Communication

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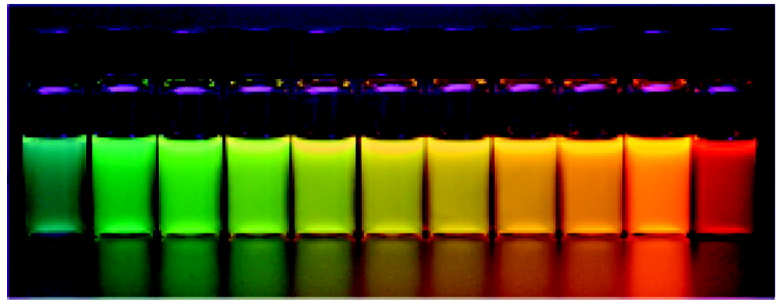

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One-Pot Synthesis, Encapsulation, and Solubilization of Size-Tuned Quantum Dots with Amphiphilic Multidentate Ligands

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Semiconductor quantum dots (QDs) are nanometer-sized particles with unique optical and electronic properties and are currently under intensive research for a broad range of applications such as solar energy conversion and molecular and cellular imaging.[1−3] Significant advances have been made in the chemical synthesis of highly crystalline and monodispersed QDs, especially with the use of organometallic and chelated cadmium precursors,[4,5] noncoordinating solvents,[6] and inorganic passivating shells.[7] However, the resulting nanocrystals are often hydrophobic and must be encapsulated and solubilized after synthesis for many important applications.[3a,8] Aqueous synthetic procedures have been used as alternative approaches to prepare water soluble QDs, using small thiol-containing molecules or polymers with carboxylic acid groups as stabilizing agents.[9−11] But these methods do not yield QDs with the fluorescence brightness or size monodispersity that are often achieved with the high-temperature organic procedures.

Here we report an "all-in-one" strategy for simultaneous synthesis, encapsulation, and solubilization of high-quality QDs. This one-pot method is based on the use of amphiphilic multidentate ligands and noncoordinating solvents such as low molecular weight polyethylene glycols (PEGs) (MW = 350 Da). The multidentate polymer ligands contain aliphatic chains and carboxylic acid functional groups and are found to act as both a cadmium precursor ligand and a nanoparticle surface stabilizer, leading to improved control of chemical reaction kinetics (Figure S1) and increased resistance to Ostwald ripening. When exposed to water, excess polymer molecules spontaneously encapsulate and solubilize the QDs without any additional materials or steps. Furthermore, this synthetic procedure allows for *in situ* growth of an inorganic passivating shell on the nanocrystal core, enabling one-pot synthesis of both type-I and type-II core−shell QDs.[12]

Figure 1 shows the schematic structures of the multidentate polymer ligands for one-pot QD synthesis and self-encapsulated QDs. A key intermediate is a cluster of chelated cadmium ions, generated by dissolving the amphiphilic polymer and cadmium oxide or cadmium acetate in noncoordinating PEGs at elevated temperatures. The reactivity of this clustered cadmium precursor plays an important role in controlling the nucleation and growth kinetics of nanocrystals. By increasing the length of the polymer backbone and the density of hydrophobic side chains, a dramatic steric hindrance effect comes into play resulting in homogeneous nucleation and growth, whereas the use of traditional monovalent ligands leads to uncontrollable and heterogeneous reactions (data not shown). By optimizing the balance between the hydrophobic and hydrophilic segments, the resulting QDs are spontaneously solubilized by a second layer of the same amphihphilic polymer when the reaction mixture is exposed to water (Figure 1b). However, if the hydrophobic grafting percentage is too high, the number of surface carboxylic acid functional groups becomes too low for water

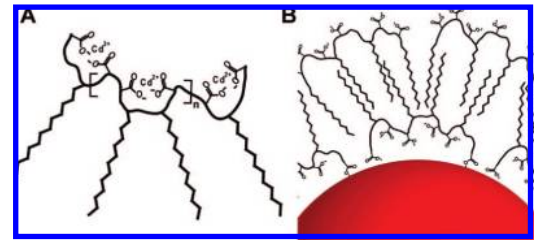

Figure 1. (A) Schematic structure of the amphiphilic multidentate ligand with multiple chelated cadmium ions (see Supporting Information for details). (B) Diagram showing multidentate ligand binding to the QD surface. The resulting nanocrystals are spontaneously encapsulated and solubilized by a second layer of the same multidentate polymer upon exposure to water. See text for detailed discussion.

solubilization. We have found that a 40% graft percentage (that is, 40% of the carboxylic acid groups are modified with hydrophobic 12-carbon aliphatic size chains) is nearly optimal for controlled nanoparticle growth and for solubilizing the capped QDs in water (Figure S2).

This improved control in reaction kinetics allows more precise tuning of the nanoparticle size and fluorescence emission wavelength across a wide range (Figure 2a). In fact, QD fluorescence emission can be consistently controlled within as little as 2 nm. This high precision will become important as QDs are increasingly adopted for multiplexed biological and clinical assays, where consistency and repeatability are critical. The use of multidentate polymer precursors also provides a new route to ultrasmall QDs; for example, CdTe cores as small as 1.5 nm with green emission (515−525 nm) can be synthesized with narrow size distributions, allowing for a very large dynamic range from the green to the far red wavelengths (Figure 2a). It is worth noting that ultrasmall QDs are often difficult to synthesize with traditional monovalent precursors due to size and kinetic control problems. Using the multidentate ligands, each polymer contains ∼15 carboxylic acid functional groups that are capable of coordinating with surface atoms. By increasing the overall binding affinity through multivalent interactions and providing steric hindrance, the polymer capping can better stabilize small particles and reduce Ostwald ripening. However, some ripening does occur at increased temperatures after long periods of time, as shown by the dark red curve obtained after 1 h at 280 °C (Figure 2b, slight tailing). Overall, transmission electron microscopy reveals uniform, nearly spherical particles without clustering or aggregation (Figure 2c), confirming the stability and monodispersity of QDs synthesized and protected with multidentate ligands.

Because QD cores show a propensity to oxidize in water, we have developed an *in situ* procedure for capping them with an inorganic passivating shell. Inorganic shells have the added benefit of increasing the quantum yield as well as opening the possibility

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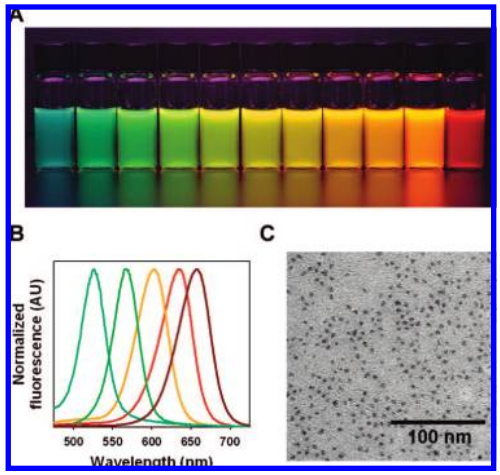

Figure 2. Fluorescence emission and electron microscopy structural properties of CdTe core QDs prepared by using multidentate polymer ligands in a one-pot procedure. (A) Series of monodispersed CdTe QDs, showing bright fluorescence from green to red (515 to 655 nm) upon illumination with a UV lamp. (B) Normalized band-edge fluorescence emission spectra of CdTe QDs with 35−50 nm full width at half-maximum (fwhm) (QY ~30%). (C) Transmission electron micrograph of CdTe cores (emission = 655 nm) showing uniform, nearly spherical particles (mean diameter = 4.2 nm, standard deviation ~10%) (Figure S2).

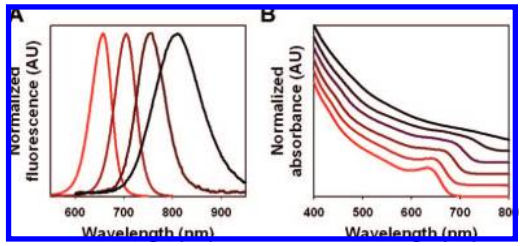

Figure 3. Type-II core−shell CdTe/CdSe QDs synthesized in one pot. (A) Normalized fluorescence emission spectra showing the transition from CdTe cores (red curve) to CdTe/CdSe core−shell QDs emitting in the near-infrared (black curve). (B) Optical absorbance showing the red-shifting and eventual loss of the first exciton peak as the CdSe shell is grown on the CdTe core, typical of type II QDs.

of band gap engineering through the selection of an appropriate shell material. In this procedure, an excess of cadmium is used to start the synthesis (the mole ratio of cadmium to tellurium is typically 2:1), and the reaction is allowed to proceed until the limiting species (tellurium) is depleted. This leaves an excess of the cadmium precursor available for incorporation into a passivating shell. CdSe is used as a model shell material for CdTe cores because the band offsets are such that CdTe/CdSe is a type-II QD with light emission in the near-infrared spectrum.[12] Fluorescence emission spectra (Figure 3a) show significant red-shifting of the original QD core emission, from 650 to 810 nm, as a shell is grown on the particle surface. Considerable broadening of the emission peak is observed with shell growth, consistent with the behavior of type-II QDs. Monitoring of the QD absorbance spectra also confirms shell growth and transition to type-II behavior (Figure 3b). For example, the distinct exciton peak seen in the CdTe cores (red curve) is gradually red-shifted and eventually disappears during shell deposition. This is expected as the CdTe/CdSe QDs should behave as indirect semiconductors near the band edge.

The roles of low molecular weight PEGs are also interesting. They not only provide an inert and noncoordinating environment for QD synthesis at high temperatures but also act as an "adjuvant" to facilitate nanocrystal dissolution in various solvents. Indeed, the QDs reported in this work are soluble in a wide range of hydrophilic and hydrophobic solvents including water, DMF, acetone, and chloroform.

In summary, we have reported a new, one-pot procedure for preparing high-quality QDs based on the use of amphiphilic multidentate ligands and short PEGs at high temperatures. The novel features associated with the use of polymeric precursors are better control of the nanocrystal growth kinetics, resistance to Ostwald ripening, and synthesis of ultrasmall dots with blue-shifted emission spectra. This synthetic procedure also allows for *in situ* growth of an inorganic passivating shell (CdSe) on the QD core, opening the possibility of band gap engineering for these nanoparticles and providing a large dynamic range for QD emission from the visible to the near-infrared.

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Supporting Information Available: Detailed procedures for one-pot synthesis of core and core−shell QDs, QD size distribution, and reaction kinetics data. This material is available free of charge via the Internet at http://pubs.acs.org.

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