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

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Abstract

We report one-pot synthesis, encapsulation, and solubilization of high-quality quantum dots based on the use of amphiphilic and multidentate polymer ligands. In this "all-in-one" procedure, the resulting QDs are first capped by the multidentate ligand, and are then spontaneously encapsulated and solubilized by a second layer of the same multidentate polymer upon exposure to water. In addition to providing better control of nanocrystal nucleation and growth kinetics (including resistance to Ostwald ripening), this 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 with tunable light emission from visible to near-infrared wavelengths.

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 for many important applications. Aqueous synthetic procedures have been used as alternative approaches to prepare water soluble QDs, using small thiol-containing molecules or polymers with carboxylic acid functional groups as stabilizing agents.[8–10] 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 quantum dots. This one-pot method is based on the use of amphiphilic multidentate ligands and noncoordinaging solvents such as low-molecular weight polyethylene glycols (PEG) (MW = 350 Daltons). 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 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.[11]

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Figure 1 shows schematic structures of the multidentate polymer ligands for one-pot QD synthesis and the 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 polyethylene glycols 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 (see Figure 1b). However, if the hydrophobic grafting percentage is too high, the number of surface carboxylic acid functional groups becomes too low for water solubilization. We have found that a 40 percent 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.

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 1–2 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, small CdTe cores emitting in the green range (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 small QDs are often difficult to synthesize with traditional monovalent precursors because of the problems with kinetic control and Ostwald ripening. In contrast, the QDs capped with multidentate ligands are strongly resistant to Ostwald ripening. In fact, each polymer has approximately 15 carboxylic acid functional groups that are capable of coordinating with surface atoms. By increasing the overall binding affinity through multivalent interactions, the polymer capping can better stabilize small nanoparticles. However, some ripening does occur at increased temperatures after long periods of time, as shown by the dark red curve obtained after 1 hour at 280°C (Figure 2b). 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 of bandgap 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 mole 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.[11] Fluorescence emission spectra (Figure 3a) show significant red-shifting of the original QD core emission, from 650 nm to 810 nm, when 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 provide not only 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 show "amphibious" behaviors and are soluble in a wide range of hydrophilic and hydrophobic solvents including water, DMF, acetone, and chloroform. The detailed results on "amphibious nanocrystals" will be reported in a separate paper.

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 polyethylene glycols at high temperatures. The novel features associated with the use of polymeric precursors are better control of the nanocrystals growth kinetics, resistance to Oswald 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 bandgap engineering for these nanoparticles and providing a large dynamic range for QD emission from the visible to the near infrared.

Acknowledgments

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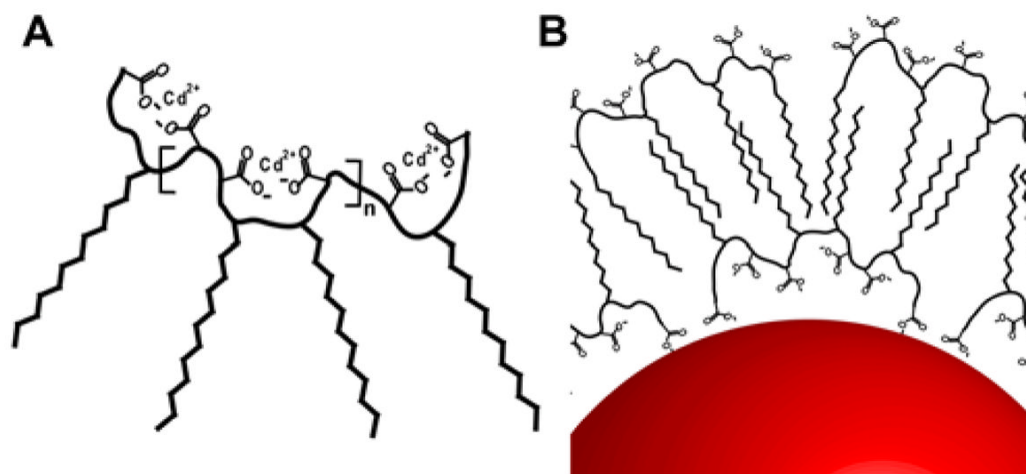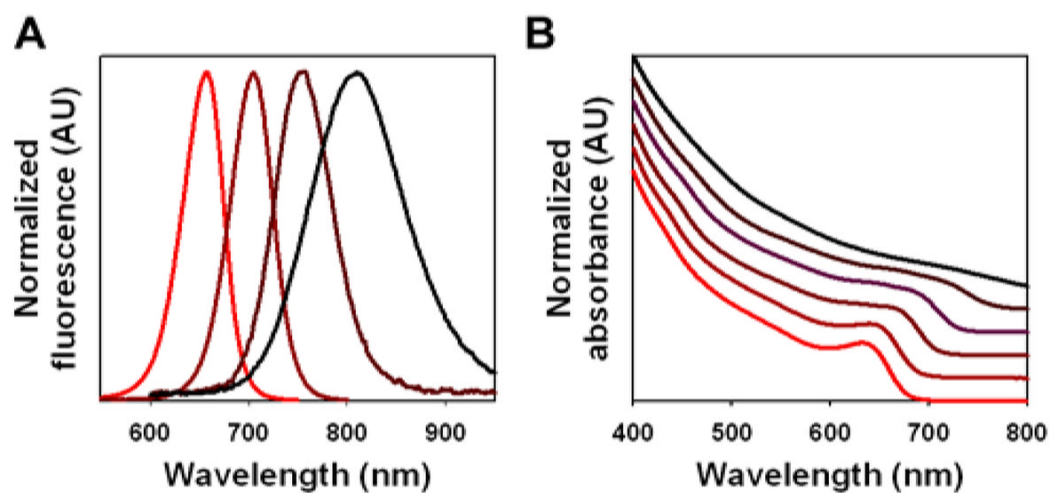
Figure 1.
(A) Schematic structure of the amphiphilic multidentate ligand with multiple chelated cadmium ions. (B) Diagram showing multidentate ligand binding to the QD surface. The resulting nanocrystals are spontaneously encapsulated and solubilized by a second layer of the same multidentate polymer upon exposure to water. See text for detailed discussion.
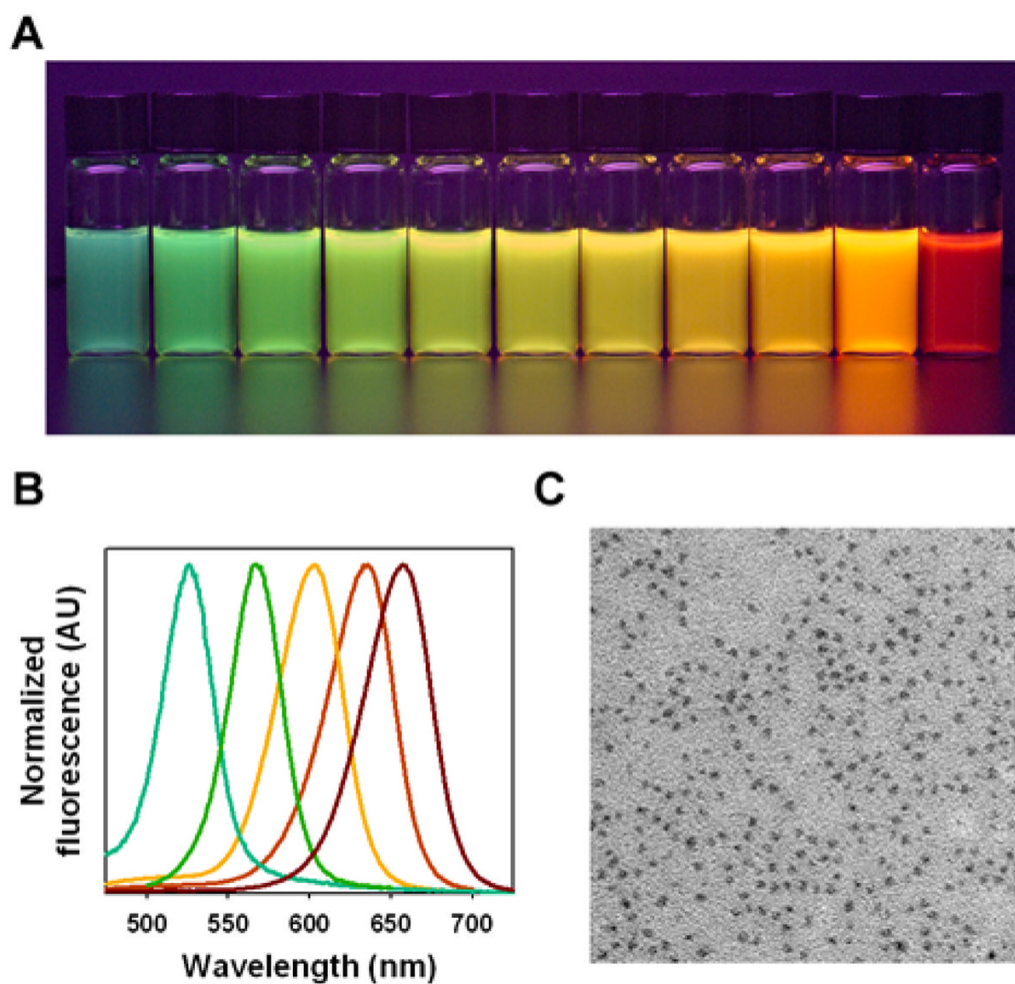
Figure 2.
Fluorescence emission and electron-microscopy structural properties of CdTe core QDs prepared by using multidentate polymer ligands in a one-pot procedure. (A) Color photograph of a series of monodispersed CdTe QDs, showing bright fluorescence from green to red (515 nm to 655 nm) upon illumination with a UV lamp. (B) Normalized fluorescence emission spectra of CdTe QDs with 35–50 nm full width at half maximum (FWHM). (C) Transmission electron micrograph of QDs showing uniform, nearly spherical particles.

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.