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

Maksym Kovalenko has been a tenure-track Assistant Professor of Inorganic Chemistry at ETH Zürich since July 2011. His group is also partially hosted by EMPA Dübendorf (Swiss Federal Laboratories for Materials Science and Technology) to support the highly interdisciplinary character of his research program. He completed graduate studies at Johannes Kepler University Linz (Austria, 2004–2007), followed by postdoctoral training at the University of Chicago (USA, 2008–2011). Present scientific focus is on the development of new synthesis methods for nanocrystals and nanoparticles, their surface chemistry engineering and assembly into macroscopically large solids. An ultimate practical goal is to demonstrate novel design of inorganic materials for rechargeable Li-ion batteries, photovoltaics and optoelectronics. From 2012, his research activities are also supported by a five-year ERC Starting Grant awarded to the project 'Chemically Engineered Nanocrystal Solids'.

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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 to 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 we focused on alternative approaches to the chemical surface functionalization and device integration of inorganic nano-materials.[3]

In this account, we will discuss contemporary problems in NC science and highlight our recent results. One motivation of our work is a growing recognition that NCs have a set of unique capabilities, such as size- and shape-tunable plasmonic, excitonic, electronic and magnetic properties of the NC core combined with versatile surface functionalization.[4] A common theme in our research, outlined in Fig. 1, is to link recent advances in the precision synthesis of inorganic NCs with the design of practically useful solid-state materials. In the world of nanoscale inorganic materials, the key principles of solid-state chemistry and molecular chemistry are bridged already at the first stage, when NCs are synthesized from molecular precursors. Arguably, inorganic NCs with 10^2–10^4 atoms/NC exceed a realistic limit for the atomic precision in the controlled single-step reaction converting molecular precursors into an inorganic material. Nevertheless, the standard variations of the size and the shape can be as narrow as a few percent, thanks to the dedicated efforts of many research groups over the last 10–20 years. Being large enough to exhibit key structural and electronic features of the respective bulk material, NCs are sufficiently small to form stable, clean and easy-to-handle colloidal dispersions. Such colloids are especially well-suited for processing into thin-film devices. Dense packing of one or several kinds of NCs can be used to construct far-from-equilibrium, macroscopically large inorganic solids – 'nanocrystal solids'. These materials may open new and exciting opportunities for modern technologies, including photo-voltaics, photodetectors, light-emitting devices, rechargeable batteries, nanostructured thermoelectrics, electronics and sensors (Fig. 2).

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 ºC, 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 $Cu_2ZnSnS(Se)_4$, 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 $Sn[NSiMe_3)_2]_2$ is produced *in situ* from $SnCl_2$ and $LiN(SiMe_3)_2$, a ^{119}Sn NMR study suggested a different reaction pathway. The true role of $LiN(SiMe_3)_2$ is
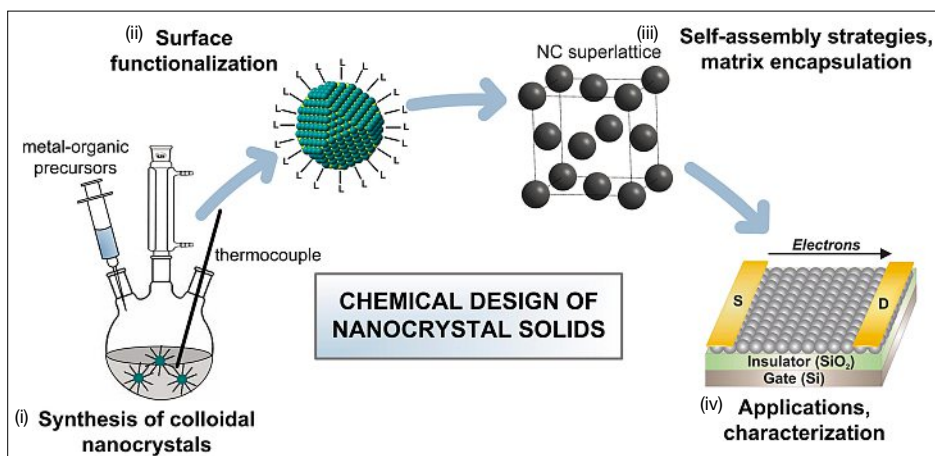

Fig. 1. Chemical design of nanocrystal solids as a highly interdisciplinary problem involving (i) colloidal synthesis of nanocrystals from organometallic and coordination compounds, (ii) surface chemistry engineering, (iii) supramolecular or reticular methods for self-organization and, finally, (iv) exploration of structure-property relationship and integration into devices.
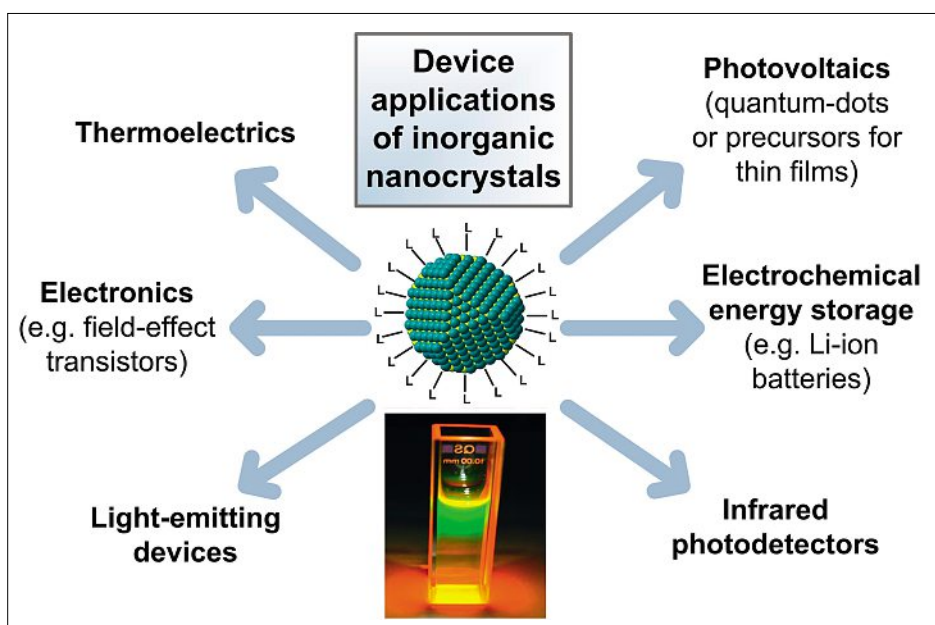

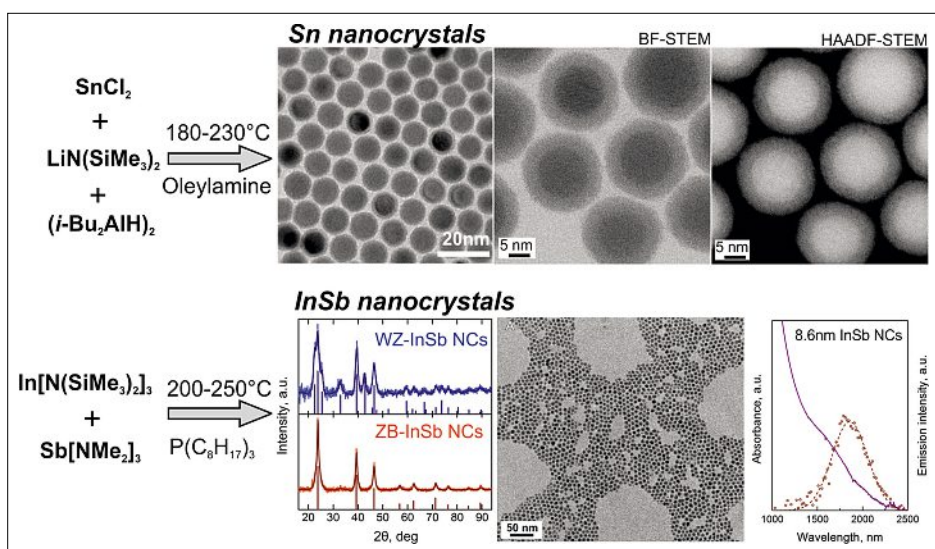Fig. 2. Prospective applications of colloidal inorganic nanocrystals in solid-state devices.

Fig. 3. Synthesis of colloidal Sn and InSb nanocrystals using metal amide precursors. Reprinted with permission from *J. Am. Chem. Soc.* **2013**, *135*, 4199. Copyright 2013 American Chemical Society.
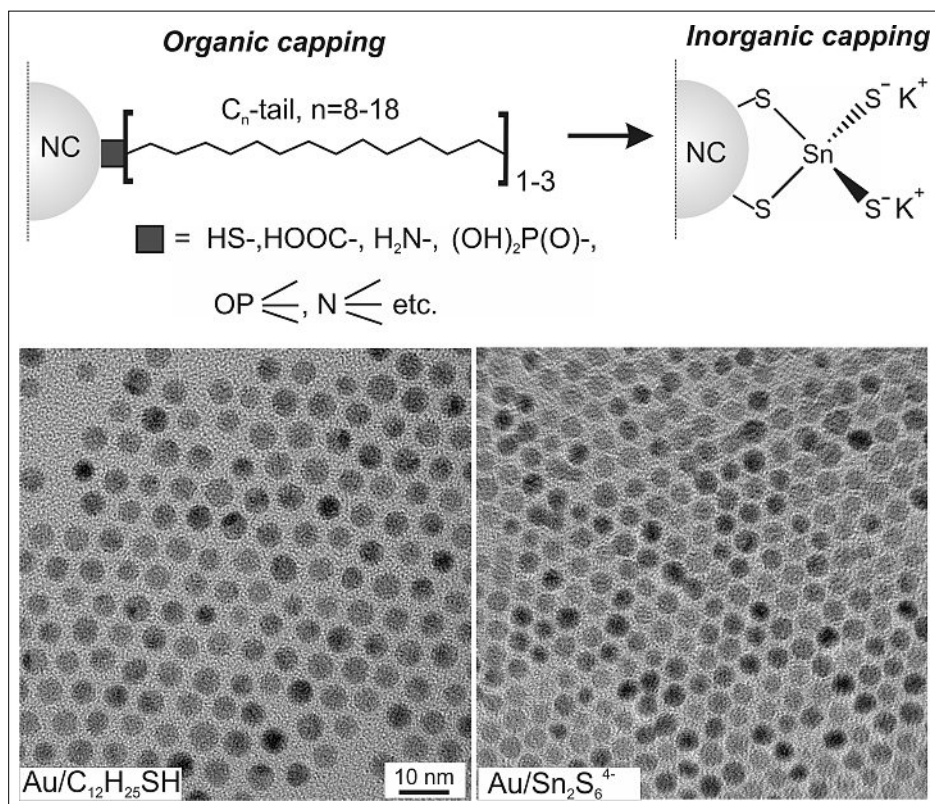
Fig. 4. Traditional organic and novel inorganic surface functionalization of colloidal nanocrystals. TEM images illustrate the compactness of nanocrystal arrays depending upon the length of capping ligands.

to deprotonate oleylamine, thus promoting the formation of Sn-oleylamido species. Nearly instant reduction by diisobutylaluminium 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 $LiNMe_2$ 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.[8] In a colloidal quantum dot state, InSb with its narrow bulk bandgap energy of 0.18 eV (300K)[9] and very large excitonic Bohr radius of 70 nm[10] 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 $P(SiMe_3)_3$, PH_3 and $As(SiMe_3)_3$.[11] Significantly lower chemical stability of Sb analogs, $Sb(SiMe_3)_3$ and SbH_3, remained the major obstacle towards the synthesis of monodisperse InSb NCs.[12] We therefore tested tris(dimethylamido)antimony, $Sb(NMe_2)_3$ as a more stable, alternative reagent.[5b] $Sb(NMe_2)_3$ 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.[13] $In[N(SiMe_3)_2]_3$ has been identified as a convenient indium precursor, with the reactivity matching well to that of $Sb(NMe_2)_3$. The reaction between $In[N(SiMe_3)_2]_3$ and $Sb[NMe_2]_3$ 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).[5b] Furthermore, this synthesis method allows the control of the zinc blende/wurzite (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}.[14] In 2009, the traditional concept of 'inorganic core-organic shell' has been revised by demonstrating that various chalcogenidometalate complexes (*e.g.* SnS_4^{4-}, $Sn_2S_6^{4-}$, $SnTe_4^{4-}$, $In_2Se_4^{2-}$, $Sn_2S_6^{4-}$, $SbSe_4^{3-}$, MoS_4^{4-}, and the like) can quantitatively replace organic molecules (Fig. 4), serving as polydentate, highly nucleophilic, small and electrically conductive capping ligands. These all-inorganic, charge-stabilized NCs exhibit high colloidal stability in polar solvents such as water and formamide. Chalcogenidometalates with decomposable cations (NH_4^+, $N_2H_5^+$) can be conveniently converted into parent metal chalcogenides, thereby forming a layer of conductive 'glue' between the NCs: $(N_2H_5)_4Sn_2S_6 \rightarrow 2SnS_2 + 4N_2H_4 + 2H_2S$. 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 S^{2-}, OH^-, NH_2^-, TeS_3^{2-}, CNS^-.[16] Oxidatively stable NCs, such as metal oxides, can be colloidally stabilized by tetrafluoroborate anion BF_4^-, a weakly nucleophilic anion that easily dissociates in polar solvents leaving 'bare', cationic NC surfaces behind. Such surface functionality can be obtained by treating organic-capped NCs with $NOBF_4$,[17] HBF_4 (or HPF_6)[16a] and Meerwein's salt Et_3OBF_4.[18]

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 $\beta \approx h\Gamma$, where h is Planck's constant and Γ is the tunneling rate between two orbitals of NC neighbors.[4,14,19] The tunneling rate can be approximated as[4,14,19a,19b]

$$\Gamma \approx \exp\left\{-2\left(2m^*\Delta E / \hbar^2\right)^{1/2} \Delta x\right\} \quad (1)$$

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 Δx and ΔE. 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 (μ), 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 10^2–10^3 S cm^{-1} in the arrays of Au NCs,[3a] band-like transport and electron mobilities up to 30 cm^2/Vs in the films of quantum dots,[3e,20] photon detectivities up to 10^{13} Jones,[3e] photovoltaic power conversion efficiencies of at least 5%,[21] and enhanced thermoelectric characteristics.[3d]

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).[3a] 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$_2$S$_6$$^{4-}$ 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,[22] binary (Fig. 5)[23] 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.[27] 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 (γ_{eff}) 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 colloidally synthesized 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 (**1**), also known as Keplerate cluster,[32] for simplicity denoted here as {Mo$_{132}$} to account for a total number of Mo atoms. The spheri-

cal core of the cluster has a composition of {Mo$_{132}$O$_{372}$Ac$_{30}$(H$_2$O)$_n$}$^{42-}$, where n is ~72: (NH$_4$)$_{42}$[Mo$_{72}$^{VI}Mo$_{60}$^{V}O$_{372}$(CH$_3$COO)$_{30}$ (H$_2$O)$_{72}$]·ca.300H$_2$O·ca.10CH$_3$COONH$_4$ (compound **1**).

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
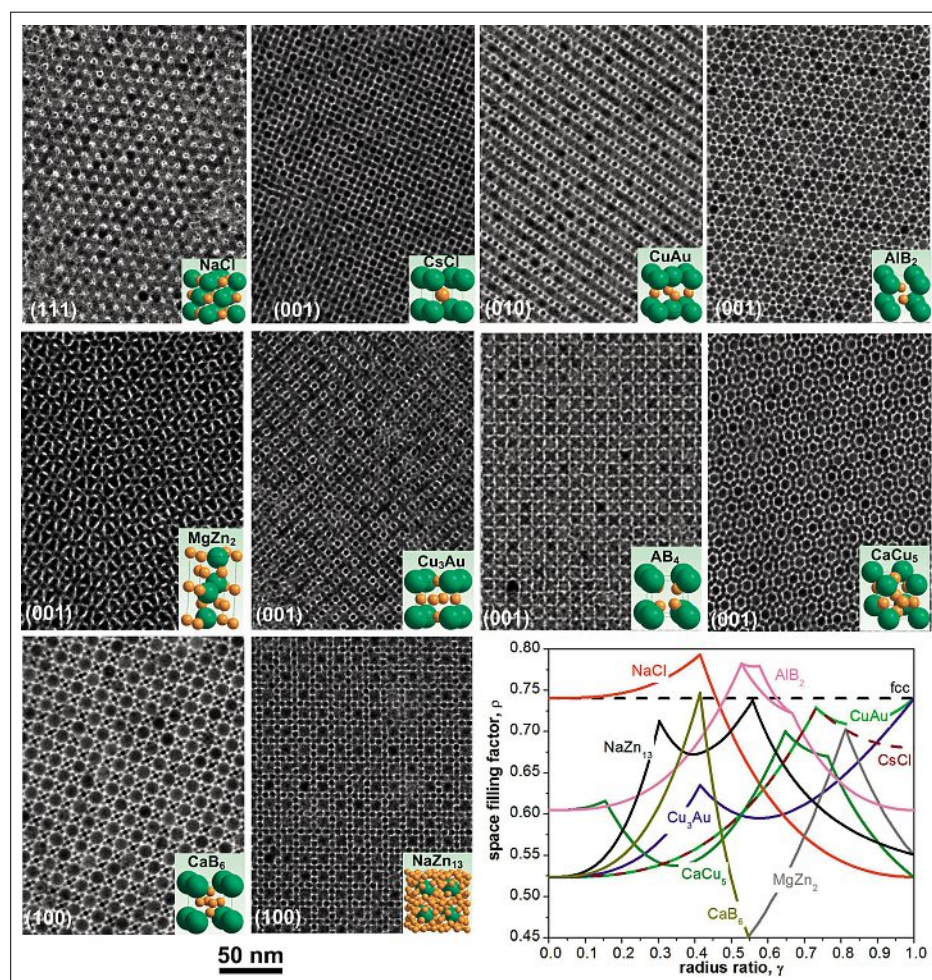

Fig. 5. Structural diversity in binary nanocrystal superlattices and space-filling curves for commonly observed binary crystal phases. Nanocrystal building blocks: Au and Pd as smaller constituents (3–5 nm) and PbSe, PbS, CdSe and Fe$_3$O$_4$ as larger counterparts (5–10 nm). Entropy factors favors a densest structure at a given size ratio (in the range of 0.4–0.8). Image is courtesy of Maryna Bodnarchuk.
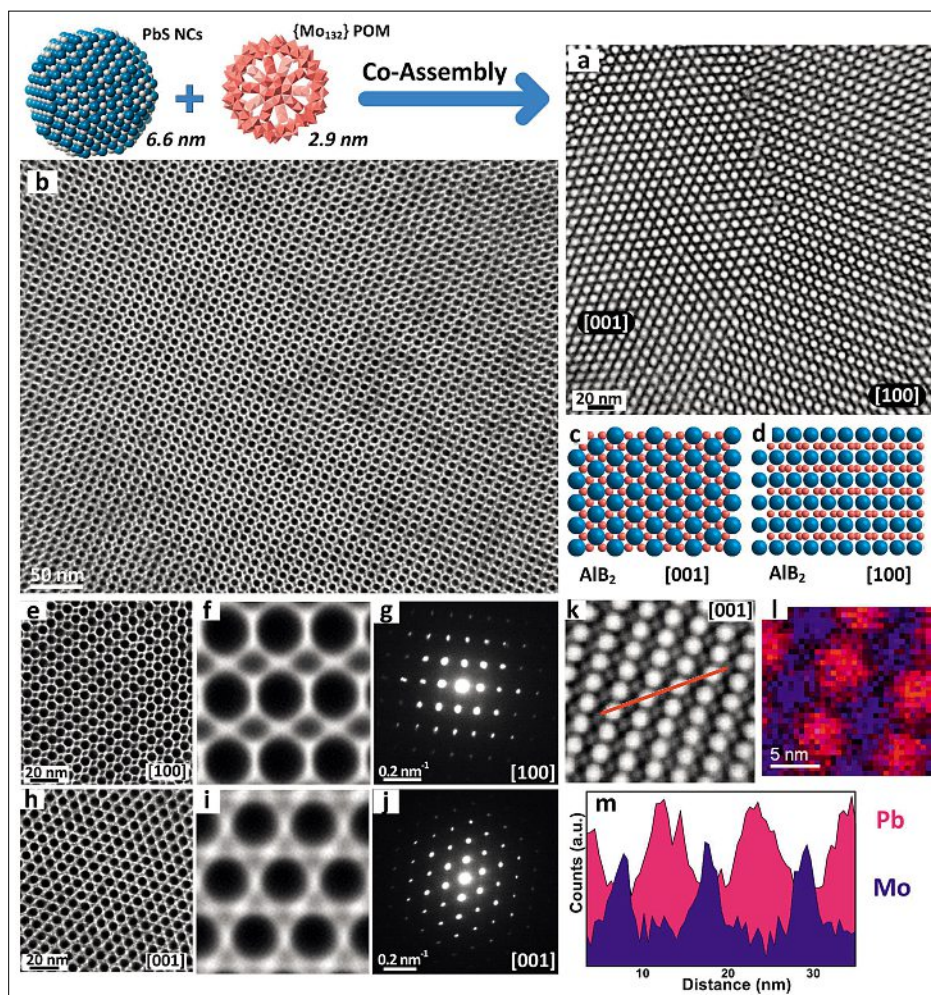
Fig. 6. Detailed structural characterization of AlB_2-type polyoxometalate/nanocrystal superlattice constructed from dodecylammonium-encapsulated $\{Mo_{132}\}$ clusters and 6.6 nm oleate-capped PbS NCs (γ_{eff} = 0.58). (a, k) HAADF-STEM and (b, e, h) TEM images at various magnifications; (c, d) crystallographic models of [001] and [100] oriented AlB_2 thin-film crystallites; (f, i) images obtained by template analysis of TEM images (e, h); (g, j) small-angle electron diffraction patterns; (l) EDX maps for Pb (red, K-line) and Pb (blue, L-line); (m) EDX line scans for Pb and Mo taken along the line shown in (k). Reprinted with permission from *Nano Lett.* **2013**, DOI: 10.1021/nl4002475. Copyright 2013 American Chemical Society.
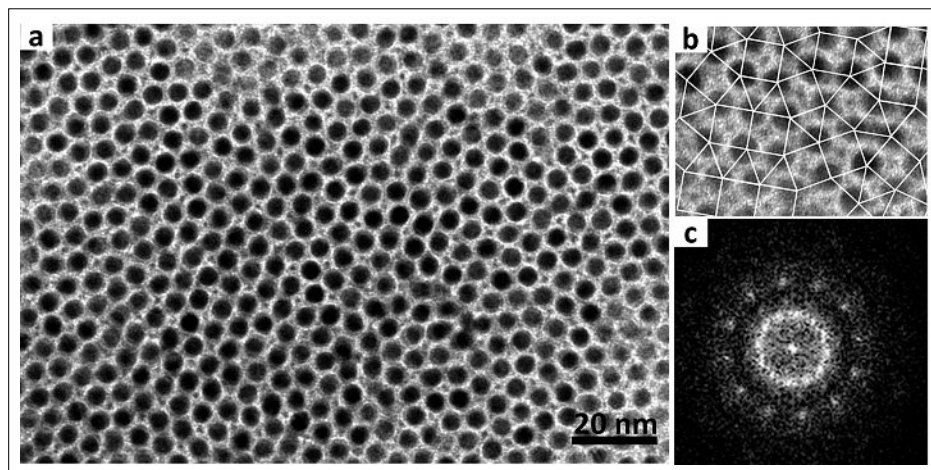

Fig. 7. Dodecagonal quasicrystalline ordering in binary mixtures of 2.9 nm DDA-encapsulated $\{Mo_{132}\}$ clusters and 8.1 nm PbS NCs and (γ_{eff} = 0.51). (a,b) TEM images and (c) FFT pattern from image (a). Reprinted with persmission from *Nano Lett.* **2013**, DOI: 10.1021/nl4002475. Copyright 2013 American Chemical Society.

size-ratios and relative concentrations of constituents, we obtained a range of binary crystals isostructural with NaCl, AlB_2 and $NaZn_{13}$ lattices (all predicted to be thermodynamically stable in hard-sphere mixtures), and also $CaCu_5$-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_5Li_{22}, enabling a theoretical capacity of 992 mhA/g,[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.[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_2, formed upon exposure to the air (Fig. 3). The contribution of SnO_2 may reduce achievable reversible capacity to that of pure SnO_2 (780 mAh/g) due to the 1st-discharge irreversible reaction $SnO_2 + 4Li = 2Li_2O + Sn$. In order to ensure electronic connectivity between current collector and all NCs within the electrode, an inorganic S^{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_2 nanomaterial and relatively high charge/discharge currents of 1000 mA/g. NCs exhibit high reversible discharge capacities of up to C_{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_{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 fluoroethylenecarbonate (FEC) additive (Fig. 8A). In order to illustrate the importance of the mean particle size, Fig. 8B compares electrodes containing 10 nm
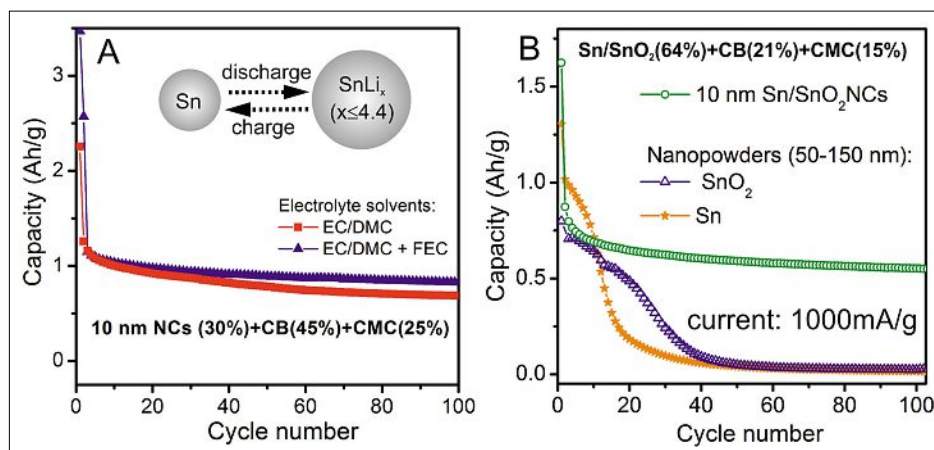
Fig. 8. Reversible discharge capacities of Sn-based Li-ion battery anodes: (a) effect of fluoro-ethylene carbonate (FEC) electrolyte additive on the performance of electrodes containing low mass fraction of 10 nm Sn/SnO$_2$ NCs and ethylene carbonate/dimethyl carbonate (EC/DMC) as main electrolyte solvents; (b) effect of the nanomaterial mean size at a high mass loading of 64%. Reprinted with permission from *J. Am. Chem. Soc.* **2013**, *135*, 4199. Copyright 2013 American Chemical Society.

and 20 nm Sn/SnO$_2$ NCs with those based on commercial Sn and SnO$_2$ nanopowders, all with the significantly higher content of an active Sn-material (~64wt%). Only 10 nm Sn/SnO$_2$ NCs maintained high Li insertion/removal cycling stability (C_{Sn}^{max} = 600 mAh/g and C_{Sn}^{min} = 443 mAh/g) after 100 cycles. Further work is in the progress to optimize formulation of the electrodes and electrolytes.

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