the theoretical calculations suggest that the radical anion of the PBI is displaced with the nearest Zn atom.

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Tunable Magnetism in 2D Semiconductor Nanostructures

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Abstract: Magnetism has been a topic of broad interest since the discoveries of motors/generators, through magneto-resistance, and up to modern times, where low dimensional materials offer support for new magnetic phenomena. The talk will focus on the influence of magnetic moments and magnetism on the magneto-optical properties in materials with reduced dimensions, exposing the influence of magnetic doping, intrinsic anisotropic effects and long-range magnetic order, with further details as below.

Magnetic self-doping in II-VI colloidal quantum dots: magnetic dopants endow the interaction between their unpaired spins and the photogenerated carriers, leading to a giant magnetization and excion's g-factor. This interaction is identified by implementing the optical detected magnetic resonance method, deepening the understanding of surface properties.

Long-range magnetic order in metal phosphor tri-chalcogenide compounds: Metal phosphor tri-chalcogenides with the general chemical formula MPX_3 (M=metal, X=chalcogenide) possess ferromagnetic or anti-ferromagnetic arrangement. Most recent magneto-optical measurements will be reported, exposing the dual relation between magnetism and electronic properties.

Intrinsic magnetism in perovskite materials: Perovskite materials are composed of organic-inorganic constituents, forming 2D and 3D structures. The discovery of unique magneto-optical properties in those materials reflects the development of intrinsic effective magnetic poles by the inversion of symmetry breaking (inducing a Rashba effect) or due to the existence of a nuclear field (the so-called Overhauser effect).

Overall, the observations designated a strong influence of magnetic effect on spin and optical properties of low-dimensional semiconductors, significantly impacting their implementation in modern spin-electronics and spin-optical devices.

Electronic and Phononic Dynamics in Halide Based Nanocrystals

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Abstract: Halide based semiconductors have enabled new opportunities for the synthesis of colloidal nanocrystals offering a surprisingly versatile construction kit for tailored optical, optoelectronic and even photo-electrochemical nanosystems.[1] Lead halide based nanocrystals show superb optical emission properties even at room-temperature. Interestingly, a simple two-band model with low effective masses is often sufficient to explain even spin-dependent relaxation phenomena.[2] Meanwhile not only nanoplatelets and cubes but also spherical quantum dots can be synthesized with impressive control leading to well-pronounced excitonic confinement effects.[3,4] Less toxic bismuth-based halide nanocrystals are mostly characterized by indirect band-structures resulting in long lifetimes and occasionally in charge separation favourable for photocatalytic processes. The soft ionic lattice easily couples to optical excitations leading to polaronic effects and in the case of short pulse excitation to the generation of coherent phonons. [5,6]

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Surface Passivation of Intensely Luminescent All-Inorganic Nanocrystals and Their Direct Optical Patterning

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Abstract: Colloidal nanocrystals (NCs) have become indispensable materials in the construction of electronic and optoelectronic devices due to their easy processability, tunable bandgap, precise controllability of components and morphology, and unique optoelectronic properties. The NCs obtained by the classical synthesis method are usually capped with organic ligands with long carbon chains. The poor electrical conductivity of these ligands limits the efficiency of carrier transport, resulting in inefficient related devices. By introducing inorganic ligands to replace the original organic ligands, the electron migration efficiency between the crystals can be effectively improved, but it will greatly affect their optical properties. Therefore, it is important to prepare and precisely assemble all-inorganic materials with high luminescence performance. Based on this, we developed a simple, versatile and mild surface treatment strategy to realize the construction of all-inorganic nanocrystals (ILANs) with high fluorescence quantum yield. The experimental results show that certain metal salts consisting of metal cations and anions without coordination can act as inorganic ligands and play a dual role in the surface treatment of nanocrystals: (i) to remove the original organic ligands and ensure the stability of nanocrystals in polar solvents; (ii) to bind to unpassivated Lewis basic sites (usually non-metallic atoms such as S, Se, etc.) to ensure that the NCs maintain high fluorescence quantum efficiency (PLQY). While the passivation of the Lewis basic sites leads to a high PLQY of ILANs, the exposed Lewis acidic sites provide the opportunity to tune the functions of NCs in situ, creating opportunities for direct optical patterning of functional NCs with high resolution. As a proof of concept, ILANs are being used in a variety of industrially applicable patterning techniques to assemble a variety of precise structures on devices. The new surface chemistry proposed in this work, together with the development of materials adapted to the patterning techniques, creates a versatile platform for building the next generation of nanocrystal-based optoelectronic devices.

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The Extreme Confinement Regime: A Critical Juncture for the Mechanical and Optical Properties of Semiconductor Quantum Dots

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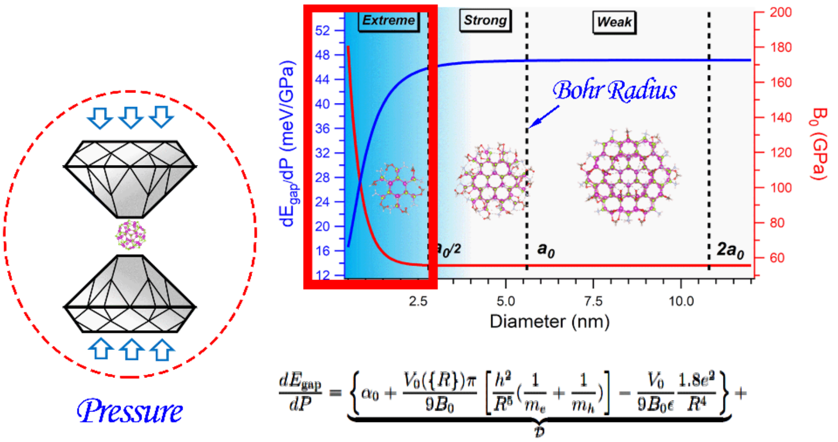
Abstract: The Bohr Radius has long been considered a defining characteristic of conventional quantum dot systems. However, our research demonstrates that as quantum dot size approaches the extreme confinement (EC) regime, the wavefunction becomes more delocalized, leading to the breakdown of the Bohr radius. Through a combination of comprehensive experiments (high hydrostatic pressure absorption and fluorescence spectra) and simulation techniques (density functional theory and molecular dynamics), we show that the EC regime is a critical juncture at which both the mechanical and optical properties of quantum dots differ significantly from conventional expectations. Specifically, the mechanical properties of CdSe quantum dots deviate from bulk values only within the EC regime, where the Brus equation's effective mass approximation is no longer valid. Furthermore, the absorption spectra of CdS clusters become increasingly sensitive to surface chemistry and solvent environments, with varying behaviors observed for the wurtzite and zincblende structures. Our findings provide new insights into how to manipulate wet chemistry synthesis conditions to adjust optical properties while maintaining stability, emphasizing the significance of the EC regime as a fundamental regime for investigating quantum dot/cluster systems.



$$\frac{dE_{\text{gap}}}{dP} = \underbrace{\left\{\alpha_0 + \frac{V_0(\{R\})\pi}{9B_0}\left[\frac{h^2}{R^5}\left(\frac{1}{m_e}+\frac{1}{m_h}\right)\right] - \frac{V_0}{9B_0\epsilon}\frac{1.8e^2}{R^4}\right\}}_{\mathcal{D}} + \underbrace{\left[\frac{h^2}{8R^2}\frac{\partial}{\partial P}\left(\frac{1}{m_e}+\frac{1}{m_h}\right) - \frac{1.8e^2}{4\pi R}\frac{\partial}{\partial P}\frac{1}{\epsilon}\right]}_{\mathcal{U}} + \mathcal{O}(P).$$

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Fusion Chemistry and Electronic Coupling in Coupled Colloidal Quantum Dot Molecules

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Abstract: Colloidal semiconductor quantum dots are robust emitters implemented in numerous prototype and commercial optoelectronic devices. For the next step towards enhancing their functionalities, we introduce the controlled fusion of two core/shell quantum dots creating an artificial molecule manifesting two coupled emitting centers.[1,2] The size effect and mechanism of the fusion reaction reveals an interesting behavior of atomic migration allowing to create a crystalline connection between the two emitting centers.[3] The nature of the fusion interface between the two emission centers is found to strongly affect the optoelectronic characteristics.[4] Accordingly, the coupled colloidal quantum dot molecules (CQDMs) present several novel behaviors differing than their quantum dot building blocks. Firstly, the presence of localized versus segregated charged- and multi-exciton states, the latter states providing elongated lifetimes and enhanced intensity due to the decreased Auger non-radiative relaxation. Secondly, such CQDMs open the path to a novel electric field induced instantaneous color switching effect, allowing color tuning without intensity loss, that is not possible in single quantum dots. Both effects are strongly influenced by the degree and character of fusion within the CQDMs. All in all, such quantum dot molecules, manifesting two coupled emission centers, may be tailored to emit distinct colors, opening the path for sensitive field sensing and color switchable devices such as a novel pixel design for displays or an electric field color tunable single photon source.

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Layered 2D Hybrid Perovskites: Molecular Design and Optoelectronics

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Abstract: Hybrid perovskites like $(C_4H_9NH_3)_2PbI_4$ have fascinating layered crystal structure with periodic nanoscale interfaces between the inorganic $\{PbI_4\}^{2-}$ and organic $C_4H_9NH_3^+$ layers. Because of these nanoscale interfaces, electron and hole are confined in atomically thin $\{PbI_4\}^{2-}$ inorganic well layers. Therefore, these layered perovskites are electronically 2D systems (quantum well), irrespective of their crystallite sizes.[1,2] Importantly, the crystal structure allows numerous combinations of different organic cations and inorganic anions. So a rational molecular design of the nanoscale interfaces, and hence, tunable optoelectronic properties are feasible. For example, if structural non-centrosymmetry is introduced in such semiconductors, then important functionalities like chirality, non-linear optical properties, ferroelectrocity, and anomalous photovoltaic effect can be achieved. In this talk, I will discuss about design principles of achiral and chiral non-centrosymmetric hybrid perovskite single crystals. The key parameter that yields the desired non-centrosymmetric structure is the rationally designed non-covalent (hydrogen- and halogen-bonding) interactions, between the organic cation sublattice and the inorganic $\{PbI_4\}^{2-}$ sublattice.[3] Furthermore, I will also discuss about how non-covalent cation-π interactions between the A-site cations can make low-dimensional hybrid metal halides completely water-stable for years.[4-5]

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Mapping the Energy Landscape from a Nanocrystal-Based Field Effect Transistor under Operation using Nanobeam Photoemission Spectroscopy

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Abstract: Nanocrystals (NCs) have become promising building blocks for cost-effective infrared optoelectronics, as it has been widely demonstrated for different device structures.[1,2] In the design of such devices, the integration of these materials requires a deep knowledge of their electronic structure.[3] For this purpose, in the field of NCs, optical spectroscopy, electrochemistry and X-ray photoemission spectroscopy (XPS) have been widely used, mainly for characterization of the pristine material. Further device optimization requires probing the NCs in their actual environment (surrounded by electrodes, coupled to transport layers, under electric field).

In this work,[4] we explored the use of nanobeam soft X-ray photoemission spectroscopy[5] to investigate a HgTe NC-based field effect transistor, where a split-gate allows the formation of a planar p-n junction.[6] The X-ray beam, focused down to a 700 nm spot, is shone on a sample mounted on a scanning stage, allowing mapping across the position. The setup also allows the application of bias inside the chamber, enabling measurement of the device *in operando*.

We showed that a direct access to the metal-semiconductor interface band bending is possible. Furthermore, through the application of gate bias, we observed a shift in the photoemission spectrum as a result of the electric-field-induced carrier doping and correlated its propagation to the NCs film thickness. The latter is crucial in the design of a device combining both carrier density tunability and light absorption. Finally, we demonstrated the generality of the method by applying it to a different material (PbS NCs) and device geometry.

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Boosting the Photoluminescence Efficiency of InAs Nanocrystals via Wide Bandgap Shell Overgrowth

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Abstract: Colloidal InAs nanocrystals (NCs) are gaining increasing interest as optimal near infrared (NIR) emitters for the next-generation optoelectronic NIR commercial devices.[1] This stems from the fact that InAs NCs are RoHS compliant and their optical bandgap can be tuned from ~700 to >1600 nm. To date, the most developed strategy to synthesize InAs NCs is based on pyrophoric, toxic and costly tris-trimethylsilyl arsine (or derivatives).[2] With the aim of lowering the costs and the hazardousness of InAs NCs' production, in the last few years several less toxic and cheaper As precursors have been explored, with the most promising one being tris(dimethylamino)-arsine (amino-As).[3]

The current challenge to start employing amino-As-based InAs NCs for practical applications is to further improve their optical properties mainly in terms of absorption peak width, photoluminescence (PL) quantum yield (QY) and Auger recombination rate. As regarding the last two points, the best procedure to optimize their PL emission is to coat them with an ad-hoc wide bandgap material capable of growing epitaxially and of forming type-I heterostructures. In this regard, we recently demonstrated an effective amino-As and $ZnCl_2$-based synthesis approach to grow InAs@ZnSe NCs with a PLQY record value of 42% (at ~860nm).[4, 5]

In this work, we pushed forward such synthesis approach with the goal of improving the control over shell growth process. Our optimized procedure allows not only to grow core@shell NCs with shell thicknesses not reached nor studied before, but also to further enhance the PLQY values of amino-As-based InAs@shell NC systems.

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Publishing in Nature Journals: An editor's view

Amos Martinez[#]

[#] Nature Materials

Abstract: I will talk about the process of preparing and submitting scientific papers and provide an editor's perspective on the editorial and peer-reviewing process, briefly discussing what editors look for when making editorial decisions.

High Performance Perovskite Nanocrystals for In-Pixel Color Conversion

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Abstract: The high absorption coefficient and impressive optical emission properties of perovskite nanocrystals are ideal for in-pixel color conversion in display applications. QD-OLED and μLED displays require the emitting layer to transmit <0.1% of the blue backlight – Helio's perovskite nanocrystals can achieve this in films less than 10 μm, while also exhibiting narrow band emission which eliminates the need for color filters. For products to be useful to display manufacturers, they must be resilient to patterning processes (UV-curing and developing with basic aqueous solutions) and have good long-term stability. Perovskite nanocrystals synthesized using proprietary techniques have been used to make red and green color converting films with over 90% Rec2020 coverage without any additional filters. Regarding the green material, we have achieved a PLQY of 84% at a peak wavelength of 532 nm and full width half max (FWHM) of 23 nm; this material shows T90 over 1500h under light and temperature stress. For red, a PLQY of 85% at 634nm and 32nm FWHM has excellent stability with a T90 over 200 h and the test is still ongoing. These measurements have been taken on perovskite nanocrystals incorporated into an acrylate matrix, analogous to the photo-patternable materials used by display manufacturers.

Quantum Dots and Upconversion Nanocrystals for Advanced FRET Biosensing and Bioimaging

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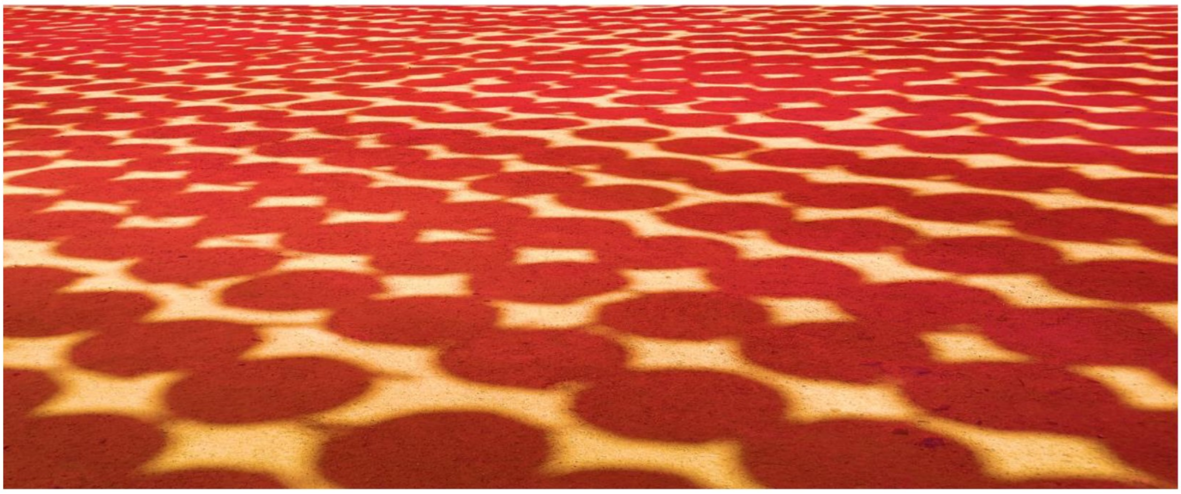
Abstract: he unique photoluminescence properties of semiconductor quantum dots (QDs) and upconversion nanoparticles (UCNPs) are ideally suited for Förster resonance energy transfer (FRET).[1-3] However, FRET is a strongly distance-dependent mechanism that only occurs within a circa 1 to 10 nm donor-acceptor distance range and both QDs and UCNP sizes (~5 to 50 nm in diameter) are everything else but negligible for such FRET distances. Adding biological recognition molecules, such as IgG antibodies (~12 nm in length), to a NP-based biosensing FRET probe can largely exceed the FRET-compatible distance range. Therefore, careful design of QD/UCNP FRET systems and their surfacebioconjugation is paramount for developing efficient biosensors that can fully exploit the photophysical properties of those NPs. I will first explain the FRET-related properties of QDs and UCNPs and then discuss our recent work concerning sensitive and multiplexed FRET biosensors with specifically designed surface coatings and engineered biomolecules for molecular diagnostics and in-vitro/in-vivo imaging.[4-9]



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Aqueous Continuous Flow Synthesis of Highly Luminescent Chalcopyrite Nanocrystals

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Abstract: In recent years the synthesis of ternary chalcopyrite I–III–VI nanocrystals (I: Cu, Ag; III: In, Al, Ga, Bi; VI: S, Se, Te) has drawn a lot of interest due to their outstanding, size- and composition tuneable absorption and photoluminescence properties.[1] They are considered as highly promising candidates for substituting toxic heavy metal containing quantum dots (QDs), such as CdSe, CdTe and PbS. Colloidal syntheses of ternary I–III–VI QDs are most often performed in organic solvents and, therefore, the obtained particles cannot be directly used in biological studies or in photocatalytic reactions taking place in water. Phase transfer from the organic to the aqueous medium involves additional steps and is often associated with a decrease in the photoluminescence quantum yield (PLQY) and colloidal stability. Therefore, direct synthesis in the aqueous phase appears as an appealing alternative. Another important factor when it comes to real-life applications of QDs is the reproducibility of the syntheses and hence the precision with which the optimized optical and electronic properties of the nanocrystals can be achieved when comparing batches. To this end, batch-to-batch variations of the QD quality in terms of emission peak position, line width and PLQY remains problematic due to the high sensitivity of many synthetic schemes to subtle changes in the experimental conditions. Continuous flow chemistry has recently emerged as a promising approach for the precision synthesis of high-quality colloidal QDs.[2] It offers the possibility to produce QDs with a higher reproducibility than batch reactions due to the more precise control of reaction conditions (e.g., heating rates, reaction time, flow rate) through improved heat and mass transfer in small tubular reactors, as well as faster and automated reactions.

We have developed a robust aqueous synthesis method for silver indium sulfide (AIS) core and AIS/ZnS core/shell QDs using continuous flow chemistry.[3] Optimization of the reaction parameters resulted in core QDs with 44% and core/shell QDs with 83% PLQY. By combining structural and optical studies we elucidated the nature and density of defect states involved in the PL emission. The extension of the synthetic approach to other I–III–VI materials will also be discussed.

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Wurtzite InP Nanocrystals Synthesized Via Cation Exchange From $Cu_{3-x}P$: size and Emission Control

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Abstract: Phosphide based nanocrystals, including InP and $Cu_{3-x}P$ are studied extensively in recent years due to their use in various applications for light emitting devices and catalysis. The synthetic design of these materials is limited in terms of size range and homogeneity. The surface of InP is also known to be prone to oxidation and defects that decrease their emission. In this work we report uniform and tunable size control of wurtzite phase InP via cation exchange from $Cu_{3-x}P$. The $Cu_{3-x}P$ nanocrystals (NCs) are synthesized by the formation of metallic Cu^0 NCs and their phosphidation to $Cu_{3-x}P$. By changing the coordination ligands and precursor concentration the NCs size is varied between 5-14 nm. The uniform $Cu_{3-x}P$ are then cation exchanged to InP and by reaction with $NOBF_4$ the photoluminescence quantum yield is increased by impurity removal and surface passivation. The NCs size range is further extended by etching with the $NOBF_4$ reaction to cover NCs diameter down to 4 nm and emission beak at 600 nm. The effect of water, acid, and halides including F^-, Cl^-, Br^- and I^- on the etching and passivation balance.

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Beyond The Sum of Their Parts: Towards Controlling Defect-Related Optical Properties of Self-Assembled Quantum Dot Supercrystals

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Abstract: Nanoparticle supercrystals extend the fascinating properties of colloidal solutions of microscopic quantum dots to the macroscopic realm and are therefore of significant interest for various optoelectronic device applications such as solar cells, LEDs, electro-optic modulators, etc.[1]

We recently reported a study on defect/strain-related optical properties in self-assembled supercrystals of lead halide perovskites. Specifically, reproducibly observed spatial gradients in the photoluminescence energies and lifetimes of CsPbBr2Cl and CsPbBr3 supercrystals were shown to result from a combination of compressive strain, a loss of structural coherence, and an increasing atomic misalignment between adjacent nanocrystals. These findings expand on the idea of quantum dots functioning as quasi-atomic building blocks in the formation of macroscopic superstructures.[2]

The poster will detail the spatially and temporally resolved optical measurements and present current efforts towards achieving precise control over the defect-related optical properties through manipulation of parameters both in the synthesis (particle size distribution, surfactant concentration) and the self-assembly (evaporation-method, -time, -temperature) of the nanoparticular building blocks.

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Self-Trapped Excitons mediated Energy Transfer to Sm^{3+} in $Cs_2AgIn_{(1-x)}Sm_xCl_6$:Bi DoublePerovskite Nanocrystals

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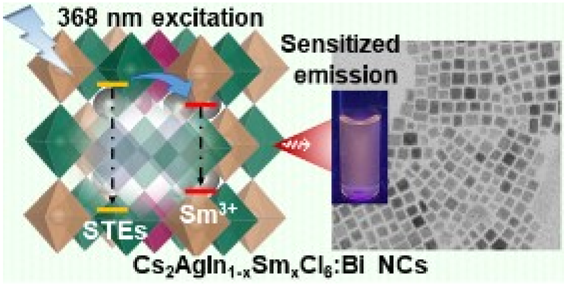
Abstract: Incorporation of Lanthanide ions (Ln^{3+}) in lead-free halide double perovskites has become an excellent strategy to overcome the challenge of weak photoluminescence. However, the excitation energy of Ln^{3+} doped $Cs_2AgInCl_6$ being too high (~250-290 nm) limits its direct excitation by commercial UV light emitting diodes (≥ 365 nm). To overcome this challenge, we employed sensitization technique by codoping Bi^{3+}(~1%) to induce the emission of Sm^{3+} at much lower excitation energy in Sm^{3+}-Bi^{3+} co-doped $Cs_2AgInCl_6$ DP nanocrystals (NCs). Spectral analysis shows that trace amount of Bi^{3+}(~1%) doping provides enhanced dual emission of self-trapped excitons (STEs) and four characteristic emissions of Sm^{3+} assigned to $^4G_{5/2}$ to ^6H_J ($J = 5/2, 7/2, 9/2$, and $11/2$) transitions. We propose a luminescence mechanism to explain the energy transfer pathway in the synthesized system. Our study demonstrates that Bi^{3+} can efficiently sensitize Sm^{3+} to modify the optical properties of lead-free DP NCs to expand their luminescence application.



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Synthesis of Bismuth Based-Perovskite Nanocrystals For CO_2 Reduction

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Abstract: Perovskite nanocrystals (NCs) have been widely considered as promising materials as light-harvesters emitters due to their wide range of benefits combining those of conventional colloidal semiconductor NCs with halide perovskite materials, including tunable bandgap, high absorption coefficients, strong photoluminescence, flexible crystal structure and low fabrication cost due to the processability from solution. Recently, perovskite NCs were successfully used for the photocatalytic CO_2 reduction, however most of them are still based on toxic lead and have limited stability in polar medium used in photocatalysis.[1] Among lead free alternatives, one of the most promising is bismuth halide perovskite $A_3Bi_2X_9$ (A=cation; X=Br, I) NCs combining good absorption in the visible range, higher stability, and much lower toxicity compared to the lead-based counterparts.[2] They can be synthesized using Hot-injection or Ligand assisted reprecipitation (LARP), however numerous challenges still exist, namely to synthesize the NCs with a small controlled size, to properly purify them, and to accurately study their crystalline structure and optical properties.

We have developed a new approach to synthesize air-stable bismuth halide perovskite NCs in ambient conditions with a high reaction rate using cesium halide NCs as the templates.[3] By optimizing synthesis protocols, we managed to obtain air-stable $Cs_3Bi_2Br_9$ and $Cs_3Bi_2I_9$ NCs of around 10 nm with a good size dispersion. In addition, by a modified hot-injection method using various ligands we have synthesized $Cs_3Bi_2I_9$ nanoplatelets under ambient condition. Synthesis details, structural and optoelectronic properties will be discussed, as well as their perspectives for the photoelectrocatalytic CO_2 reduction application.

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Polymer-Coated Magnetic Nanocrystal Hydrogels And Aerogels: A Universal Approach

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Abstract: The assembly of inorganic nanocrystals (NCs) into macroscopic self-supported networks, either hydrogels or aerogels, constitute a new interesting type of materials characterized by their low density, large specific surface area and open porous structure.[1] Therefore, in these materials it is possible to exploit the nanoscopic properties of the building blocks in the macroscopic scale, either preserving these properties or exhibiting collective properties that are not present neither in the NCs alone nor in the bulk material. In particular, magnetic nanocrystal (MNC) based gels are of special interest because it is possible to exploit synergistically the nanoscopic magnetic properties of the MNC building blocks (e.g. superparamagnetism) with that of the gels and they can be manipulated by external magnetic fields.

In this work, firstly we present a successful and universal gelation procedure which allows to obtain highly porous hydrogels and aerogels regardless of the NC composition, size or shape.[2] For that, an amphiphilic polymer coating strategy[3] is used prior to gelation, to perform the water transfer of the NCs avoiding ligand exchanges. The water transfer is necessary to obtain the hydrogels, interesting for biomedical applications, and ligand exchanges could cause undesirable changes in the NC surface and therefore in their properties. Finally, the obtained polymer-coated MNC-based gels are shown in detail, focusing on their fabrication, structural and magnetic characterization (Figure 1). The importance of the structure and the magnetic interactions between the NCs in the final gel properties will be highlighted and different applications will be discussed.

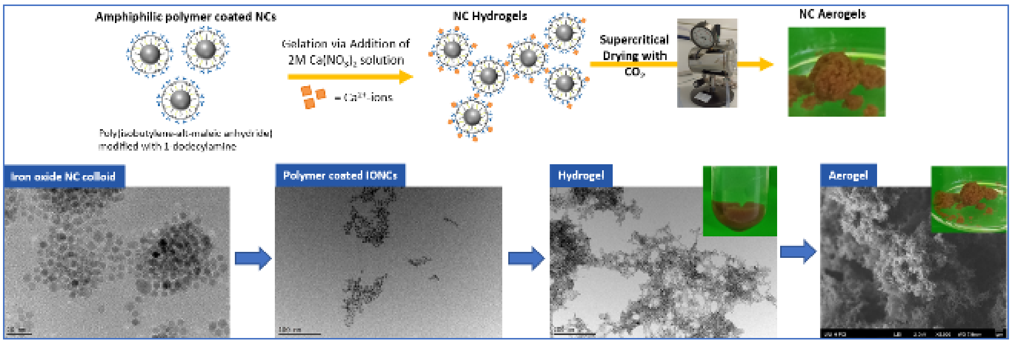

Figure 1. Scheme of the polymer-coating strategy and formation of the hydrogels and aerogels (top). TEM images of the γ-Fe2O3 NC colloid, polymer-coated γ-Fe2O3 NCs, hydrogel and SEM of the aerogel (bottom).

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Aqueous Synthesis of Advanced CeO_2-Based Nanostructures

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Abstract: Nanosized cerium oxide (CeO_2, a rare-earth semiconductor) is known for its oxygen storage capacity. It allows the material to work as an oxygen buffer, extending its applicability both in the nanocatalysis field for oxidation reactions; and in biomedicine, where it is manly used as ROS scavenger and holds great potential as modulator of oxidative stress in living organisms.[1] This work presents the optimized formulation of colloidal CeO_2 nanocrystals, the mechanistic description of the synthetic process and its key parameters to attain the production of the minimal stable size for monocrystalline colloidal and biocompatible nanoparticles, their complete physicochemical characterization and the extension of the material's functionality through two derivation strategies: lanthanide doping (Yb^{3+}, Er^{3+}) and hybridization to plasmonic metals (Au and Ag)[2] via different synthetic approaches to produce several types of hybrid architectures (core-shell, heterodimers, hollow structures, trimers, etc…) of controlled size. To assess the prospects of these materials as nanocatalysts, their catalytic activity has been tested for different processes[3] such as the degradation of organic dyes, CO_2 reduction, and H_2O_2 degradation among others. Finally, the origin of its oxygen storage capacity has been described through the characterization of the Ce 3*d* and O 1*s* spectra in XPS and Ce L_3 edge in XANES, where, notably, no Ce^{3+} states paired to the presence of oxygen vacancies have been recorded.[4]

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Ligand Exchange Quantification on Colloidal III-V Quantum Dots

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Abstract: The implementation of III-V colloidal quantum dots (QDs) in optoelectronic devices is rapidly increasing due to their unique photophysical properties. While the implementation of In-based III-V semiconductor materials such as InAs and InSb colloidal QDs in optoelectronics requires a deep understanding of their surface binding motif, less studies have paid considerable attention to revealing the surface chemistry of this group of binary quantum dots compared to the more prevalent II-VI and IV-VI groups. Among those few studies, an acid-based mediated ligand exchange[1] has been previously reported for tetrahedrally-shaped InAs QDs by introducing the surface to aliphatic acids, resulting in partial replacement of the surface by the conjugate bases in an X-for-X manner. In this regard, we have applied the same mechanism to further analyze the surface chemistry of IR-active InAs and InSb colloidal QDs. It turns out that introducing the surface of such QDs to an alkanethiol (Dodecanethiol) and a carboxylic acid (Undecylenic acid) leads to different surface reactions due to different surface terminations of each QD type, which has been validated by a series of H-NMR spectra as well as X-ray photoelectron spectroscopy. The fact that two different synthesis procedures of InAs QDs lead to the same surface chemistry reactions is an appealing outcome that could be used later on to develop a more insightful realization of III-V QDs surface chemistry as a candidate for infrared-based optoelectronic devices.

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Fatty Acid Capped, Metal Oxo Clusters as The Smallest Conceivable Nanocrystal Prototypes

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Abstract: Group 4 metal oxo clusters $M_6O_4(OH)_4(RCOO)_{12}$ (M = Zr or Hf) are interesting materials with applications in 3D-printing, MOF's and catalysis.[1] We regard them as the smallest conceivable nanocrystals, since their inorganic core still resembles the crystalline oxide structure and it is capped with organic ligands, similar to colloidal nanocrystals. Clusters are atomically precise, presenting a clear advantage over nanocrystals, even when the latter are reasonable monodisperse.

Despite their potential, oxo cluster synthesis is not well developed. Only short and rigid ligand were explored and single-crystal XRD was the main characterization technique to obtain structural information. However, cluster with long ligands do no crystallize, rendering single-crystal diffraction obsolete.

Here we present the first comprehensive strategy on how to fully characterize zirconium oxo clusters, including both the inorganic core and the organic ligand shell.[2] We optimized the synthesis, achieving high yield and reproducibility, and extended the library of possible ligands to typical ligands of the nanocrystal field. In order to obtain structural data, detailed Pair Distribution Function (PDF) analysis was used. The organic ligand shell is probed via NMR, TGA and IR. Our results were found to be applicable for hafnium oxo clusters as well. Finally, when applying these clusters as catalysts in esterification reactions, it was found that they outperform nanocrystals 5-fold. Additionally, we can tune the ligand shell to avoid side products during the esterification reaction.

We thus present here atomically precise oxo clusters not only as interesting models for oxide nanocrystals but even as superior nanomaterials.

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Adjusting The Composition of Noble Metal-Based Chalcogenide Nanocrystals: Synthesis And Applications of Multinary Phases

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Abstract: The optimization of a material functionality requires both the rational design and precise engineering of its structural and chemical parameters.[1] Colloidal chemistry is an excellent synthetic choice for the synthesis of homogeneous and compositionally complex novel nanostructures with potential application in several fields.[2] We have exploited here several surfactant-assisted synthetic strategies in order to chemically transform our starting silver and copper chalcogenide nanocrystals into compositionally more complex nanostructured systems, such as hybrid and ternary I-I-VI semiconductor nanocrystals with different stoichiometries. Among them, a synthetic approach has been explored, in which the employment of solely nanostructures as precursor materials is considered. Our results indicate the formation of new ternary materials, both with stoichiometric and non-stoichiometric compositions. The use of advanced atomic-resolution electron microscopy techniques was key for their appropriate characterization and elucidation of formation mechanisms. The work is complemented with the assessment of their potential as active materials for energy conversion devices and as contrast agents in clinical diagnosis.

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Monoalkyl phosphinic acids as ligands in nanocrystal synthesis and its binding affinity towards nanocrystal surfaces

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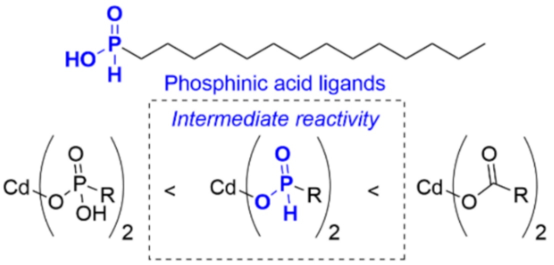
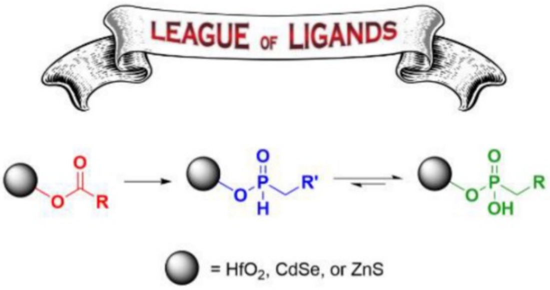
Abstract: Ligands play a crucial role in the synthesis and/or stabilization of colloidal nanocrystals. Nevertheless, only a handful molecules are currently used, of which oleic acid being the most typical example. Here we show that monoalkyl phosphinic acids are another ligand class.



We put forward monoalkyl phosphinic acids as an alternative ligand class, similar to carboxylic acids and phosphonic acids. After presenting the ligand synthesis for several selected substrates, we proceed to show the intermediate reactivity of the phosphinic acids in CdSe quantum dot syntheses. The nanocrystals synthesized with phosphinic acids are also easier to purify since there is no gel formation. Very small (2–3 nm) CdSe quantum dots with low polydispersity and high photoluminescence quantum yields can be easily accessed with phosphinic acid ligands. CdSe and CdS nanorods were also synthesized using phosphinic acids, whereby the rods showed high purity an d uniformity.



In addition, we investigate the ligand-NC interaction on both metal oxide (i.e., HfO_2) as metal chalcogenide (i.e., CdSe and ZnS) NCs. Given their intermediate acidity, phosphinic acids (pKa ≈ 3.08) bind to the surface with an affinity between carboxylic and phosphonic acids. Using solution NMR, we quantify the X-for-X ligand exchange via the alkene resonance of the oleyl chain (carboxylic and phosphonic acid), and the ether resonance of the 6-(hexyloxy)hexyl phosphinic acid. We conclude that the monoalkyl phosphinic acids quantitatively displace carboxylate ligands and are in equilibrium with phosphonates (although phosphonate binding is favored). These results show that monoalkyl phosphinic acids are suitable reagents to efficiently functionalize nanocrystal surfaces.

In conclusion, by careful design new type of ligands can be created, and can tailored towards specific functionalities such as solubility matching or intermediate reactivity and binding strength.

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New Synthesis of Coupled Molecules CdSe/ZnS@CdSe/ZnS And CdSe@CdSe With Used Silica Template

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Abstract: In analogy to atoms and molecules colloidal quantum dots (QDs) known as zero-dimensional objects can used as a building blocks of so called "artificial molecules". Recent advance in the synthesis protocols provide possibilities to organize colloidal QDs into such super-structures. First syntheses of colloidal molecules where obtained on simple addition of difunctional linkers to the colloidal QDs solution obtaining monomers, dimers, trimers and larger aggregates.[1] J. Cui at all.[2] provided more intentional synthesis protocol involving silica template. This procedure enabled high efficiency and selectivity of dimer formation. In this work we proposed modification of Cui procedure that allows one to get even better results. In our procedure the TEOS silica modified by MPTMS is used as a template for combining colloidal QDs. Synthesized QDs dimers were characterized using single particle spectroscopy providing important physical premises on changes in the relaxation kinetics implicated by the QDs coupling represented hire by exciton tunneling between them.[1,3,4] Deeper insight in to the impact of near field coupling on the relaxation kinetics is also gained by the Kinetic Monte Carlo (KMC) simulations. All reported results are here discussed using fluorescence lifetime-intensity distribution (FLID) maps showed on Figure 1.

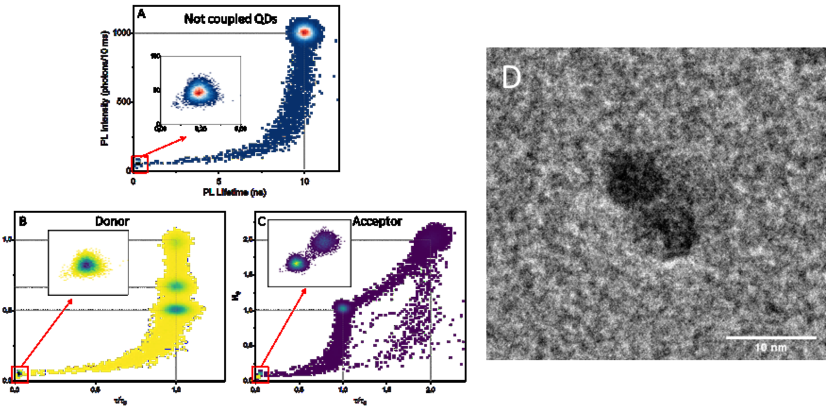

Figure 1. FLID maps made from KMC calculation for (A) single QDs, and for dimers (B) QDs as perform role the donor and (C) acceptor in coupled system. (D) TEM image of CdSe/ZnS@CdSe/ZnS molecules.

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Scale-up Syntheses of Magnetic Ferrite Nanoparticles with Different Shapes and Enhanced Performance for Magnetic Hyperthermia Applications

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Abstract: Magnetic iron oxide nanoparticles (Fe_3O_4-MNPs) have been a topic of great interest given their potential use for magnetic hyperthermia treatment (MHT).[1] This cancer therapy is based on the heat released by MNPs when exposed to alternating magnetic fields (AMFs).[2] The performance of MNPs in MHT is evaluated by measuring the specific absorption rate (SAR), which is related to MNP's heat dissipation under an AMFs. The SAR value strongly depends on the design of MNPs (i.e., shape, size distribution, crystallinity, saturation magnetization(Ms)).[1] Indeed, several synthetic routes have been developed to produce MNPs in order to increase their heating and magnetic performances. Among them, thermal decomposition is a common method used to produce monodisperse MNPs showing high Ms, maintaining good control over shape and composition.[3] However, it is limited by the amount of final product which is in the mg-scale per synthesis, very far from clinical need. In this work, to scale up the production of MNPs to gram-scale, we exploit the solvothermal method. The synthesis solution is composed by an alcohol solvent, carboxylic acid, primary amine, iron precursor, and shape-directing agent4. In particular, we found out that benzaldehyde and its derivatives can promote the formation of cubic-like nanoparticles; instead, by using aliphatic aldehydes, spherical and hexagonal shapes are formed. Moreover, the replacement of the primary amine with secondary or tertiary amines favors the formation of stars-like shape. The method developed is simple and straightforward, giving the possibility to carry out multiple syntheses obtaining MNPs in gram-scale amounts with benchmark MHT performance.

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Tailored Fluorescent Carbon Dots For Sensing Applications

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Abstract: Carbon dots (CDs) are relatively new emerging subclass of fluorescent nanoparticles that have demonstrated impact in multiple fields thanks to their unique optical properties and excellent biocompatibility. Since CDs were first synthesized and characterized[1] this field of study has witnessed an impressive development and continuing intense attention, but nonetheless still requires further improvements of the materials quality and a more systematic and deeper understanding of the photophysics that is involved to rationally design CDs for various applications. Novel fluorescence sensing nanomaterials are poised to solve problems in many disciplines. Fluorescence sensing which takes advantage of the bright and colorful fluorescence and nontoxic nature of CDs has been an extremely popular research topic in a literature. There is constantly rising need for technologies that enable reliable and accurate sensing of many fundamental parameters and analytes. Apart from conventional organic dyes or semiconductor nanocrystals, CDs with their attractive functional properties, such as broad-band optical absorption, strong fluorescence, superior resistance to photobleaching, high chemical stability, low toxicity, excellent biocompatibility, and flexible designability, are promising next-generation fluorescence nanoprobes for sensing. Therefore, rational design of surface functionalized carbon dots through presynthetic design tailored for targeted sensing is of high importance. In this work we will demonstrate the examples of realization of fluorescence lifetime nanosensors targeted for alcohols, ionic strength, and mercury, based on tailored surface-functionalized CDs.

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Optical Binding-Driven Photo-Sculpting With Silver Nanorods For Luminescence Enhancement

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Abstract: ince the discovery of optical trapping, strong light-matter interactions have set the basis for nano- and micro-manipulation methods. Recently, Huang *et al.* [1,2] described a new type of light-matter interaction called Optical binding employing NIR lasers and gold nanorods. In this work, we present a method for controllably creating silver micropatterns by pulsed laser radiation of plasmonic silver nanorods (AgNRs). The photo-sculpting process leads to optical binding forces transporting AgNRs in the surroundings, while the electronic thermalization results in photo-oxidation, melting and ripening of the AgNRs into well-defined 3D structures (Figure 1A), that we called Airy castles due to their structural similarity with a diffraction-limited Airy disk (Figure 1B). During the process emissive Ag nanoclusters are formed, allowing the visualization and examination of the aggregation process using luminescence microscopy. We comprehensively examine the factors that define the photo-sculpting process, namely, the concentration and shape of the AgNRs, as well as the energy power and repetition rate of the laser. Finally, we investigate the potential applications by measuring the metal-enhanced luminescence of a europium-based luminophore using the Airy castles, obtaining an enhancement of at least 20 times,[3] turning it to a very interesting tool with a great potential in future nanosensors and nanophotonics applications.

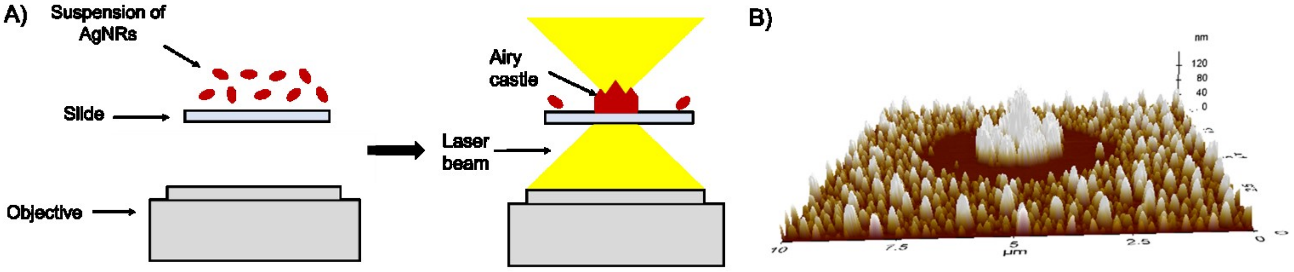

Figure 1. A) Scheme of photo-sculpting formation of Airy castles B) AFM Image of an Airy's castle.

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Microcrystalline Two-Dimensional Layered Perovskite Heterostructures

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Abstract: Two-dimensional layered perovskites (2DLPs) represent an emerging class of materials where a semiconducting metal-halide octahedral layer is sandwiched between two layers of bulky organic cations.[1,2] To take advantage of the highly anisotropic character of this material class the formation of lateral instead of vertical heterostructures is a promising approach to achieve e.g. charge separation in the two-dimensional plane. The low mobility of halide anions in 2DLPs compared to their 3D counterparts significantly suppresses the interdiffusion of ions across the heterojunction, opening a pathway toward realizing stable heterojunctions.[3] Here, we report on a facile two-step solution-based method for the formation of microcrystalline lateral heterostructures of the form PEA_2PbBr_4-PEA_2PbI_4. The formation of the low band gap material PEA_2PbI_4 at the edges of the high band gap material PEA_2PbBr_4 leads to a significant band offset at the heterojunction that could enable a directional charge or energy flow from the center towards the edges of the heterostructure. The influence of different solvents and solvent mixtures as well as the respective ion sources on the optical and structural properties are reported. The results indicate that the formation of the lateral heterostructures is based on a dissolution-recrystallization process that can be fine-tuned by the respective solvent or solvent mixture. The fabrications of such 2DLPs heterostructure offer an opportunity to investigate charge-transfer phenomena at the heterojunction and the interchange between these materials, which could lead to their applications in photocatalytic reactions among others.

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Size-Dependent Energy Levels Alignment and Carrier Delocalization in Indium Phosphide Based Core/Shell Quantum Dot

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Abstract: Colloidal quantum dots (QDs) have been a research subject for over 30 years now. Due to their unique size-dependent optical properties, QDs found their way into displays, lasers, and photodetectors. Recently, InP-based QDs have emerged as an alternative to the widely deployed CdSe-based QDs. Similar to CdSe-based QDs, InP QDs are formed through hot-injection, and core/shell heterostructures are grown to enhance the optical properties, *e.g.*, the photoluminescent quantum efficiency. To understand the different factors that determine these properties, linear and non-linear optical spectroscopy is most useful. By analyzing the interaction of QDs with light, extensive information on the energy and oscillator strength of the band-gap transition, the alignment of the energy levels, and the intricate balance between radiative and non-radiative recombination can be obtained.

In this study, a set of InP/ZnSe/ZnS core/shell/shell QDs with different InP-core sizes and different ZnSe shell thicknesses was analyzed using femtosecond pump-probe spectroscopy. The double shelling results in QDs with a near-unity photoluminescence quantum efficiency, yet it also raises the question of how energy levels in core and shell interact. This information can be derived from transient absorption spectroscopy which probes, *i.e.*, the absorbance of the QDs after photo-excitation. By analyzing the transient absorption spectra, supported by k·p calculations and 2-photon photoluminescence excitation spectroscopy, we assign 4 different bleach bands to specific electronic transitions, estimate the energy levels alignment and describe carrier delocalization into the ZnSe shell.

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Biexciton Blinking in CdSe-based Quantum Dots

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Abstract: Experiments on single colloidal quantum dots (QDs) have revealed temporal fluctuations in the emission efficiency of the single-exciton state. These fluctuations, often termed "blinking", are caused by opening/closing of charge-carrier traps and/or charging/discharging of the QD. In the regime of *strong* optical excitation, multiexciton states are formed. The emission efficiencies of multiexcitons are lower because of Auger processes but a quantitative characterization is challenging. Here, we quantify fluctuations of the biexciton efficiency for single CdSe/CdS/ZnS core–shell QDs. We find that the biexciton efficiency "blinks" significantly. The additional electron due to charging of a QD accelerates Auger recombination by a factor 2 compared to the neutral biexciton, while opening/closing of charge-carrier traps leads to an increase of the nonradiative recombination rate by a factor 4. To understand the fast rate of trap-assisted recombination, we propose a revised model for trap-assisted recombination based on reversible trapping. Finally, we discuss the implications of biexciton blinking for lasing applications.

Efficient Photochemical System Based on Au-nanopartcicles/Cyanine J-Aggregates Plexcitons

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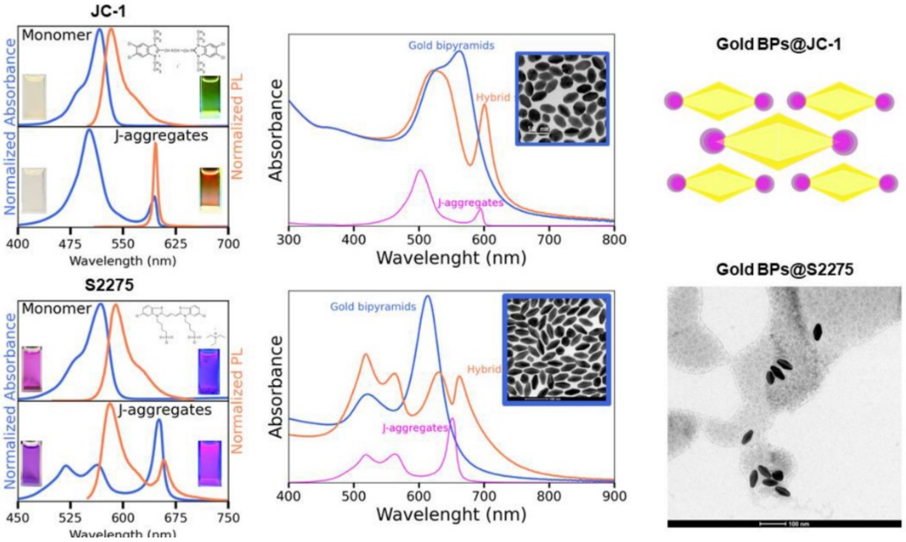
Abstract: owadays, gold nanostructures properties are widely analyzed due to their potential for a wide variety of applications. In particular, their ability to focus and confine optical energy in regions smaller than the wavelength size, make them ideal to develop light-harvesting devices.[1] The coupling of these structures with J-aggregates pursues to take advantage of their Frenkel exciton. This kind of macromolecule presents a red-shifted and arrowed absorption band, and the monomeric species have a high extinction and polarizability.[2] The quasiparticles involved in the strong coupling process are known as plexcitons: they are defined as the combination of plasmons and excitons, and their interaction triggers in hybrid states' formation of light-matter.[3]

The aim of this work is the characterization of the nanostructures, molecules, and the resulting hybrid systems and the analysis of their potential application as efficient photochemical systems. We present the comparison of JC-1 and S2275' hybrids properties. They were characterized using their absorbance and luminescence spectra, and luminescence lifetime. From the absorbance spectra we can estimate the Rabi splitting energy, the cooperativity factor (C), and the Hopfield coefficients. These calculated parameters allow us to describe the resulting systems.

As a final step, we will apply the hybrid systems in a photocatalytic reaction to test their potential as hot-carriers' generators and measure their efficiency.



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Passivation of III-V And II-VI Quantum Dots by Metal Fluorides

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Abstract: Colloidal quantum dots (QDs) are promising down shifters for solid state lighting devices provided that their photoluminescence quantum yield (PLQY) can be maintained over thousands of hours. To achieve this level of performance, we have explored the passivation of QDs using oleylammonium fluoride, which improves the PLQY of II-VI and III-V QDs and core shell materials. Photochemical acidolysis of InP QDs with oleylammonium fluoride produces PH_3 and InF_3 coproducts and increases the PLQY up to 83 % while narrowing of the absorption and luminescence spectral features (PL FWHM as low as 42 nm). The metal fluoride content of the products was measured by reaction with Me_3Si-Cl which liberates Me_3Si-F which can be characterized using ^1H and ^{19}F NMR spectroscopy. In the presence of Bu_3P ligands, phosphine bound chloride terminated InP QDs are obtained. The chemical formulae of these QDs has been determined using ^1H, ^{31}P, and ^{19}F NMR spectroscopy and will be described. It is hypothesized that the small size and the electron withdrawing properties of the fluoride ion support high surface coverages and prevent nonradiative recombination pathways.

From Surface Chemistry to Surgery: Dual-Modality Nanocrystals for the In Vivo Detection of Sentinel Lymph Nodes

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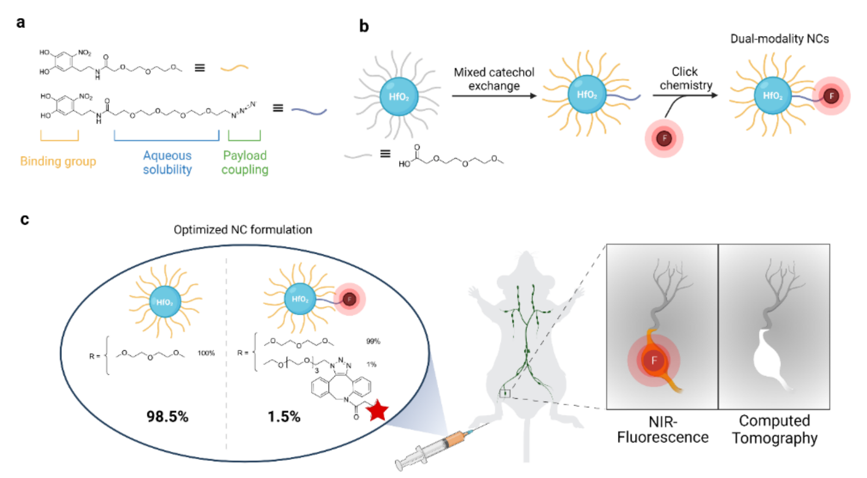
Abstract: In the surgical treatment of breast cancer the primary tumour is removed together with the so-called sentinel lymph nodes (SLNs), the lymph nodes that have the highest probability of being invaded by cancer cells. The current clinical standard to identify SLNs uses a combination of 99m-Technetium labelled nanocolloids and blue dyes. This workflow comes with downsides such as inflexible procedures, exposure to radioactivity for both the patient and surgical team, allergic side-reactions and long-lasting skin discoloration. Here, we develop dual-modality hafnium oxide nanocrystals (NCs) as alternative to the current clinical standard and demonstrate the *in vivo* detection of SLNs in mice using X-ray computed tomography and near-infrared fluorescence.[1] We first functionalize the NCs with our recently developed catechol-derived ligands,[2] providing colloidal stability in competitive biological buffers at concentrations up to 300 mg NCs/ml. In the following step, we further improved the surface chemistry of the NCs by synthesizing an azide-terminated catechol ligand, and apply strain-promoted click chemistry to covalently link clinically used fluorophores to the NCs to create a dual-modality imaging-probe. Next, we performed an *in vivo* evaluation of the dual-modality NCs in mice, the SLN is selectively detected via both imaging modalities 15-30 minutes post-injection of the probe, while higher echelons remain undetected. We further confirmed our findings by performing a longitudinal statistical study on a test group (N = 6). Moreover, a comparison between the probe and 99m-Technetium nanocolloids reveals similar lymphatic drainage while utilizing faster, cheaper and more readily available imaging infrastructure, which could facilitate clinical integration.



Project overview. a: Design and synthesis of ligands for nanocrystal functionalization. b: Ligand exchange strategy and payload coupling. c: In vivo proof-of-concept.

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Disproportionation Induced by Lewis Base: The Case of Metal Chloroalkoxide Complexes of Group IV

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Abstract: Colloidally stable metal oxide nanocrystals of group IV, such as titania, zirconia and hafnia, can be obtained by reacting metal tetrachloride and metal isopropoxide together with trioctylphosphine oxide (TOPO), at high temperatures.[1] However, in order to control the properties of the nanocrystals, such as size, shape and elemental composition, it is important to understand the reaction on a fundamental level. Part of the mechanism was recently elucidated and the metal chloroalkoxide $ZrCl_2(OiPr)_2$ was proposed as intermediate.[2] Further insights into nucleation and growth showed the formation of an amorphous phase which converts within minutes into nanocrystals.[3]

Here we study the interaction between the metal chloroalkoxide precursor and TOPO to further understand the reaction mechanism. By mixing MCl_4 and $M(OiPr)_4$ in different ratios, the Lewis acidic chloroalkoxide species, $MCl_x(OiPr)_{4-x}$, (with x=1-3), can be synthesized. When these complexes react with 2 equivalents of TOPO, a peculiar Lewis base-driven disproportionation is observed via phosphor Nuclear Magnetic Resonance Spectroscopy (^{31}P NMR). Not only does the starting complex coordinate with TOPO, but also the more acidic one does, which contains more chlorine atoms, $MCl_{x+1}(OiPr)_{4-x-1}(TOPO)_2$. Since species that are not coordinated with TOPO cannot be detected, it can be deduced that the less acidic complex $MCl_{x-1}(OiPr)_{4-x+1}$ is also formed, and therefore the mass balance rule is not violated. A mechanism was suggested for this ligand redistribution and tested for the case of zirconium. The good fit of the proposed equilibria, consisting of a complexation reaction and disproportionation, to our data, confirms our hypothesis.

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Silver-Based Semiconductor Nanoparticles for Novel Transistor Structures

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Abstract: Smartphones, computers, televisions, radios - transistors can be found in almost every electrical device. Therefore, these small, electronic semiconductor components are among the most important active components of electronic circuits. Nowadays, such electronic components should become smaller, more flexible, and more powerful. However, a high-performance, flexible, thin-film transistor technology is still missing.

Semiconductor nanocrystals (NCs) have the potential to achieve a breakthrough in transistor performance, as they overcome the intrinsic low carrier mobility of organic semiconductors. In the last decades, different functional nanoparticles have been studied in detail. It is possible to precisely control the physical and electronic properties of NCs via parameters such as size, shape and composition. Using them in vertical transistor structures with their ultrashort channels is promising, as studies with CdSe NCs have shown recently.[1]

In this work, we strive to use different NCs for vertical transistors, which allow to easily realize high-performance devices without nanostructuring. Therefore, NCs like Ag_2S or $AgInS_2$ are synthesized to replace the widely studied but more toxic Cd-containing materials. Commonly, the as-synthesized NCs are capped with insulating hydrocarbon-containing ligands, which have to be removed in an additional thermal or chemical step. However, this postsynthetic treatment often results in the formation of defects or the removal does not work completely. To avoid the necessity of such a step and to improve the electronic communication, the modification with inorganic ligands is the second focus of this work. The materials are then characterized in terms of their film-forming properties and electronic parameters.

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Single Particle Dynamics of ZnS Shelling-Induced Replenishment of Carrier Diffusion for Individual Emission Centers in $CuInS_2$ Quantum Dots

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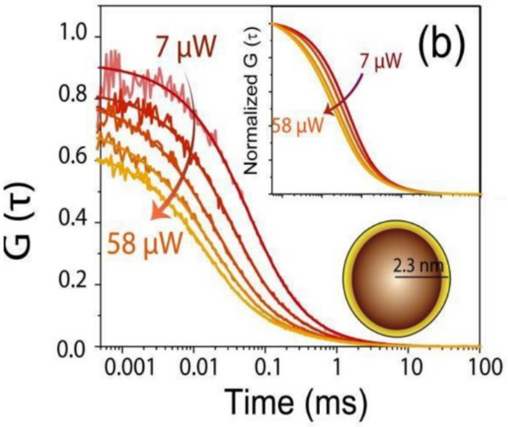
Abstract: Water soluble Copper Indium Sulphide (CIS) and Core/Shell CIS/ZnS QDs are prepared by a previously reported green method with required modifications.[1] Fluorescence Correlation Spectroscopy (FCS) of freely diffusing QDs are performed at interband (λex=405 nm) and Intraband (λex=532 nm) excitation wavelengths to investigate blinking and photoactivation phenomenon. For interband excitation, The power dependent FCS study showed a decrease in the blinking timescale and an increase in the number of particles in the confocal volume whereas reverse has been observed for intraband excitation. This criss-cross observation varies from that of previous studies in II-VI QDs.[2,3] The Time correlated single photon counting (TCSPC) tuned with FCS set forth a technique of Fluorescence Lifetime Correlation Spectroscopy(FLCS).[4] Each lifetime components are separated using FLCS and from each emission centers individual Autocorrelation Functions (ACF) are constructed. The ACFs of the high lifetime component nearly matches showing a small perturbation in the Cu mediated radiative recombination states. The 10-30 ns lifetime surface states clearly shows differing ACF showing that the Shelling has an enormous impact on the surface states, but has a little impact on the core states. The Cross Correlation Function (CCF) constructed between the different emission centers shows no correlation between those two states.

This indicates that the two states- one containing the Cu trap state mediated recombination and other containing the excitonic recombination attributed the surface states are fundamentally different from each other and there is nearly no correlation between the states.



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Spatiotemporal Microscopy of Energy Carrier Transport

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Abstract: Optoelectronics applications require control over the generation, separation, and extraction of photoexcited charges. Yet, in many material systems, energy carrier transport must navigate efects of various natures over a broad range of length and time scales. There are many approaches to inferring microscopic energy transport through energetic, temporal, or spatial markers, but each faces limitations. Moreover, heterogeneous systems are often elusive to simple kinetic models that reveal fundamental transport parameters. To understand the principles that govern electronic and thermal relaxation dynamics in complex systems relevant to optoelectronic applications, advanced experimental techniques and theoretical models rooted in fundamental physical phenomena are needed. This presentation will focus on the following questions: How do heterogeneous environments and interfaces impact microscopic energy transport and conversion? How can we access information about energy carriers that traditionally do not have clear spectroscopic signals? I will describe pump–probe optical measurements and modeling of carrier transport in nanocrystal and semiconductor films.

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Trion Emission in CdSe Nanoplatelets Activated by Hole Trapping Copper Dopants

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Abstract: The photoluminescence of quasi-2D CdSe nanoplatelets shows unique signatures like a strong dual emission below 100 K. While the high energy emission line is usually attributed to the neutral exciton, a popular explanation for the lower energetic one are negative trions. The ability of controlling trion emission opens attractive opportunities for single-photon emitters, since trions do not possess a dark state that broadens or dephases the emission like it is the case for neutral excitons.[1] It has been shown that the intensity of the trion line can be controlled by adding electron donors in the dispersion, which supports trion formation.[2] Though, to the best of our knowledge, it has not been shown, that trion emission can be controlled by doping the nanoplatelets.

In this work we show that copper dopants incorporated into the lattice have the ability of tuning the ratio between the exciton and the trion photoluminescence lines. We observe stronger trion emission in four monolayer thick copper doped CdSe nanoplatelets compared to their respective undoped counterparts. We hypothesize that this effect is caused by the built-in Cu^{1+} ions, which create a hole trapping state with a large recombination lifetime. The subsequent electron excess in the nanoplatelets averaged over time is thus expected to assist trion formation. This hypothesis is supported by single particle studies of undoped and doped nanoplatelets that are linked to temperature and power dependent ensemble measurements. This allows further insights into, *e.g.*, the trion energy and the probability of the emitting transitions.

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Bioactive Gold-Polythiophene Hybrid Nanoparticles as Electrochemical Biosensing

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Abstract: The monitoring of blood glucose has a great significance in clinical diagnosis. A series of customizable and portable sensors designs has been developed since Clark and Lyons proposed the first concept of glucose enzyme electrode 40 years ago.[1] Conventional fabrication often requires multi-step fabrication process with thermal sintering and harmful chemicals. Alternative processing methods such as inkjet printing waste less material and provide opportunities for bespoke designs.[2] A variety of materials that can be formulated as inks and additively applied to a wide range of substrates.

In this contribution, we discuss printable sinter-free gold nanoparticle (AuNPs) inks that are suitable for glucose biosensing. A conductive polythiophene (P3KHT) was immobilized on quasi-spherical gold nanoparticles. Glucose oxidase (GOx) was covalently bound to the functional carboxylate groups in the polymer side chain via EDC/NHS coupling. Colorimetric assays revealed a higher enzymatic affinity of AuNPs@P3KHT-Gox towards glucose compared to free Gox. Electrochemical biosensors were fabricated by inkjet printing on PET (polyethylene terephthalate). The electrochemical detection showed selectively for glucose and a linear current response for glucose concentrations in a range of 2 mM to 14 mM, suitable for detection of blood glucose concentration in human.[3]

Our results indicate that gold-polythiophene hybrid nanoparticles are suitable not only for glucose detection. They can be modified for other biologically relevant targets such as antibodies, oligonucleotides and peptidomimetics, for example for stem cell growth.

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Multi-Color Amplified Spontaneous Emission from Electrically Excited Colloidal Quantum Dots

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Abstract: Chemically synthesized, continuously-graded quantum dots (cg-QDs)[1] have emerged as a promising gain medium for solution-processable laser diodes thanks to strong suppression of Auger recombination and large optical gain cross-sections. When incorporated into a light-emitting diode with a current-focusing structure, these materials showed intense two-band electroluminescence (EL) due to the band-edge (1S) and the excited-state (1P) transitions in the case of both d.c.[1] and pulsed (ms pulse duration) excitation[2]. These observations indicated the realization of broad-band, long-lived optical gain in the QD medium. However, neither amplified spontaneous emission (ASE) nor lasing have been achieved because optical losses were too high and were not fully compensated by optical gain generated in the QD layer.[2,3] To tackle this problem, we increase modal gain by employing novel compact cg-QDs (ccg-QDs) and simultaneously modify the device structure by incorporating a low-loss photonic waveguide.[3,4] As a result, we are able to achieve strong net optical gain and realize ASE with electrical pumping. The regime of ASE is indicated by multiple observables including a super-linear EL-intensity growth above the ASE threshold, preferential TE polarization of emitted light, as expected for amplified modes, manifold line narrowing, increased optical coherence, and a high output intensity of up to ~2 kW cm^{-2}.[4] The effect of ASE is observed at three distinct energies that correspond to the 1S, 1P, and 1D transitions. This demonstration opens the door to applications of QDs in spectrally tunable laser diodes and color-selectable, narrow-band, highly directional ASE light sources.

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Detecting Metabolites With Antenna Enhanced Infrared Absorption

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Abstract: Changes in tumor health are reflected by minute changes in the metabolite composition of the tumor; to monitor a tumor the metabolite composition should be observed fast, label-free and non-invasively.[1]

Infrared (IR) absorption offers such analysis by informing qualitatively and quantitatively about characteristics molecular vibrations in the IR region without destroying the sample. IR spectroscopy has been successfully employed to distinguish between healthy and non-healthy patients.[2] Toward detecting more subtle metabolic differences at the onset of disease or during treatment, lower concentrations need to be detected. The infrared signal may be enhanced via localized surface plasmon resonances (LSPR) on the surface of gold nano-antennas leading to surface-enhanced infrared absorption (SEIRA).

For SEIRA the LSPR frequency must match the frequency of the molecular vibration.[3] Therefore, to identify metabolites in the IR with SEIRA the whole IR range should be covered by a range of LSPR. Rod-shaped antennas display LSPR in the IR with a linear dependence of their length to the resonance frequency. Each metabolite with its corresponding molecular vibration needs to be enhanced by a corresponding IR antenna on the substrate.[3] In the size ranges for IR antennas, top-down production is a popular production process, because the size can easily be tuned to the application at hand. This allows for identification of a sensor geometry for each metabolite of interest. By combination of design elements, the sensor may sense more than one molecule at the same time, moving towards the analysis of the metabolic tumor profile.

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Spin-Exchange Photoemission From Manganese-Doped Quantum Dots

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Abstract: Photoemission underlies many applications including photocathodes, free-electron lasers, and photocatalysis. This process typically relies on a photoelectric effect,[1] which requires high-energy photons. An alternative mechanism for photoemission is Auger ionization,[2] in which an 'energy-donor' electron relaxes from a conduction to a valence band by transferring its energy (defined by a bandgap, E_g) to an 'acceptor' electron. The acceptor carrier is hence excited to a higher-energy state within the material (Auger up-conversion) or even ejected from it (Auger ionization).[3] The latter process, however, is difficult to realize *via* a single-step process as an electron affinity is normally higher than E_g.

Here, we demonstrate highly efficient electron emission due to a two-step Auger process occurring in manganese-doped CdSe colloidal quantum dots (CQDs). Importantly, this process is driven by low-photon-energy, visible-range light,[4] a favorable distinction from a photoelectric effect which usually occurs only under ultraviolet illumination. The observed process relies on two sequential spin-exchange energy-transfer events involving two excited Mn ions. Due to extremely short time scale of this process (~100fs time scale)[5] it outcompetes phonon-assisted intra-band cooling. As a result, the high-energy electron produced by the first energy-transfer step can be promoted further to a 'vacuum' state *via* a second Auger-re-excitation step. Exploiting these large spin-exchange energy-transfer rates, we achieve photoemission with a 3% efficiency per absorbed photon, which is orders of magnitude greater than that for undoped CQDs. These observations suggest that manganese-doped CQDs can serve as light-driven electron sources in traditional (e.g., photocathodes) and less traditional (e.g., photoreduction chemistry) applications.

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Magneto-Plasmonic Nanoparticles Enabling Novel Medical Imaging Techniques

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Abstract: Nanostructured surfaces and nanoparticles can boost the performance in many different fields of application, leading to a growing demand for novel nanoparticles with physical properties engineered to optimize a particular application. Here, we report on the utilization of nanoparticles with both, magnetic and optical properties, as probes for biosensing and as contrast agent for medical imaging. We present novel imaging and biosensing technologies as well as nanoparticles with physical properties that are tailor-made to the employed imaging techniques.

The new magneto-plasmonic imaging technique enables the background reduction in optical coherence tomography and photoacoustic imaging and is based on magnetic excitation and plasmonic signal generation (see Figure 1), which enables molecular imaging with ultra-high contrast. We present two types of novel multifunctional nanomaterial with defined optical and magnetic properties, see Figure 2. Both nanoparticle types have an elongated shape, are ferromagnetic and show plasmon resonances. The maxima of the plasmon resonances are engineered to the excitation wavelength of the imaging system. In addition, we demonstrate the transfer of the different particles into aqueous solution and methods for protein biofunctionalization that are required for the aimed medical imaging.

Finally, alternative possible areas of application of these nanomaterials will be discussed, ranging from biology and medicine to electronics, photovoltaics and photocatalysis.

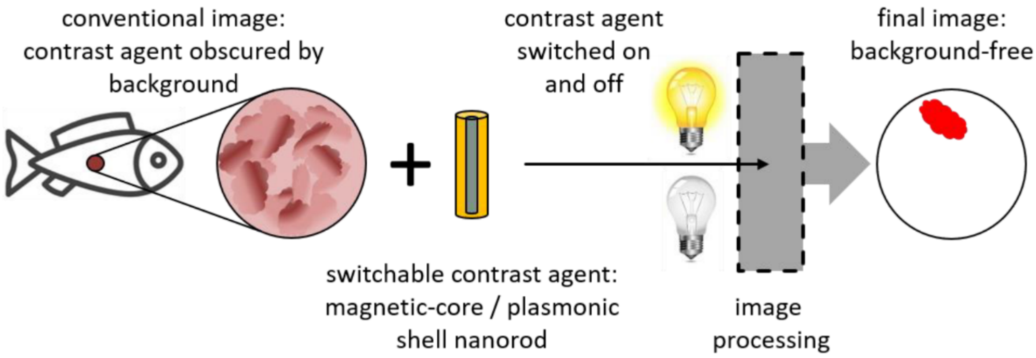

Figure 1. Schematic illustration of the imaging principle.

Defects Matter: The Role of Different Processing Parameters on Solution-Processed Thermoelectric Materials

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Abstract: In recent years, solution processes have gained considerable attention as a cost-effective and scalable method for producing high-performance thermoelectric materials. In this strategy, powder material is prepared in a solution, then purified and processed thermally to render the desired dense polycrystalline material. Despite the importance of detailing how each of these steps has been done, we found that strictly following many publish works often results in blanks in the procedure where we have to decide our own methodology. Surprisingly, those missing details in the synthetic methods can be key to controlling material performance.

Herein, we evaluate the effect of the most relevant parameters within the synthesis, purification, pre-consolidation thermal treatments, and consolidation on the material composition and microstructure. Then we correlate our findings with the changes observed on the transport properties. Our case study is SnSe produced by an aqueous synthetic method. We selected this material as it is one of the most relevant materials in thermoelectrics. The synthetic strategy was chosen due to its low cost and extended use in producing particles.

High Thermoelectric Performance at Room Temperature in Ag_2Se Achieved Through a Solution Synthesis

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Abstract: Currently, the library of high-performance thermoelectric materials near room temperature is very limited. Silver selenide has been explored as one of the most promising candidates. However, large discrepancies in the reported thermoelectric properties impede the proper evaluation of its performance. This divergence arises from the difficulty of controlling the defects present in the material, such as vacancies, interstitial atoms, dislocations, grain boundaries, precipitates, etc.

Defect engineering is strongly linked to the synthetic method and synthesis conditions used. In the case of powder consolidation, typically by spark plasma sintering, yet no unanimity in the sintering temperature is given. Furthermore, temperatures are selected, where uncontrolled selenium evaporation and silver migration determine the different types and densities of defects.

In this work, we propose a new synthetic approach based on the synthesis of Ag_2Se nanoparticles in a solvent mixture of amines and thiols. The resulting powder is then consolidated using spark plasma sintering at different temperatures. This synthetic approach allows bypassing fluctuations in stoichiometry and hence charge carrier concentration. Moreover, microstructural defects, such as dislocations, grain boundaries, and lattice strain, can be tuned by small variations in the sintering temperature around the phase transition. This work highlights the opportunities for control provided by solution synthesis and that besides stoichiometry, the microstructure is crucial for tuning the transport properties.

Band Structure Engineering In Z-Scheme Photocatalysts For The Efficient Green Hydrogen Generation

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Abstract: Z-scheme photocatalysts, one of the most attractive photocatalysts, are composed of two different photocatalysts with relatively small bandgap for achieving both visible light absorption and efficient overall water splitting without hole scavenger. One of the major roadblocks for the practical application of Z-scheme photocatalyst has been the lack of control of carrier transfer between two photocatalysts, which play a pivotal role for efficient water splitting.

In this study, we investigated the effect of band structure engineering in $CuIn_{1-x}Ga_xS_2/BiVO_4$ Z-scheme photocatalyst on their carrier dynamics and hydrogen evolution rate. In order to systemically control the band structure, we prepared $CuIn_{1-x}Ga_xS_2$ nanocrystals with varying Ga content ($0 \leq x \leq 1$) as a hydrogen evolution photocatalyst to control the charge transfer from CIGS to $BiVO_4$ nanocrystals. We characterized carrier dynamics of prepared Z-scheme photocatalysts using transient absorption spectroscopy (TAS) and their hydrogen generation rates. Then, we demonstrated a correlation between the band structure and photocatalytic efficiency for each $CuIn_{1-x}Ga_xS_2/BiVO_4$ photocatalyst with different Ga content. As a result, it reveals that the ratio of Ga to In affects the band bending of the $CuIn_{1-x}Ga_xS_2/BiVO_4$ heterostructure and plays a critical role in determining whether the charge transfer mechanism is type-II charge transfer or Z-scheme charge transfer. The efficient Z-scheme charge transfer leads to high hydrogen evolution rate, while type-II charge transfer lowers hydrogen evolution rate.

Evidence of Long-Lived Delocalized Electrons in $CuInS_2$ and $CuInS_2/CdS$ Nanocrystals

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Abstract: $CuInS_2$ nanocrystals (NCs) are attractive for bioimaging, photovoltaic, and photocatalysis applications due to their broad absorption spectra, wide photoluminescence tunability, and microsecond-long luminescence lifetimes.[1] The decay dynamics of the photogenerated carriers in colloidal $CuInS_2$ NCs has been extensively studied at the sub-nanosecond regime, but studies focusing on longer timescales remain scarce. In this work, we investigate the exciton dynamics of $CuInS_2$ and $CuInS_2/CdS$ NCs up to 10 μs using transient absorption (TA) and time-resolved photoluminescence spectroscopies. In agreement with previous reports,[2] the transient absorption spectra consist of a ground-state bleach (GB) and a photoinduced absorption (PIA) band at lower energies. Interestingly, the TA signals decay faster when an electron scavenger (p-benzoquinone) is added to the solution. In contrast, addition of a hole scavenger (ethanol) does not induce observable changes in the TA spectra. Hence, we attribute both the GB and PIA signals to conduction band electrons, which is consistent with the coupled decay dynamics reported in the literature for timescales longer than 1 ns.[2] This assignment contradicts the idea that the broad near-infrared PIA corresponds to localized hole states. Intriguingly, the GB recovery is slower than the photoluminescence lifetime, suggesting that the photogenerated carriers are transiently stored and released from excited dark states at time scales faster than the temporal resolution of our TA measurements. . This observation is consistent with the self-trapped exciton model recently proposed by Adi Harchol et al.[3]

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Colloidal Quantum Dot Laser Diodes: Three Decades in the Making

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Abstract: It has been 30 years since the first demonstration of lasing with semiconductor nanocrystals embedded in glass matrices[1] – the samples akin to standard colored glass filters. Following this discovery, it took three years to realize lasing with epitaxial QDs[2] and six more years to demonstrate the effect of amplified spontaneous emission (ASE) – a precursor of lasing – with colloidal QDs.[3]

So far, all reported studies into colloidal QD lasing have utilized optically excited samples. However, most of the prospective technological applications require electrically pumped devices, that is, laser diodes. The realization of such devices is complicated by multiple problems, widely deemed insurmountable. These include extremely fast nonradiative Auger recombination of optical-gain-active multicarrier states, poor stability of QD films under high current densities required for lasing, and unfavorable balance between optical gain and optical losses in electroluminescent (EL) devices wherein a gain-active QD medium is a small fraction of an overall device stack comprising multiple optically lossy charge-transport layers.

Here we resolve these problems and achieve strong ASE with electrically driven QDs.[4] To demonstrate this effect, we employ compact, continuously graded QDs with strongly suppressed Auger recombination incorporated into a low-loss photonic waveguide integrated into a pulsed light-emitting diode capable of operating at current densities of up to ~2000 A cm^{-2}. These prototype ASE-type laser diodes exhibit strong, broad-band optical gain and demonstrate low-threshold, room-temperature ASE which leads to intense, edge-emitted EL whose instantaneous power reaches ~200 mW.

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Solution-Synthesized Thermoelectric Materials and Devices

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Abstract: Thermoelectric materials can convert waste heat into electricity and mitigate the energy crisis. 'Nano' strategies have been adopted in thermoelectric materials since two decades ago, yet limited paradigms such as quantun confinment of electrons and grain-boundary scattering of phonons are established. This is probably ascribed to the conventional solid-state synthetic routes. We attempted to invent some new "nano" strategies for optimizing thermoelectric materials, through our solution-phase syntheses. These new protocals include single-atom materials, low-temperature efficient doping, surface-energy-induced restructuring of the unit cell, pore engineering through shape control of nanocrystals and Kirkendall effect, *etc.* [1-5]

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Zwitterionic Polymer Coatings for Stable and Stealthy Nanocrystals in Bioimaging and Magnetic Micromanipulation

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Abstract: Inorganic nanocrystals such as gold, iron oxide and semiconductor nanocrystals have unique optical or magnetic properties that make them very promising for cancer detection, imaging and therapeutic applications. The surface ligands of these nanoparticles play a critical role in their application and control the nanoparticle interaction with biomolecules and cells. I will present the development of zwitterionic copolymer ligands containing a multidentate anchoring block that provide a stable binding to the surface of different inorganic nanocrystals, enabling prolonged biological applications. The nature of the zwitterion group has a strong influence on antifouling properties, ranging from specific interactions with some biomolecules to a complete suppression of interactions with serum biomolecules, cytosolic components and macrophage cells. This enables various applications including intracellular targeting of fluorescent quantum dots, in vivo tracking of individual circulating cells, or micromanipulation in the nucleus of living cells using magnetic nanoparticles.

Repeated Topical Administration of 3 nm Cerium Oxide Nanoparticles Reverted Disease Atrophic Phenotype and Arrested Neovascular Degeneration In AMD Mouse Models

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Abstract: Increased oxidative stress in the retina and retinal pigment epithelium is implicated in age-related macular degeneration (AMD). Antioxidant cerium oxide nanoparticles (CeO_2NPs) have been used to treat degenerative retinal pathologies in animal models, although their delivery route is not ideal for chronic patient treatment. In this work, we prepared a novel formulation for ocular topical delivery that contains small (3 nm), non-aggregated biocompatible CeO_2NPs. In vitro results indicate the biocompatible and protective character of the CeO_2NPs, reducing oxidative stress in ARPE19 cells and inhibiting neovascularization related to pathological angiogenesis in both HUVEC and in in vitro models of neovascular growth. In the in vivo experiments, we observed the capacity of CeO_2NPs to reach the retina after topical delivery and a subsequent reversion of the altered retinal transcriptome of the retinal degenerative mouse model DKO*rd8* towards that of healthy control mice, together with signs of decreased inflammation and arrest of degeneration. Furthermore, CeO_2NP eye drops treatment reduced laser-induced choroidal neovascular lesions in mice by lowering VEGF and increasing PEDF levels. These results indicate that CeO_2NP eye drops are a beneficial antioxidant and neuroprotective treatment for both dry and wet forms of AMD disease.

The Design of Multifunctional Nanomaterials And Devices Through Nanocrystal Self-Assembly

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Abstract: The advances in organizing ensembles of monodisperse colloidal nanocrystals (NCs) with controlled composition, size, and shape now represents a new strategy for mesoscale materials synthesis. We can consider the NCs to act as "artificial atoms" with tunable electronic, optical, magnetic properties that allow the development of a new periodic table for design at the Mesoscale. These NCs are ideal building blocks for incorporation into new thin films, microresonators, and integrated devices. In this talk, I will briefly outline the current state of the art in synthesis, purification, and integration of single-phase NCs and core-shell (heterostructures and heterodimer) NCs emphasizing the design of semiconductor building blocks, rare-earth-based phosphors, and magnetic NCs with tunable shapes (spheres, roads, cubes, discs, octahedra, etc. I will then share how these tailored NCs can be directed to assemble into single-component, binary, ternary NC superlattices providing a scalable route to producing multifunctional thin films and 3D solids. The modular assembly of these NCs allows the desirable features of the underlying quantum phenomena to be enhanced even as the interactions between the NCs allow new delocalized properties to emerge. Synergies in the electronic and optical coupling between NCs will be emphasized as we push toward the realization of artificial solids with a new 3D structure. Recent progress in using emulsion-based assembly methods for continuous production and tuning of stimuli-responsive, optically tunable photonic resonators from the dense NC "superparticles" will be discussed.

Driving Nanohybrid Synthesis and Hierarchical Assembly at Interfaces with Surface Chemistry Anisotropy

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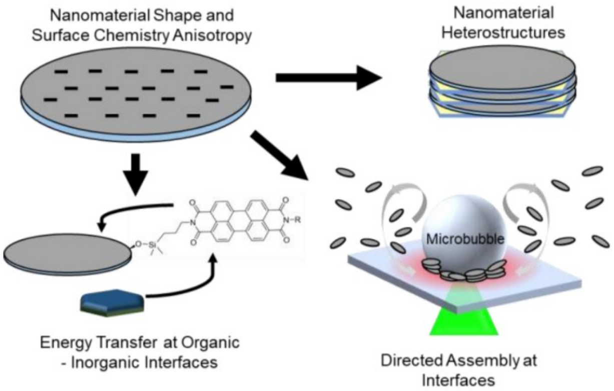
Abstract: Morphological and surface chemistry anisotropy of certain nanomaterials can permit colloidal modification strategies which target specific interfaces. Colloidal modification of specific nanoparticle interfaces can provide a chemical environment that favors the nucleation and growth of other materials at the modified interface. For example, growth of semiconductors such as In_2S_3[1,2] and BiOI[3] at the interface of tube- and disc-like nanomaterial templates can result in nanomaterial hybrids with drastically improved photocatalytic properties, while the aqueous dispersibility of the template is maintained. Charged 2D materials are particularly well-suited for controlling the crystal growth habit of a number of different materials, and the charge of the template can also introduce ionic selectivity to the function of the material.[4,5] Furthermore, the edge groups of certain 2D layered materials such as layered silicates provide a site for covalent attachment of energy donor and acceptor pairs to the edges of these discoidal particle, providing a platform to explore co-facial aggregation and basal separation due to solvent composition or surfactant modification.[6] Finally, perspectives on how such anisotropic modification strategies can be used to influence the hierarchical structure of assemblies formed at the interface of a laser-driven microbubble are presented, towards the directed hierarchical assembly of functional nanomaterials at interfaces.[7,8]



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Testing the Limits of Collective Excitations in Perovskite Quantum Dot Superlattices

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Abstract: Collective excitations in Perovskite cesium lead bromide ($CsPbBr_3$) nanocrystals have garnered significant attention due to their ability to facilitate rapid and coherent emission, surpassing that of standard isolated nanocrystals. In 1954, Dicke formulated the theoretical framework for superradiance and superfluorescence, describing the correlated spontaneous emission of closely-packed quantum emitters. Self-assembled perovskite superlattices have exhibited collective emergent phenomena characterized by fast, narrow, and coherent emission. However, the physical parameters that restrict this phenomenon are not yet fully understood, as all experiments demonstrating superfluorescence have utilized diffraction-limited laser sources. Overcoming this challenge, we present a novel approach to investigating correlated phenomena with nanometer spatial resolution by utilizing a pulsed free electron beam to trigger superfluorescence in lead-halide perovskite superlattices. This method extends the limits of observation and offers new opportunities to study collective correlations with SEM resolution. An imidate revelation is spectral non-homogenuity of nanocrystals at the edges of superrlattices which limits collective excitations and potentially superfluorescence.

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Self-Assembly of Superionic Nanoparticles Into Static And Out-of-Equilibrium Materials

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Abstract: Self-assembly of inorganic nanoparticles (NPs) into ordered structures ("superlattices") has led to a wide range of nanomaterials with unique optical, electronic, and catalytic properties. Various interactions have been employed to direct the crystallization of NPs, including van der Waals forces, hydrogen bonding, as well as electric and magnetic dipolar interactions.[1] Among them, Coulombic interactions have remained largely unexplored, owing to the rapid charge ligand exchange between NPs bearing high densities of opposite charges. In this talk, I will describe a new method[2] to assemble such "superionic NPs" under conditions that preserve their native surface charge density. Our methodology was used to assemble oppositely charged NPs into high-quality superlattices exhibiting Catalan shapes.[3] The methodology can be applied to a wide range of charged nanoparticles of various sizes, shapes, and compositions. I will also discuss different ways to employ electrostatic interactions to assemble NPs into transient assemblies,[2,4] whose lifetimes depend on and can be controlled by the availability of small-molecule ionic "fuels".

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Dynamics and Emergent Complexity in Colloidal Nanocrystal Superstructures

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Abstract: Functional materials built from nanocrystals and nanocrystal superstructures are enabling new applications in renewable energy conversion, optoelectronics, nanomedicine, and more. Essential to the realization of materials-by-design is to elucidate synthetic pathways and understand the kinetics of structural transitions. The process of nanocrystal assembly, analogous to a chemical reaction, usually traverses a complex free-energy landscape before reaching the equilibrium or steady-state structure. Therefore, we must begin to think of assembly as a reaction pathway connecting multiple nonequilibrium intermediates. Fully understanding these pathways requires real-space, real-time characterization with meaningful spatiotemporal resolution, which is not by possible with existing ex-situ characterization or scattering-based methods. In the first part of this talk, I will discuss our recent advances on direct imaging of nanocrystal assembly using in-situ liquid cell transmission electron microscopy. The interaction potential between nanocrystals can be readily tuned by changing the nonaqueous solvent, which enabled observation and quantitative analysis of nonclassical crystallization pathways toward nanocrystal superstructures. In the second part, I will introduce our recent studies on structural diversity in gold nanotetrahedron superstructures that emerged from simultaneous control of nanocrystal core dimensions, surface chemistry, and assembly conditions.

Cadmium Chalcogenide Nanoplatelet Stacks from Various Media

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Abstract: Cadmium chalcogenide nanoplatelets (NPLs) possess not only unique optical properties but also a high tendency to self-assemble into ordered stacks in direction of their thickness. Here, we investigate the emergence of new collective properties such as a charge carrier transport which can arise due to the self-assembly.[1,2] As smaller distances between the NPLs should enhance the transport within the stacks we focused on minimizing these. We applied ligand exchanges with a mixture of $CdBr_2$ and different amines to minimize the inter-NPL distance, since the stacks form by interpenetration of long aliphatic chained ligands of neighboring NPLs. Hereby, the inter-NPL distance could be reduced by more than half (below 1 nm).[2] Further, this indeed led to enhanced charge carrier transport in photo-electrochemical experiments. The ligands not only influence the distances in the stack but also the solubility in different media. Since many applications and processes such as photo-catalysis and various gelation methods require aqueous systems, we investigated a new stacking process directly in aqueous media. Here, to phase transfer the NPLs to aqueous solution we performed a ligand exchange, followed by controlled destabilizations with different antisolvents.[3] Due to the fact, that the stacking process is highly dependent on the ligand interactions with each other and the antisolvent, we monitored the stacking process and ligand shell in different polar and non-polar media through different characterization method such as dynamic light scattering, transmission electron spectroscopy, X-ray photoelectron spectroscopy, and infrared spectroscopy.

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Polymorphous Packing of Pentagonal Nanorods

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Abstract: Packing solid shapes into regular lattices can yield very complex assemblies, not all of which achieve the highest packing fraction. In two dimensions, the regular pentagon is paradigmatic, being the simplest shape that does not pave the plane completely. In this work nanoprisms with pentagonal cross section have been assembled in large supercrystals in which the long-predicted ice-ray and Dürer packings (with packing fractions of 0.921 and 0.854, respectively) were encountered. A variety of novel polymorphs that can be obtained from these two configurations by a continuous sliding transformation and exhibit an intermediate packing fraction were also evidenced. Using a model of the sliding transformation, and comparing data from this model with experimental data, the packing fraction of a section of the crystal can be finely determined. Beyond the fundamental interest of this result, fine control over the density and symmetry of such plasmonic assemblies opens the perspective of tuning their optical properties, with potential applications in metamaterial fabrication, catalysis, or molecular detection.

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Polymer Templated Synthesis of Functional Nanostructures

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Abstract: In my talk I will discuss synthetic approaches toward fabrication of nanomaterials relevant for catalytic, photocatalytic, sensing, and optical applications. I will review the potential of a new method based on infiltration of polymer templates with inorganic precursors for direct fabrication of highly porous materials in a form of conformal coatings and scale-up three- dimensional structures for design of high performing catalysts, optical coatings, and sensing materials. I will discuss the strategies that can be utilized to improve the catalytic performance of nanocatalysts. These strategies include surface modification of catalytic nanoparticles with organic molecules and ionic species.

Tuning the Shades of Red Emission in InP/ZnSe/ZnS Nanocrystals with Narrow Emission Profile for Fabrication of Light-Emitting Diodes

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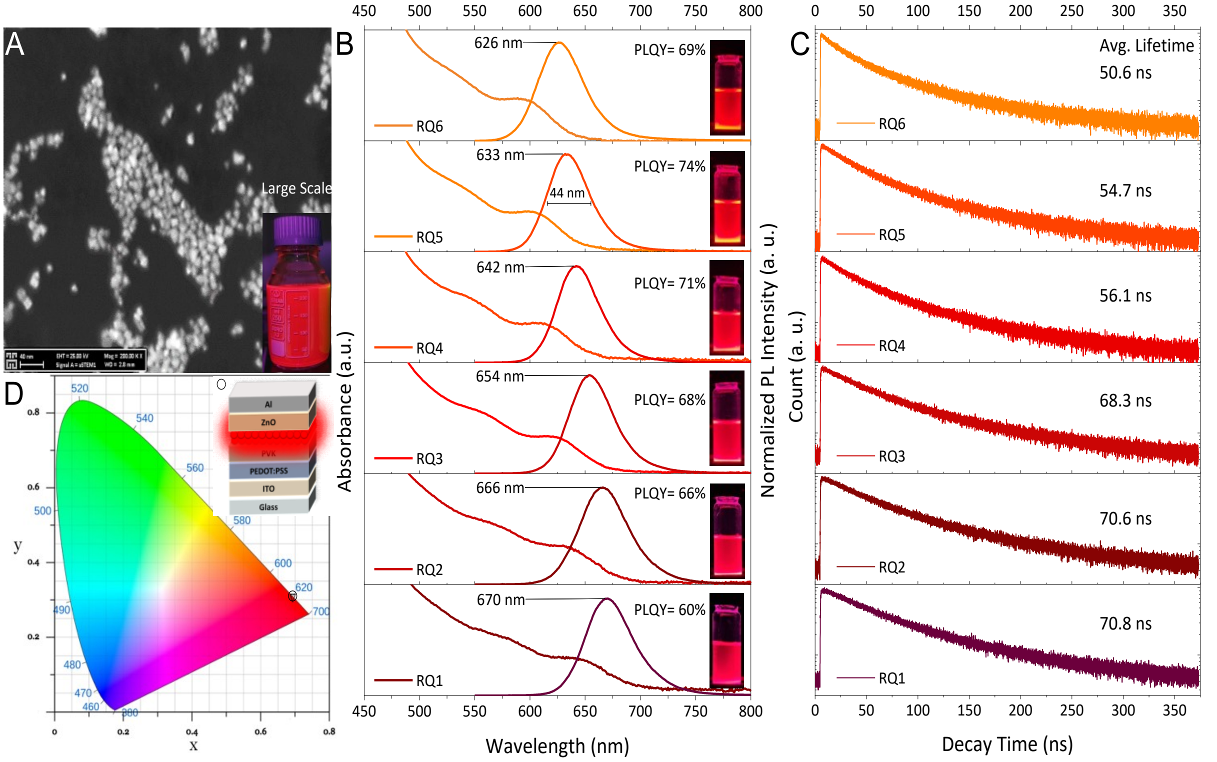
Abstract: While Cd-based luminescent nanocrystals (NCs) are the most mature NCs for fabricating efficient red light-emitting diodes (LEDs), the toxicity-related limitation is their inevitable property, making it necessary to find a promising alternative. From this perspective, multi-shelled red-emissive InP NCs are promising nanomaterials to be employed as an emissive layer in electroluminescent (EL) devices.[1] However, due to the presence of oxidation states, they suffer from a wide emission-profile, limiting their performance. This study uses tris(dimethylamino)phosphine as a low-cost aminophosphine precursor and a dual HF-treatment to represent a cost-effective, one-pot, up-scaled hot-injection synthesis of purely red-emissive InP-based NCs. The HF-etching process was performed twice to reduce the formation possibility of surface oxidizing agents at interior layers. The InP core structures were coated with thick shells of ZnSe/ZnS to prevent charge delocalization and create a narrow size distribution with lower surface/interface defects. The colloidal NCs were 11 nm in size (Figure A), with an intense emission signal as narrow as 44 nm across the entire red-wavelength (626-670 nm) with emission quantum efficiencies of 74% at 633 nm and 60% for far-red wavelengths of 670 nm (Figure B) which are one of the best results reported yet for red InP-based NCs prepared via a one-pot method.[2-4] Also, samples showed relatively long emission-lifetimes of 50-70 ns with biexponential decay-profiles (Figure C). To demonstrate their practical ability in optoelectronics, we fabricated red-emissive InP-based LED. It showed external quantum efficiency of 1.16%, luminance of 1039 cd.m^{-2}, and current efficiency of 0.88 cd.A^{-1} (Figure D).



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Engineering Polymorphs in Colloidal Metal Dichalcogenides for Efficient Electrochemical Activity

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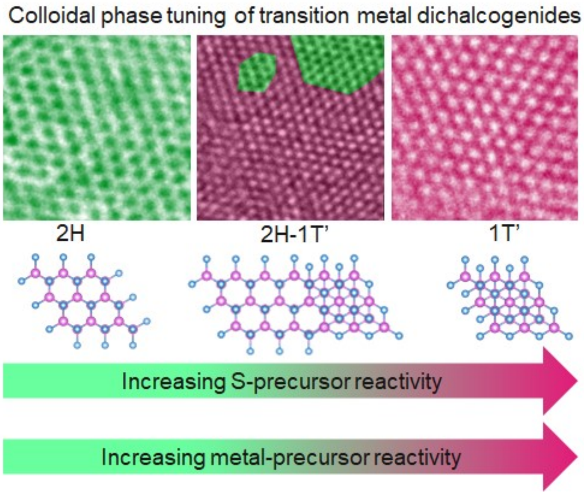
Abstract: Controlling the crystal phase in layered transition metal dichalcogenides (TMD) is critical for their diverse, flexible applications.[1] However, due to the thermodynamic stability of 2H over other polymorphs, fine synthesis control over polymorphism in TMD is challenging, restricting the entire range of characteristics associated with other polymorphs.[2] Herein, we present a solution-based crystal phase engineering approach for layered transition metal disulphide nanosheets by modulating the reactivity of the molecular precursors. By tuning precursor-ligand chemistry, 2H, 1T' and polytypic MoS_2 and WS_2 are synthesised. The flexibility to selectively modify the reactivity of S and metal precursors allowed control over the proportion of specific phases in synthesised nanosheets. The formation of 1T' is facilitated by the highly reactive metal and S source, whereas less reactive sources lead to the formation of thermodynamically stable 2H. We provide in-depth mechanistic insights that enable improved predictive synthesis of particular phases. In addition, we carried out a retrosynthetic approach that predicted chemical intermediates during the nanosheet formation, leading to the specific polymorph formation. Furthermore, we demonstrate the advantage of the polytypic transition metal sulfide nanosheets over the monophasic nanosheets displaying better catalytic performance with higher onset potentials and diffusion-limited current density during the oxygen reduction reaction (ORR). Our synthesis approach has the potential to be extended to various TMDs compositions, enabling exquisite control over polymorphism in TMDs.



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Magic from Magic-Sized Clusters

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Abstract: Magic-sized clusters (MSC) are identical inorganic cores that maintain a closed-shell stability, inhibiting conventional growth processes. Because MSCs are smaller than nanoparticles, they can mimic molecular-level processes, and because of their small size and high organic-ligand/core ratio, MSCs have "softer" inter-particle interactions, with access to a richer phase diagram beyond the classical close packed structures seen with larger particles. In this talk I will highlight some remarkable behavior we have recently found in both of these areas. We have found that MSCs have the ability to undergo a chemically-induced, reversible isomeric transformation between two discrete states. The diffusionless reconfiguration of the inorganic core follows a first order kinetic rate driven by a distortion of the ligand binding motifs. These MSCs also display a surprising ability to self-organize into hierarchical assemblies which span over six orders of magnitude in length scale. The films are optically active with g-factors among the highest reported for all semiconductor particles. Because identifying the physical origin of the chirality for a highly-structured chiroptical active film is a challenging, we developed a stepwise method for extracting the chiroptic-CD signal from the raw data that contains linear anisotropic effects, derived using Mueller matrix and Stokes vector conventions, and find that the likely origin of the chirality is from exciton coupling between adjacent MSCs. Beyond optical properties, the multiscale self-organization behavior of these MSCs displays similarities to biosystems, providing a new platform for the design and study of materials.

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Analysis of Semiconductor Magic-Size Clusters in Crude Reaction Mixtures using Analytical Ultracentrifugation

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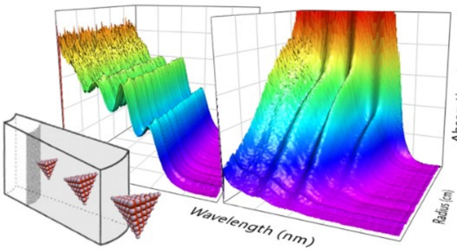
Abstract: The early stages of semiconductor nanocrystal synthesis are often characterized by the occurrence of small clusters with an atomically defined size and shape, commonly called magic-size clusters in reference to the much better-understood magic number clusters of metals like gold. A major reason for the difficulties in obtaining a proper analysis is the low stability and transient nature of these ultrasmall particles. Efforts to isolate and purify them often lead to destabilization and a broadening of the size distribution.

We have employed analytical ultracentrifugation (AUC) using a multiwavelength detector to analyze samples of magic-size clusters in crude reaction mixtures, without the need of purification.[1] AUC yields information on the sedimentation and diffusion behavior, size, shape, and composition. With additional access to the whole UV/vis absorption spectra during centrifugation, it is possible to separate and identify individual magic-size clusters.



Using the technique, we were able to confirm the structural model of zincblende tetrahedra terminated by {111} surfaces for the family of CdSe clusters obtained from colloidal synthesis following two different, published protocols.[2,3] The mean values for the stoichiometry determined by AUC fall within seven atoms of the tetrahedron model.[4]

Analytical ultracentrifugation thus constitutes an elegant, independent, high-resolution, and statistically significant method to show the stepwise growth of magic- size clusters.

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Colloidal Synthesis of Noble-Metal-Based Hollow Multicomponent Nanocrystals

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Abstract: The ability to produce noble metal nanocrystals (NCs) with fine control of their physical, chemical and structural properties is crucial for expanding their applicability in many areas, including optoelectronics, energy harvesting, catalysis, chemical and biological sensing, imaging and biomedicine. The intrinsic properties of NCs can be tailored by controlling their morphology (size and shape), composition (monocomponent vs alloys) and structure (solid vs hollow). Exciting is the case of hollow NCs, where virtually all the atoms of the structure are on the surface, where a large part of electronic, optical and catalytic processes occur. In this regard, hollow NCs offer additional properties, such as resonant cavities, increased surface areas and reduced densities.

Despite its fundamental and technological importance, synthetically controlling the structure, morphology, and composition of metallic hollow NCs is still challenging. The processes to obtain hollow NCs are low-yielding, restricted compositions, and often undesired polycrystalline surfaces and require high temperatures. Therefore, new synthetic strategies are needed to fully develop the benefits of controlling matter at the nanoscale. Herein, we present our latest results on producing hollow NCs based on galvanic replacement. By adjusting the synthetic parameters involved in the reaction, we can precisely control the final morphology of multicomponent hollow NCs. Moreover, the catalytic properties of these types of structures, including the role played by the particle composition, structure, and morphology, were widely investigated, providing fundamental insights into key features that influence the activity, selectivity, durability and reusability of catalysts.[1-5]

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Colloidal Semiconductor Nanocrystals as Platforms for Quantum Information Science

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Abstract: Colloidal semiconductor nanocrystals (NCs) provide platforms to pack the functions of photon and spin qubits within individual particles.[1] Quantum states can be sculpted as quantum confined excitons, delocalized over the NC volume, or encoded in charge and spin states, localized at defects of dopants within the NC core. Advances in synthetic methods allow near-atomic-scale precision in tailoring NC size, shape, and composition; in engineering NC heterostructures; and in introducing defects and dopants. As colloids, directed and self-assembly enables the deterministic positioning of single NCs on surfaces and their solution-based integration in optical cavities. Here, I will describe the use of template-assisted self-assembly to deterministically position single NCs in arrays and study their optical and quantum properties. For example, in collaborative work to silica-coat CdSe/CdS core/shell NCs, we show their scalable assembly and single-photon excitonic emission.[2] We also use this method to position individual milled nanodiamonds containing nitrogen-vacancy (NV) centers, allowing the statistical study and correlation of the spin and charge properties of these point defects with their creation and structure.[3] Finally, we also explore colloidal NCs as wide bandgap hosts for candidate point defects. We synthesize copper-doped, colloidal ZnS (ZnS:Cu) NCs with primarily sub-bandgap, red emission.[4] Through temperature-dependent optical spectroscopies and through theory, we show the red emission is consistent with the creation of Cu_{Zn}-V_S complexes, an impurity-vacancy point defect structure analogous to other well-known quantum defects with desirable optical and spin dynamics.

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Single Particle Photoluminescence Spectroscopy as a Tool to Identify Nanocrystal Orientation

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Abstract: For decades high resolution transmission electron microscopy has been used to gain insight to the crystal orientation of single nanocrystals. However, this technique does not allow a correlation between geometric and spectroscopic signatures. This works reports an approach for the determination of the complete 3D orientation of semiconductor nanocrystals containing an anisotropy axis by means of polarization resolved single particle photoluminescence spectroscopy.[1]

We chose colloidal CdSe/CdS core-shell quantum dots of wurtzite crystal structure. Manganese doping ensures an enhanced sensitivity of the photoluminescence polarization to magnetic fields. At zero magnetic field, a distinct linear polarization pattern is observed while applying a magnetic field enforces circularly polarized emission with a characteristic saturation value below 100%. These polarization features are shown to act as a specific fingerprint of each individual nanocrystal. Model calculations evidence how the orientation of the crystal $\vec{c}$ axis in the lab frame plays a crucial role for the polarization emitted by each single nanocrystal. We demonstrate the need to measure the full set of Stokes parameters for describing the complete polarization state of the nanocrystal photoluminescence and show how these parameters can be used to determine the 3D orientation of the crystal $\vec{c}$ axis in the fixed lab reference frame. Although the experiments have been performed on manganese doped II-VI quantum dots, this idea can be easily transferred to other doped and undoped nanocrystals exhibiting a distinct anisotropy axis.

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Shape Transformation of Colloidal Nanocystals: From Stars to Cubes Studied by X-Ray Scattering Analyses

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Abstract: Controlling the morphology of nanocrystals[1-3] during the synthesis and the ability to analyse this morphology of a significant number of particles is one key research interest in. Besides the more common transmission electron microscope (TEM), small angle X-ray scattering (SAXS) is a leading technique to analyse the morphology of colloidal nanocrystals with sub-nanometre resolution.[3-5] Unlike TEM the probed sample in SAXS experiments is usually orders of magnitude larger, giving the data more statistic relevance. From the scattering data the average size is easily deducible, however using modern *ab initio* bead modelling techniques, also the 3D mean shape of an expressive sample of nanocrystals, seen in all directions, can be retrieved from the SAXS data.[4,5]

In this study the size and shape of varyingly complex superparamagnetic iron oxide nanocrystals (FeO NCs),[2] as well as the crystallographic growth direction are analysed. FeO NCs in the size range from 20–40 nm with nearly perfect cubic to star-like shape with eight arms are investigated.[2,6] Complementary X-ray diffraction experiment support the findings from the SAXS data. The excellent congruence of the results is demonstrated by comparison to TEM micrographs. The 3D SAXS mean shapes allows, however, to gain additional information on the internal dimensions of the FeO NCs that are not visible in the TEM analysis alone.[6]

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Nanocrystal-Based Active Nanophotonics for on Chip Spectral Filtering

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Abstract: Thanks to their low temperature growth and lack of epitaxy constrain for their growth, nanocrystals offer energy effective and toxicity reduce opportunity for the design of infrared active material compared with existing technologies. Over the past decade, significant progress have been obtained pushing the concept from absorption in the infrared to advanced devices including focale plane array. Recently, we demonstrate that such sensor can present cost below 100 €, a decade lower than their counterpart based on InGaAs. While the cost of sensor becomes almost negligible, the surrounding environment and in particular the optics remains prohibitive. Thus including the optics, directly at the wafer level, appears of high interest. Here, we show how active spectral filtering function can be obtained from photonics structure coupled to infrared active nanocrystals.

Driving multielectron redox catalysis with photoexcited nanocrystals

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Abstract: The synthetic tunability of electronic structure and surface chemistry of semiconductor nanocrystals make them attractive light absorbers for light-driven chemistry. A variety of architectures have been constructed where nanocrystals are coupled with multielectron redox catalysts to drive reactions like H_2 generation, CO_2 reduction, N_2 reduction, and water oxidation with light. In these systems, light absorption in nanocrystals is followed by charge transfer to catalysts, which then use them for redox transformations, and/or to sacrificial carrier scavengers. Interfacial charge transfer between the nanocrystal and the catalyst and its competitiveness with other relaxation pathways in nanocrystals are of paramount importance to the overall photochemical reactivity. In this talk, I will focus on our efforts to elucidate both the kinetics of charge transfer and the kinetics and mechanisms of the competing photophysical pathways in nanocrystal-based systems for light-driven multielectron chemistry. This work entails transient absorption spectroscopy measurements, extensive kinetic modeling to extract rate constants of relevant processes in these heterogeneous systems, and, for some systems, contributions from theory.

White Light Emission from Low Dimensionality Halide Perovskites

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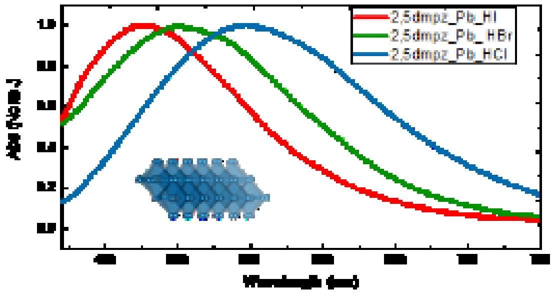
Abstract: Hybrid halide perovskites are a novel class of semiconductor materials with promising and versatile optoelectronic properties, enabled by their chemically adjustable structures and dimensionality. The diversity in the metal ions, halide anions, and organic spacers enable a wide range of materials with highly tunable properties and variable dimensionalities. These materials are studied for various applications such as solar cells, detectors, and light-emitting diodes. The ability to control and adjust the optical properties for a required application is significant. Thus, an improved understanding of the structure and optical mechanisms is crucial.

Specific low-dimensionality hybrid halide perovskites exhibit white-light emission at room temperature, associated with self-trapped excitons (STE), making them ideal candidates for illumination applications. We study the correlation between structural motifs of low dimensionality (2D, 1D) halide perovskites and their STE emission. Initially, we focus on the distortion and connectivity motifs of the metal-halide octahedra as a driving force for the appearance of STE emission. We further study how the composition and specifically exchanging the halide anions while maintaining a 1D structural motif favorable for broad emission affect the STE properties.



1D Halide perovskite compounds with different halide anions (I, Br, Cl), all showing broad emission associated with STE

Colloidal Synthesis and Photophysics of Strongly Light-Emitting Zirconium-Halide Based Nanocrystals

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Abstract: Recent advances in lead-free perovskite(-inspired) semiconductors include the family of A_2BX_6 materials (A and B are mono- and tetravalent cations, respectively, and X is a halide anion). Mostly, those A_2BX_6 materials are little emissive with typical photoluminescence quantum yields in the single-digit range[1,2] or lower,[3,4] which limits their application for example in light-emitting diodes or as scintillator materials.

The only intrinsically, strongly emitting A_2BX_6 compounds, which are able to challenge the optical properties of lead halide perovskites, incorporate Zr on the B-site. We report on the colloidal synthesis of phase-pure Cs_2ZrX_6 (X = Cl, Br) nanocrystals (NCs),[5] which are strong blue-white (Cl) and green-white (Br) light emitters, exhibit tunable emission, which is not limited by anion-exchange as in standard lead halide perovskites, and are solution-processable into thin films suitable for device applications. We uncover the photophysics behind the emission in Cs_2ZrX_6 NC thin films by means of temperature-dependent steady-state and time-resolved photoluminescence measurements and find striking differences to the emission properties reported on the closely related Cs_2ZrCl_6 NCs[6] and nanograins.[7] We hypothesise that difficulties arising on working with Cs_2ZrX_6 NCs have so far limited additional works on this interesting material and suggest remedy to enable and uncover the true potential of Cs_2ZrX_6 NCs in device applications. Our experimental work is supported by density functional theory calculations, from which we conclude on why Cs_2ZrX_6 NCs are so highly emissive.

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