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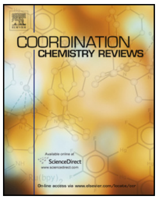

Review

Inorganic chemistry solutions to semiconductor nanocrystal problems

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ABSTRACT

The optoelectronic and chemical properties of semiconductor nanocrystals heavily depend on their composition, size, shape and internal structure, surface functionality, etc. Available strategies to alter these properties through traditional colloidal syntheses and ligand exchange methods place a premium on specific reaction conditions and surfactant combinations. In this invited review, we apply a molecular-level understanding of chemical precursor reactivity to reliably control the morphology, composition and intimate architecture (core/shell vs. alloyed) of semiconductor nanocrystals. We also describe our work aimed at achieving highly selective, low-temperature photochemical methods for the synthesis of semiconductor–metal and semiconductor–metal oxide photocatalytic nanocomposites. In addition, we describe our work on surface modification of semiconductor nanocrystal quantum dots using new approaches and methods that bypass ligand exchange, retaining the nanocrystal's native ligands and original optical properties, as well as on spectroscopic methods of characterization useful in determining surface ligand organization and chemistry. Using recent examples from our group and collaborators, we demonstrate how these efforts have lead to faster, wider and more systematic application of semiconductor nanocrystal-based materials to biological imaging and tracking, and to photocatalysis of unconventional substrates. We believe techniques and methods borrowed from inorganic chemistry (including coordination, organometallic and solid state chemistry) have much to offer in reaching a better understanding of the synthesis, functionalization and real-life application of such exciting materials as semiconductor nanocrystals (quantum dots, rods, tetrapods, etc.).

1. General introduction

In this special issue of *Coordination Chemistry Reviews* dedicated to quantum dots, we would like to more broadly give a general overview of how we have tried to address three important

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issues in the wider field of colloidal semiconductor nanocrystals (dots, rods, etc.). More specifically, we highlight recent work by our group on: (1) chemical reactivity-based, bottom-up control of the relative rates of nucleation of different nanocrystalline phases, and thus of semiconductor nanocrystal morphology, composition and architecture; (2) low-temperature, highly selective photochemical routes to the synthesis of precisely heterostructured semiconductor-based catalysts and composites, and (3) novel methods for surface modification of quantum dots that seek to control functional group loading (valence) per nanocrystal, while at the same time developing the tools needed to gain a deeper understanding of surface ligand organization. Our progress in these three areas has already allowed us, in some cases, to explore specific applications that were very difficult based on prior knowledge. This is the case for our use of giant nonblinking quantum dots in biological imaging and tracking, as well as for the use of semiconductor–metal heterostructures in solar-to-chemical energy conversion (photocatalysis) of biomass-relevant substrates.

2. Rational control of semiconductor nanocrystal morphology

The properties of semiconductor nanocrystals are heavily dependent on their specific morphology, even if their chemical composition remains unchanged [1–3]. Currently, available synthetic methods used to produce specific shapes and morphologies rely heavily on the use of very specific surfactants [4], tweaking of many different reaction conditions (reaction time and temperature, etc.) [5,6], and the presence (by luck or choice) of hard to track and difficult to remove chemical impurities in commonly used solvents and surfactants. Instead of relying on such a random mix of seemingly irreproducible (or hard to reproduce) parameters, we believe the field has much to gain from having working scales of chemical reactivity for readily available families of useful molecular precursors. This would obviate the need for time-consuming testing of several different reaction conditions or unrelated precursors at random as is currently practiced in the field of solution phase nanomaterial synthesis.

According to Hammond's postulate [7], the transition state energy for the rate-determining step of a nanocrystal formation reaction (nucleation) is closest to that of the molecular precursors involved than to the much more stable nanocrystalline products (effectively a thermodynamic sink). This implies that the transition state during nanocrystal formation resembles the initial molecular precursor much more than it does the final nanocrystalline lattice. This fact came to our attention during our work on axially anisotropic, compositionally graded nanorods, and forms the basis of our work on molecular programming. Molecular programming is a relatively new area of nanoscience where chemical precursor reactivity can be manipulated by simple chemical group substitution, allowing us to fine-tune the relative rates of nucleation of one or more phases, and thus to control the final shape, composition, and intimate architecture of different nanocrystalline materials. In this way, the formation rates of different nanocrystalline phases and the outcome of several nanomaterial preparations can be adjusted through a conceptually simple, "bottom-up" molecular chemistry approach.

2.1. Disubstituted dichalcogenide precursors

Highly soluble dichalcogenide precursors (R-E-E-R, where R = alkyl or aryl, E = S or Se) were recently used for the synthesis of nanocrystals with several different structures and shapes [8–11]. While using disulfide and diselenide precursors to prepare CdS or CdSe nanocrystals, we noticed that spherical, elongated or tetrapodal nanocrystals formed depending on the specific dichalcogenide employed [12]. To sort these differences out, we carried out reactions using a series of differently substituted disulfide and diselenide precursors under otherwise identical reaction conditions (i.e., using the same cadmium oleate precursor and precursor concentrations, in octadecene solvent, with the same concentration of oleic acid and oleylamine surfactants). While some of the alkyl disulfides yielded spherical CdS particles, diethyl disulfide produced elongated CdS shapes, and dimethyl disulfide afforded CdS tetrapods (Scheme 1). We also noted that the use of diphenyl disulfide yielded no nanocrystals at all.

In order to nucleate cadmium chalcogenide nanocrystals upon reaction with a cadmium precursor, all of the carbon—chalcogen (C—E) and chalcogen—chalcogen (E—E) bonds present in a dichalcogenide precursor (R-E-E-R, E = S or Se) must break. This prompted us to computationally study the C—C and C—S (or C—Se) bond dissociation energies (BDE) in these precursors at the density functional theory (DFT) level of theory with the BMK functional [13]. Our results revealed that diallyl and dibenzyl disulfides had the weakest carbon—chalcogen bonds, while diphenyl disulfide exhibited the strongest carbon—chalcogen bonds. The chalcogen—chalcogen BDEs did not appear to change significantly across either disulfide or diselenide series, except for the diphenyl cases, which had unusually weak chalcogen—chalcogen bonds.

In view of these results, we built a dichalcogenide reactivity scale based on C—E (C—S or C—Se) bond dissociation energies (Fig. 1), and found that this scale correlated exceedingly well with our initial morphology observations and kinetics measurements. In short, dichalcogenides with very weak C—E bonds such as diallyl disulfide are very reactive and lead to quick formation of large CdS clusters. Dichalcogenides with intermediate strength C—E bonds such as ditertbutyl disulfide react somewhat slower to produce small CdS quantum dots (Scheme 1). Dichalcogenides with stronger C—E bonds such as dimethyl disulfide react very slowly, mildly and selectively to produce anisotropic structures such as CdS tetrapods (Scheme 1). In contrast, a precursor with a prohibitively strong C—E bond such as diphenyl disulfide tends to be unreactive and does not – by itself – produce any CdS nanocrystals, however it is very good at generating phenyl-thiol radicals because it has a very weak S—S bond (see below).

In light of our experimental and computational observations, we hypothesized that the reason why some of the more mildly reacting dichalcogenides may give rise to anisotropic structures could have something to do with the release of thiyl radicals in solution. Because this would depend on the ease of breaking the chalcogen—chalcogen (S—S or Se—Se) bond, we thought that diphenyl disulfide, which has the weakest S—S bond of all precursors we studied, must form such radicals (PhS·) most easily. Indeed, mixed precursor experiments using a combination of intermediate reactivity precursors such as tBu-S-S-tBu (which usually give dots) and unreactive Ph-S-S-Ph (which by itself does not react with cadmium) only produces multipod structures [4]. Powder X-ray diffraction (XRD) measurements (Fig. 2) indicated that both zinc blende and wurtzite phases were present in the tetrapod samples. This was previously attributed to growth of hexagonal (wurtzite) arms from the {1 1 1} facets of a cubic (zinc blende) core. While the zinc blende phase is slightly more stable than the wurtzite phase at low temperatures [14,15], whether specific precursor types can directly influence the crystal structure of the nanocrystalline products will require further investigation. Experimental and computational trends on a similar series of dialkyl and diaryl diselenide precursors mirrored those of the disulfides, but all BDEs were around 5 kcal/mol lower, as anticipated due to selenium's larger size and longer (weaker) bonds.