Chemical Design of Nanocrystal Solids

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Abstract: This account highlights our recent and present activities dedicated to chemical synthesis and applications of inorganic nanostructures. In particular, we discuss the potential of metal amides as precursors in the synthesis of metallic and semiconductor nanocrystals. We show the importance of surface chemical functionalization for the emergence of collective electronic properties in nanocrystal solids. We also demonstrate a new kind of long-range ordered, crystalline matter comprising colloidal nanocrystals and atomically defined inorganic clusters. Finally, we point the reader’s attention to the high potential benefits of size- and shape-tunability of nanocrystals for achieving higher performance of rechargeable Li-ion battery electrodes.

Keywords: Nanocrystals · Self-assembly · Semiconductors · Superlattices · Synthesis

Introduction and Motivation

Very early in the course of my undergraduate studies in 1999–2004, I was thrilled by the chemistry of nanoscale inorganic materials. I was surrounded by solid-state chemists (Chernivtsi National University, Ukraine), who grew large single crystals of a renowned semiconductor material, CdTe. At the same time, I was much impressed by the 1996 paper of Andrey Rogach and his co-workers from the University of Hamburg,[1] where a simple aqueous synthesis of sub-10 nm colloidal CdTe nanocrystals (NCs) was demonstrated. Compared to a grey-colored chunk of bulk CdTe, colloidal 2–7 nm CdTe crystallites fascinated by their size-tunable absorption and emission colors spanning the entire visible spectral range due to quantum size effects. Owing to three-dimensional quantum confinement of electrons and holes, such ultra-small semiconductor crystallites are also known as colloidal ‘quantum dots’. By 2004, when I started my PhD project (Johannes Kepler University Linz, Austria), a new challenge that also became a major goal of my thesis was to synthesize narrow-bandgap colloidal quantum dots active in the near and mid-infrared spectral regions, thereby enabling the use of colloidal semiconductors in solution-processed quantum-dot photodetectors, lasers and solar cells.[2]

At about the same time, an entire research community quickly realized the fundamental importance and experimental difficulty in engineer efficient electronic communication between individual quantum dots in their compact ensembles. This led me to spend several years of my postdoctoral research training at the University of Chicago (USA), where I was much impressed by the 1996 paper of Andrey Rogach and his co-workers from the University of Hamburg,[1] where a simple aqueous synthesis of sub-10 nm colloidal CdTe nanocrystals (NCs) was demonstrated. Compared to a grey-colored chunk of bulk CdTe, colloidal 2–7 nm CdTe crystallites fascinated by their size-tunable absorption and emission colors spanning the entire visible spectral range due to quantum size effects. Owing to three-dimensional quantum confinement of electrons and holes, such ultra-small semiconductor crystallites are also known as colloidal ‘quantum dots’. By 2004, when I started my PhD project (Johannes Kepler University Linz, Austria), a new challenge that also became a major goal of my thesis was to synthesize narrow-bandgap colloidal quantum dots active in the near and mid-infrared spectral regions, thereby enabling the use of colloidal semiconductors in solution-processed quantum-dot photodetectors, lasers and solar cells.[2]

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Synthesis of Colloidal Nanocrystals

Rational synthesis of uniform NCs remains an important task for synthetic inorganic chemists. Herein we discuss our recently developed routes to monodisperse Sn and InSb NCs (Fig. 3) using amides of metals and metalloids as precursors. [5]

Monodisperse inorganic NCs are typically synthesized by reacting appropriate molecular precursors in high-boiling organic solvents at temperatures ranging from 25 to 380 °C, under oxygen- and moisture-free conditions. The nucleation and the growth can be conveniently initiated by either hot-injection of precursors into a hot solvent (Fig. 1) [6] or by heating-up the reaction mixture [7]. Capping ligands, also known as stabilizers or surfactants due to their multifunctional role, are added before the NC synthesis. Surfactant molecules dynamically adhere to the NC surface during the nucleation and growth, regulate NC size, provide chemical and colloidal stability and, therefore, are inevitable components of NC systems. Commonly used ligands include long-alkyl chain (C\(_8\)–C\(_{18}\)) amines, phosphines and thiols as well as carboxylic and phosphonic acids (Fig. 4). The shape of NCs is a complex interplay between the underlying crystal structure and passivation of crystal facets by the surface ligands. Colloidal synthesis allows unprecedented size uniformity and greatly benefits from the vast variety of solvents, precursors and surfactants, and experimental ease of solution-phase chemistry. Furthermore, liquid-phase storage and handling of nanoparticles is of paramount importance for occupational and environmental safety. The steep learning curve in the synthetic art and the rapid progress in atomic-level characterization techniques such as aberration-corrected electron microscopy, allows one to expect further rapid advances in NC synthesis.

The choice of molecular precursors is a major consideration in the synthesis of a new kind of NCs. Our present focus is on the use of metal alkylamides and silylamides as precursors in the synthesis of NCs with previously inaccessible compositions and/or morphological uniformity. The first example, tin (Sn), is a non-toxic, inexpensive, naturally highly abundant element that is extensively used in metal alloys such as solder, in photovoltaic semiconductors such as kesterites Cu\(_2\)ZnSn(Se\(_2\))\(_4\), in transparent conductive oxides and as anode material for the next-generation rechargeable Li-ion batteries (LIB). A new synthesis of monodisperse, 10–30 nm large Sn NCs (Fig. 3), exploits Sn-oleylamido complexes as precursors [5a]. Although we initially thought that Sn[N(SiMe\(_3\))\(_2\)]\(_2\), is produced in situ from SnCl\(_2\) and Li[N(SiMe\(_3\))\(_2\)]\(_2\), a \(^{119}\)Sn NMR study suggested a different reaction pathway. The true role of Li[N(SiMe\(_3\))\(_2\)]\(_2\) is
to deprotonate oleylamine, thus promoting the formation of Sn-oleylamido species. Nearly instant reduction by disobutylaluminum hydride leads to monodisperse Sn NCs. In accord with this mechanism, identical results in terms of reaction yield and size/shape uniformity were obtained using LiNMe₂ as a base. We believe that metal-oleylamido complexes may act not only as precursors but also as surface-capping monolayers.

Synthesis of high-quality III-V colloidal NCs represents a long-standing challenge in the chemistry of colloidal quantum dots. In a colloidal quantum dot state, InSb with its narrow bulk bandgap energy of 0.18 eV (300K) and very large exciton Bohr radius of 70 nm is a viable alternative to toxic Pb and Hg chalcogenide NCs, especially at infrared wavelengths beyond 2000 nm. Furthermore, InSb exhibits extremely high room-temperature electron mobilities up to 78 000 cm²/Vs. To date, most successful synthesis routes to InP and InAs NCs have employed highly reactive precursors such as P(SiMe₃), PH₃ and As(SiMe₃). Significantly lower chemical stability of Sb analogs, Sb(SiMe₃), and SbH₃ remained the major obstacle towards the synthesis of monodisperse InSb NCs. We therefore tested tris(dimethylamido)antimony, Sb(NMe₂), as a more stable, alternative reagent. Sb(NMe₂), is readily available as a commercial precursor for metal-organic chemical vapor deposition (MOCVD), in particular for growing epitaxial InSb at temperatures as low as 285 °C. In[N(SiMe₃)]₂ has been identified as a convenient indium precursor, with the reactivity matching well to that of Sb(NMe₂). The reaction between In[N(SiMe₃)]₂ and Sb[NMe₂], at 200–300 °C in a weakly coordinating solvent such as trioctylphosphine yielded uniform sub-10 nm InSb NCs with a standard size-deviation of 10–15% (Fig. 3).

Furthermore, this synthesis method allows the control of the zinc blende/wurtzite (ZB/WZ) polymorphism by adjusting the In-to-Sb molar ratio of the precursors. Notably, bulk InSb is exclusively reported in its zinc-blende phase. In agreement with expected quantum-size effects, optical absorption spectra of InSb NCs dispersed in the near-IR-transparent tetrachloroethylene exhibited a single peak/shoulder, tunable in the range of 1250–1750 nm (1.0–0.7 eV) by adjusting the average NC size from 5.6 to 8.6 nm. InSb NCs also exhibit band-edge photoluminescence, as exemplarily shown by the largest studied size of 8.6 nm with the emission peak at 1900 nm (Fig. 3). The emission intensity is, however, very weak, presumably due to surface oxidation of InSb NCs. Further work is needed to extend the optical response to mid-IR wavelengths and to improve the chemical stability of InSb NCs by overcoating with wide-bandgap, chemically stable semiconductors such as ZnSe or ZnTe.

**Nanocrystal Surface Chemistry**

One of the most pressing challenges, critically dependent on the NC surface chemistry, is efficient electronic coupling between individual NCs in densely packed NC solids. Commonly used long-chain organic molecules (Fig. 4) act as bulky and electrically insulating barriers, hindering charge transport and rendering NC solids fully insulating with electrical conductivities in the range of 10⁻¹¹–10⁻¹⁴ S cm⁻¹. In 2009, the traditional concept of ‘inorganic core-organic shell’ has been revised by demonstrating that various chalcogenidometalate complexes (e.g. SnS₂⁺, Sn₃S₆⁺, SnTe₄⁺, In₅S₇⁺, SnS₆⁺, SbSe₄⁺, MoS₆⁺, and the like) can quantitatively replace organic molecules (Fig. 4), serving as polyelectrolyte, highly nucleophilic, small and electrically conducting capping ligands. These all-inorganic, charge-stabilized NCs exhibit high colloidal stability in polar solvents such as water and formamide. Chalcogenidometalates with decomposable cations (NH₄⁺, N₂H₄⁺) can be conveniently converted into parent metal chalcogenides, thereby forming a layer of conductive ‘glue’ between the NCs: (N₄H₄)Sn₄S₆ → 2SnS₂ + 4NH₃ + 2H₂S. Milliron and coworkers proposed an alternative method for anchoring chalcogenidometalates to the NC surface via ligand exchange directly in the films of organically-functionalized NCs.[15] The success of chalcogenidometalates as capping ligands stimulated recent extension to metal-free Sₓ, OH, NHₓ, TeSₓ, CNS+x. Oxidatively stable NCs, such as metal oxides, can be colloidally stabilized by tetrafluororboron anion BF₄⁻, a weakly nucleophilic anion that easily dissolves in polar solvents leaving ‘bare’, cationic NC surfaces behind. Such surface functionality can be obtained by treating organic-capped NCs with NOBF₄ and Meerwein’s salt EtOBF₄.[16]

Electrical transport through the compact NC solid is of central consideration for efficient electronic and optoelectronic devices. Regardless of the exact mechanism of charge-transport, one has to consider quantum mechanical coupling between the neighboring quantum dots, which can be expressed in terms of the coupling energy β = hΓ, where h is Planck’s constant and Γ is the tunneling rate between two orbitals of NC neighbors.[1,13] The tunneling rate can be approximated as β = kₓΓ, where m* is the electron effective mass, ΔE and Δx are the height of tunneling barrier and the inter-NC distance. Ligand
engineering using small and electronically transparent chalcogenide ligands has a direct effect by decreasing $\Delta S$ and $\Delta E$. Furthermore, the size and shape uniformity of quantum dots has a pronounced effect as well, due to reduced site-to-site dispersion of energy levels. The efficiency of charge transport is characterized by carrier mobility ($\mu$), experimentally estimated by Hall-effect measurements or from the output characteristics of field-effect transistors with NC solids as a channel layer. In contrast to traditional organic capping, all-inorganic design allows superior (opto) electronic characteristics to be attained: metallic conductivities of $10^{2} - 10^{4}$ S cm$^{-1}$ in the arrays of Au NCs,$^{[34]}$ band-like transport and electron mobilities up to 30 cm$^{2}$Vs$^{-1}$ in the films of quantum dots.$^{[2b,28]}$ Photon detectivities up to $10^{13}$ Jones$^{-1}$ photovoltaic power conversion efficiencies of at least 5%$^{[21]}$ and enhanced thermoelectric characteristics.$^{[34]}$

Presently we aim to gain a better understanding of inorganic capping on a molecular level through systematic and direct spectroscopic methods (liquid- and solid-state NMR, FT-farIR and Raman spectroscopy) combined with atomistic computational studies. The next challenge is to obtain three-dimensional periodic packing of all-inorganic NCs. So far, long-range ordering has been observed only for inorganic-capped 5 nm Au NCs (Fig. 4).$^{[34]}$ A strong long-range electrostatic repulsion may be preventing crystallization upon the solvent evaporation, leading to randomly packed solids. Learning more about delicate balance of attractive and repulsive forces in the Au NCs–Sn$_{x}$S$_{y}$ colloids may help towards rational design of all-inorganic NCs superlattices.

**Entropy-driven Crystallization for Binary Nanocrystal Superlattices and Beyond**

Recently, a new research field of ‘artificial solids’ has emerged from the entropy-driven self-assembly of various organic-ligand capped NCs into long-range ordered, single-component binary (Fig. 5)$^{[22]}$ or even ternary$^{[24]}$ and quasicrystalline structures$^{[25]}$ upon the evaporation of the solvent. Besides tunable stoichiometry and symmetry, multicomponent superlattice is an ultimately perfectly homogeneous mixture of NCs. At present time, great efforts are put into revealing the details of the crystallography,$^{[10,26]}$ thermodynamics$^{[27]}$ and kinetics$^{[28]}$ of NC self-assembly, development of assembly methods to cover large areas$^{[29]}$ and improvement of electronic coupling.$^{[3a,16b,20]}$ Recent studies on binary NC superlattices showed that entropy often dominates the assembly of sterically stabilized NCs.$^{[21]}$ The gain in free volume entropy upon ordering of hard spheres into densely packed lattice is greater than the decrease in configurational entropy, thus providing a net positive change in the system’s total entropy. The effective size ratio ($\gamma$), between two components in a binary mixture can serve as a structure-directing factor (Fig. 5). Because the size-ratio is a primary consideration in the crystallization of hard-spheres, we recently explored a possibility to co-crystallize NCs with other inorganic species of comparable dimensionality. A new kind of long-range ordered binary superlattices comprising atomically defined inorganic clusters and colloidal synthetized NCs had been demonstrated (Fig. 6).$^{[30]}$ Our choice of polyoxometalates (POMs) as cluster building blocks was motivated by their structural diversity and emergent catalytic properties.$^{[31]}$ In the proof-of-the-concept system, colloidal semiconductor NCs (PbS, CdSe, PbS/Cds; 4–11 nm) were combined with 2.9 nm giant polyoxomolybdate cluster (I), also known as Keplerate cluster.$^{[32]}$ For simplicity denoted here as [Mo$_{72}$] to account for a total number of Mo atoms. The spherical core of the cluster has a composition of [Mo$_{12}$O$_{37}$Ac$_{3}$(H$_{2}$O)$_{4}$]$^{4+}$, where n is ~72: (NH$_{4}$)$_{2}$$^{2+}$Mo$_{12}$O$_{37}$(CH$_{3}$COO)$_{10}$(H$_{2}$O)$_{13}$·ca.300H$_{2}$O·ca.10CH$_{3}$COONH$_{4}$ (compound I).

In order to ensure electrostatically neutral and hydrophobic surface, as required to prepare sterically stabilized colloids in non-polar solvent, NH$_{4}^{+}$ cations were replaced by hydrophobic dodecylammonium cations (DDA$^{-}$) using a known procedure of Volkmer et al.$^{[33]}$ Superlattices were grown by controlled evaporation of a solvent from the colloidal mixture of POMs and NCs. Unambiguous crystallographic assignment of thin-film binary superlattices required thorough analysis by transmission electron microscopy (TEM) and electron diffraction, as well as by scanning electron microscopy (STEM) in high-angle annular dark-field mode (HAADF-STEM), along with spatially resolved energy dispersive X-ray spectroscopy (EDX-STEM). All identified crystal structures can be well rationalized on the basis of dense packing principles of sterically-stabilized particles with predominantly hard-sphere-like interparticle interactions. By varying the

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**Fig. 5. Structural diversity in binary nanocrystal superlattices and space-filling curves for commonly observed binary crystal phases. Nanocrystal building blocks: Au and Pd as smaller constituents (3–5 nm) and PbSe, PbS, CdSe and Fe$_{3}$O$_{4}$ as larger counterparts (6–10 nm). Entropy factors favors a densest structure at a given size ratio (in the range of 0.4–0.8). Image is courtesy of Maryna Bodnarchuk.**
size-ratios and relative concentrations of constituents, we obtained a range of binary crystals isostructural with NaCl, AlB\textsubscript{2} and NaZn\textsubscript{13} lattices (all predicted to be thermodynamically stable in hard-sphere mixtures), and also CaCu\textsubscript{5}-type lattice and aperiodic quasicrystals with 12-fold (dodecahedral) symmetry (Fig. 7). These results are very likely to motivate further efforts to co-crystallize NCs with other kinds of inorganic cluster materials such as fullerenes and magic-sized metallic and semiconductor clusters.

Precisely Engineered Colloidal Nanocrystals as Li-ion Storage Medium

Most of today’s applications of rechargeable LIBs such as e-mobility and portable electronics face growing demands for significantly improved performance, especially in terms of volumetric and gravimetric energy density, improved cycling performance and rate capability. Due to the formation of Sn\textsubscript{5}Li\textsubscript{22}, enabling a theoretical capacity of 992 mAh/g,\textsuperscript{[6]} tin and tin-containing materials are being actively researched as a viable alternative to the state-of-the-art graphite anodes (theoretical capacity of 372 mAh/g). High theoretical capacities of group-IV elements such as tin and silicon are outweighed by the mechanical instabilities and pulverization of electrodes caused by the large, up to 300%, volumetric changes upon full lithiation. Size-reduction of the active material to sub-50 nm range can help mitigate these difficulties.\textsuperscript{[34]} For this reason, highly monodisperse Sn NCs, shown in Fig. 3, represent an ideal system for studying the effects of precisely tunable NC morphologies on the Li-ion insertion and storage processes. As-synthesized Sn NCs are covered with the passivating layer of SnO\textsubscript{2}, formed upon exposure to the air (Fig. 3). The contribution of SnO\textsubscript{2} may reduce achievable reversible capacity to that of pure SnO\textsubscript{2} (780 mAh/g) due to the 1\textsuperscript{st}-discharge irreversible reaction SnO\textsubscript{2} + 4Li = 2Li\textsubscript{2}O + Sn. In order to ensure electronic connectivity between current collector and all NCs within the electrode, an inorganic S\textsuperscript{2−}-capping was applied to NC surfaces and NCs were mixed with conductive carbon additive and polymeric binder. Further tests were carried out at low (30%) and high (64%) mass fraction of an active Sn/SnO\textsubscript{2} nanomaterial and relatively high charge/discharge currents of 1000 mA/g. NCs exhibit high reversible discharge capacities of up to C\textsubscript{Sn,max} = 1000 mAh/g for the cells containing 30wt% Sn (Fig. 8). Taking into account a possible contribution of amorphous carbon due to its capacity of up to 200 mAh/g, the most conservative estimate is C\textsubscript{Sn,min} = 700 mAh/g. Apparently, at this electrode composition, long-term cycling stability was primarily limited by the electrolyte composition, as can be seen from the effect of fluoroethylene carbonate (FEC) additive (Fig. 8A). In order to illustrate the importance of the mean particle size, Fig. 8B compares electrodes containing 10 nm
and 20 nm Sn/SnO₂ NCs with those based on commercial Sn and SnO₂ nanopowders, all with the significantly higher content of an active Sn-material (~64 wt%). Only 10 nm Sn/SnO₂ NCs maintained high Li insertion/removal cycling stability (C₁₀₀₀₀ = 600 mAh/g and C₄₀₀ = 443 mAh/g) after 100 cycles. Further work is thus in progress to optimize formulation of the electrodes and electrolytes.

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