Nanostructures

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All-Inorganic Nanocrystal Arrays

*Stephanie L. Brock**

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In a bid to create conductive nanoscale devices using solution-phase chemical strategies, Talapin et al. have created 2D all-inorganic nanocrystal (NC) arrays by replacing the traditional (insulating) organic surface ligands of NCs created by solution-phase arrested-precipitation routes with inorganic clusters; subsequent self-assembly yields organized networks. Once annealed, electron transport between particles becomes facile, mediated by the conductive inorganic interfaces, thus enabling formation of, for example, semiconducting NC-based field-effect transistors.[1]

In the creation of nano-objects, there are two general strategies: physical and chemical. Physical methods typically involve gas-phase deposition of components onto substrates. These may be lithographically patterned to nanoscale dimensions, or NC lattices may arise spontaneously from epitaxial strain between the film and the support, leading to island formation. Key advantages of this approach include the ability to form ordered superstructures of nanofeatures in a parallel fashion and the fact that the nanoscale features can be "wired" to the outside world through the interfaces created. However, the menu of sizes and shapes that can be achieved is somewhat limited, governed by difficulties in lithography of very small features or by the characteristics of the growing particle/substrate interface.

If you really want to build small (less than 50 nm) NCs, with exquisite control of size and shape, the solution-phase chemical route is the way to go. In this case, molecules react in solution to form small bits of solid, the growth of which is controlled by solvent characteristics. In addition to spherical NCs, diverse shapes such as tetrapods and rods can be generated with a high degree of uniformity, just by tuning the growth conditions. Syntheses commonly take place between room temperature and 380 °C using organic solvents or surfactants that can coordinate to the particles, thus controlling growth while minimizing aggregation. This approach, and the obligatory organic capping ligands that result, is optimal for potential applications relying on optical or magnetic signaling (e.g. luminescent sensors and MRI contrast agents) but falls decidedly short when you want to create solid-state electronic devices. Indeed, one major disadvantage of this route has been a lack of methodologies for assembling individual NCs into extended, macroscopic, structures. A second problem has been how to "wire" the individual units into an integrated structure, because the key feature that enables exquisite control of particle size and shape (the solvent) also passivates the surface.

The ability of solution-phase NCs to organize into ordered arrays or superlattices was first reported 1n 1995 for CdSe NCs.[2] Since that time, this method has been refined and extended to a wide range of materials as well as to the assembly of more complex structures, including multicomponent arrays.[3,4] While the images of these kinds of lattices are stunning, their conductivity is decidedly poor. Upon careful examination of Figure 1 A, the reason is clear. The high-contrast NC is surrounded by a low-contrast matrix. This matrix, the interface between the particles, arises from the organic capping agents. In prior work, Talapin and Murray showed that dramatic improvement in conductivity can be achieved by treatment of the arrays with hydrazine.[5] The hydrazine effectively replaces the ligands at the particle surface, bringing the particles closer together and facilitating electronic interactions. Nevertheless, interparticle interactions are better described as "interface-blocked" rather than "interface-mediated".

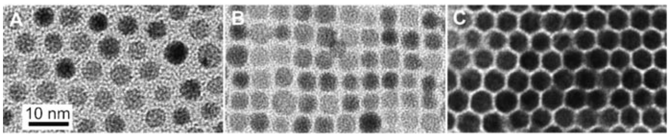

Figure 1. Electron micrograph images of A) a dodecanethiol-capped Au NC 2D lattice; B) a $[Sn_2S_6]^{4-}$-capped Au NC 2D lattice; C) a 3D superlattice of $[Sn_2S_6]^{4-}$-capped Au NCs. From reference [1], reprinted with permission from AAAS.

The recent approach adopted by Talapin et al. to address this problem is simple and elegant: replace the organic capping ligands of NCs with molecular metal chalcogenides (MMCs) originally developed by Mitzi et al. for liquid-phase deposition of semiconductor films. The Mitzi method involves dissolution of metal chalcogenide extended structures with excess chalcogen into pure hydrazine solutions, from which hydrazinium salts of MMCs can be isolated.[6] A representative reaction is shown in Equation (1). Mitzi uses the

$$2\,SnS_2(s) + 2\,S(s) + 5\,N_2H_4(l) \rightarrow [N_2H_5]^+{}_4[Sn_2S_6]^{4-} + N_2(g) \qquad (1)$$

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[*] Prof. S. L. Brock
Department of Chemistry, Wayne State University
Detroit, MI 48202 (USA)
E-mail: sbrock@chem.wayne.edu

hydrazine solutions of MMCs for spin-on film formation; after annealing, uniform chalcogenide films with thicknesses on the order of about 50 Å are achieved by a process summarized in Equation (2). Thin films of $SnS_{2-x}Se_x$ exhibited electron mobilities in excess of $10\,cm^2V^{-1}s^{-1}$, making these considerably more conductive than films deposited using other solution methodologies.

$$[N_2H_5]^+_4[Sn_2S_6]^{4-} + \text{heat} \rightarrow 2\,SnS_2(s) + 2\,H_2S(g) + 4\,N_2H_4(g) \qquad (2)$$

Talapin et al. exploit MMCs for the creation of a series of inorganic NCs capped with inorganic ligands. The all-inorganic NCs are made by treating a nonpolar solution of conventionally prepared NCs capped with nonpolar groups, such as dodecanethiol-capped Au particles, with a solution of MMCs in hydrazine or dimethylsulfoxide. Stirring results in phase transfer of the NCs from the nonpolar into the polar phase as the MMCs replace the organic ligands, thus conferring solubility in polar solvents. The scope of the reaction is truly impressive: Talapin et al. have looked at a range of NC compositions and shapes, as well as MMC formulations (see Figure 2). Unlike conventional capping ligands, the MMCs are anionic, resulting in negatively charged particles, and it is these electrostatic interactions that are responsible for the colloidal stability. Importantly, the NCs retain the optical properties that are characteristic of their size, thus indicating that quantum confinement effects (for semiconducting NCs) or surface plasmon resonance effects (for metal NCs) are retained.

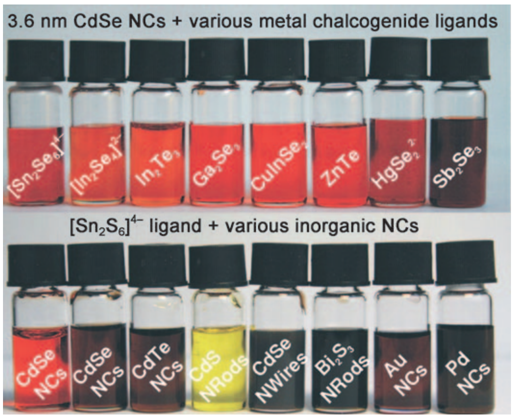

Figure 2. Solutions of CdSe NCs capped with eight different compositions of MMCs, and of eight different types of NCs combined with the $[Sn_2S_6]^{4-}$ ligand (NRods = nanorods, NWires = nanowires; the color difference between the first two CdSe NC solutions is due to the different particle diameter (3.6 vs. 5.8 nm)). From reference [1], reprinted with permission from AAAS.

Like their organically passivated precursors, the MMC-capped NCs can be induced to assemble into either 2D or 3D superlattices (Figure 1 B,C); however, the distance between particles is considerably smaller (compare to Figure 1 A), which would be expected to significantly facilitate interactions. In the case of CdSe semiconducting NCs, this proximity results in a clear red shift in the absorbance spectrum owing to quantum mechanical coupling between particles (i.e., the apparently large band gap arising from quantum confinement effects is narrowing, approaching the behavior of a bulk-phase semiconductor). In the case of Au, the plasmon band that is responsible for the wine-red color of colloidal gold solutions (and gold-containing stained glass) is completely suppressed, a signature of electronic delocalization.

The best conductivity might be expected if the MMCs and hydrazinium counterions that form the interface between NCs were thermally converted to a conducting chalcogenide [see Eq. (2)]. Indeed, heating CdSe NCs capped with $[Sn_2S_6]^{4-}$ ligands to 200 °C yielded CdSe NC/SnS_2 composites. These composites, when incorporated into field-effect transistors, had reasonable electron mobilities (on the order of $10^{-2}\,cm^2V^{-1}s^{-1}$) and showed gating behavior and photoconductivity. Moreover, the characteristics of the films are strongly dependent on the ratio of CdSe to $[N_2H_5]^+_4[Sn_2S_6]^{4-}$ employed in the ligand-exchange process: high concentrations of the MMC led to continuous SnS_2 film formation around the NCs and enhanced conductivity owing to the presence of a more facile electron pathway. Because of the ability to vary the characteristics of the individual components, the possibility to optimize the component characteristics for enhanced synergy is very high.

While promising, the NC-MMC method is but one approach to the problem of how to “wire” particles together. Indeed, we have at our disposal a long-standing traditional route for NC assembly that obviates heterogeneous interfaces altogether: sol-gel reactions. Though commonly employed with silica, a number of conducting oxide formulations have also been made, such as manganese and vanadium oxides and RuO_2/silica composites.[7] In contrast to the superlattices above, the gel structures are disordered and consist of an interpenetrating network of nanoscale matter and nanoscale porosity. Like the superlattices, the methodology enables considerable flexibility; components can be mixed within the solid nanonetwork, and secondary phases can be selectively deposited on the pore walls. In direct analogy to the NC-MMC superlattices reported by Talapin et al., even pure metal chalcogenides can be induced to form gels,[8–10] which should enable the consequences of these complementary approaches on the resultant properties to be assessed.

Which approach is likely to be the most successful? The answer will depend on the application: whether it is better to have dense, organized structures or airy, disorganized structures. The NC-MMC approach may be better for dense circuitry, transistors, photodiodes, and so forth, while gel structures can be expected to be uniquely suited for 3D batteries and capacitors. One thing is clear: interfaces matter, and our ability to modify these interfaces at the nanoscale, whether by physical or chemical processes, is critical for the development of viable nanotechnologies. In this regard, the recent efforts of Talapin et al. represent a major step forward.

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