One-Pot Synthesis of High-Quality Zinc-Blende CdS Nanocrystals

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The formation of high-quality semiconductor nanocrystals, with well-controlled size and shape, as well as well-confined surface passivation, can be achieved by controlling the thermodynamics and kinetics during the nucleation and growth of nanocrystals.[1,2] However, the separation of the nucleation and growth stages is a prerequisite of producing high-quality nanocrystals. When nucleation occurs concurrently with the growth of nanocrystals, samples with broad size distributions are often expected.

In colloidal synthesis, chemists have invented a state-of-the-art method to separate the nucleation stage from the nanocrystal's growth stage.[3] The key part of this synthetic method is the injection of room-temperature organometallic precursors into well-stirred, hot organic solvents. Nucleation takes place immediately after the injection and continues until the temperature and the precursor concentration drop below a critical threshold. In this case, the nucleation time is determined by the rate of the injection and the mass transfer in the reaction systems. Therefore, rapid precursor injection and strong stirring would lead to a short nucleation time and thus achieve a separation between nucleation and growth stages.[3] This method has led to synthesis of a variety of high-quality nanocrystals ranging from II−VI (e.g., CdS and CdSe) and III−V (e.g., InP and InAs) to IV−VI (e.g., PbS and PbSe) semiconductors, which are of great importance to applications such as biological labeling, LEDs, lasers, and solar cells.[3−6]

However, this injection-based synthetic method is not suitable for large-scale, industrial preparation (e.g., hundreds of kilograms), even though it can be scaled up to the order of grams.[2] Industrial preparation of nanocrystals has to be carried out in batch reactors that could be tens of thousands of times larger than those in research laboratories.[7] In this industrial case, the rapid injection of precursors is very difficult to achieve. Moreover, the limitations of mass transfer in the industrial reactors further diminish the merits of the injection method. Therefore, this injection-based synthetic method is problematic in producing high-quality nanocrystals at an industrial scale. To overcome this difficulty, new synthetic methods that do not require the injection of precursors have to be developed.

Although many reports have detailed one-pot synthesis of semiconductor nanocrystals without precursor injection, the quality of the as-prepared nanocrystals is not comparable to that of the nanocrystals made by the injection method.[8] Herein, we report a one-pot colloidal synthesis of high-quality CdS nanocrystals. This synthetic method is based on a new concept of controlling the thermodynamics and kinetics of the nanocrystal nucleation stage. The separation between nucleation and growth is automatically achieved in a homogeneous reaction system by adding two reagents, here called nucleation initiators (tetraethylthiuram disulfides, I_1; and 2,2′-dithiobisbenzothiazole, I_2). These initiators have been used as accelerators to increase the reactivity of sulfur in rubber vulcanization for more than 70 years.[9]

In a typical experiment, cadmium acetate hydrate (0.1 mmol, from Aldrich), myristic acid (0.2 mmol), and octadecene (ODE) solutions with sulfur (0.05 mmol), I_1 (6.25 μmol), and I_2 (3.13 μmol)
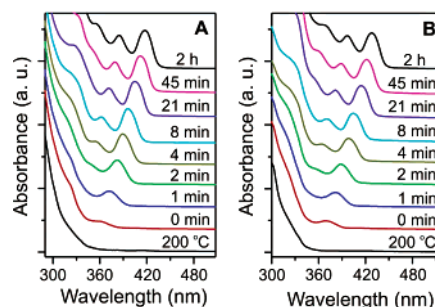

Figure 1. Temporal evolution of the absorption spectrum of CdS nanocrystal growth at $S:I_2$ ratios of 1:1/16 (A) and 1:1/8 (B).

were respectively added into a three-neck flask with ODE (the ratio of $S:I_2 = 1:1/16$, and the total amount of ODE = 5 g). The mixture solution was heated at 120 °C with gentle stirring under vacuum (∼30 mTorr). A clear solution was obtained after 2 h. Under an Ar flow, the resulting solution was heated to 240 °C at a rate of 10 °C/min. After the temperature reached 240 °C, serial aliquots were taken for kinetic studies. No nucleation occurred when the temperature was below 200 °C (Figure 1A). Small nanocrystals (i.e., nuclei) did appear when the reaction temperature reached 240 °C. As the particles grew, their size distribution continued to decrease, and a very narrow size distribution was reached after 4 min. The subsequent growth kinetics was similar to that in the injection-based synthesis.[4a] Here, the narrow size distribution of particles can be maintained for at least 12 h while nanocrystals continue to grow. No detectable new nucleation occurred during particle growth, and the concentration of nanocrystals in the reaction solution was kept nearly unchanged. Taken together, these results demonstrate that the nucleation and growth stages are clearly separate in this noninjection-based synthesis.

The nucleation initiators (I_1 and I_2) play an important role in this synthesis, partly because they can affect the reactivity of the precursors (i.e., cadmium myristate and S). Without these initiators, a large quantity of white precipitate was often obtained in the synthesis after the temperature reached 240 °C. On the other hand, increasing the amount of I_2 led to faster nanocrystal growth, but the general kinetic feature of the nucleation and growth stages stayed unchanged (Figure 1B). In addition, the amount of I_2 affects the number of stable nuclei. The greater the amount of I_2, the smaller the number of stable nuclei found in the synthesis (Figure 2A). Importantly, this result allows the final particle sizes in the synthesis to be controlled. With the same amount of precursors, a smaller number of nuclei resulted in nanocrystals with a larger final size, and vice versa. A reaction with a $S:I_2$ ratio of 1:3/8 yielded large particles with a first absorption peak at 460 nm and a good size distribution (Figure 2C).

The quality of the CdS nanocrystals formed by this method is at least comparable to that of the best CdS nanocrystals made by injection-based methods.[4] After non-size-sorting separation, the CdS nanocrystals exhibit up to four absorption peaks, indicating their
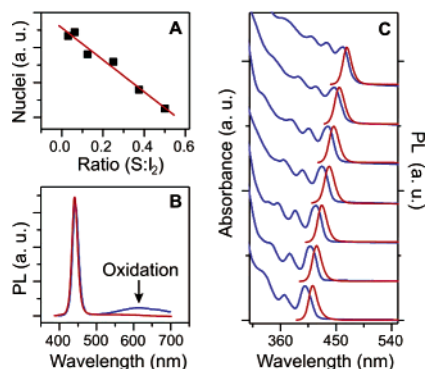
Figure 2. (A) Number of stable nuclei in the synthesis with different S:I$_2$ ratios (Supporting Information). (B) PL spectra of CdS nanocrystals before (in blue) and after (in red) oxidation. (C) Absorption (in blue) and PL (in red) spectra of the as-prepared CdS nanocrystals with different sizes.

very narrow size distributions (Figure 2C). However, the photoluminescence (PL) of the CdS nanocrystals still contains a noticeable quantity of surface-trap emission like the particles made by the injection method (Figure 2B).[4b] Amazingly, after a gentle oxidation reaction under laboratory fluorescent lights, the surface-trap emission of these CdS nanocrystals was totally eliminated; also the quantum yield of the band-gap emission was slightly enhanced, and up to 12% was found with a quinine-sulfate standard (Figure 2B). Such yield is 2−3 times higher than the best reported yields for CdS nanocrystals.[4b] Using this oxidation processing method, we have prepared differently sized monodisperse CdS nanocrystals without surface-trap emission, with the first absorption peaks of these particles ranging from 400 to 460 nm (Figure 2C).

Interestingly, the CdS nanocrystals made by this new method have a different crystal structure than those made by the injection method (zinc blende vs wurtzite, respectively).[4] Although these two crystal phases could produce similar X-ray powder diffraction (XRD) results in nanocrystals, the XRD pattern herein shows unambiguous evidence that the particles are of a zinc blende structure: (a) the (200) diffraction is clearly shown as a shoulder at 30.8°; (b) the valley between the (220) and (311) is deep; and (c) the (531) peak is shown at 102.8°, but in the case of wurtzite crystals, the strong peak should appear at 107.8° (215) in this high-angle regime (Figure 3A).[3a] This structural assignment is consistent with the TEM observation (JEOL-JEM 2010 operated at 200 kV). The nanocrystals with a first absorption peak at 456 nm appeared as cubes with an edge length of 3.8 nm and a standard deviation (σ) of 7% (Figure 2B). A cubic shape is very easily formed for the zinc blende crystals, which are enclosed by {100} faces, but not for the wurtzite ones (Figure 3A, inset).

Moreover, the results from electron diffraction (ED) provide further evidence for recognizing the zinc blende crystal phase. The high uniformity of these cubic nanocrystals allows the formation of superlattices. Superlattices with sizes up to a few microns were generated by slow evaporation of a concentrated nanocrystal solution (toluene/hexane = 1:1) on TEM grids (Figure 3C). One set of four orthogonally aligned diffraction spots shown in the ED represents an ordered distance of 0.21 nm, corresponding to the lattice spacing of the (220) faces in zinc blende CdS. In contrast, a set of six hexagonally aligned diffraction spots should be expected for the counterpart of zinc blende (220) faces, the (110) faces in a wurtzite structure.

In summary, this paper reports a one-pot synthetic method for producing high-quality CdS nanocrystals. We have demonstrated
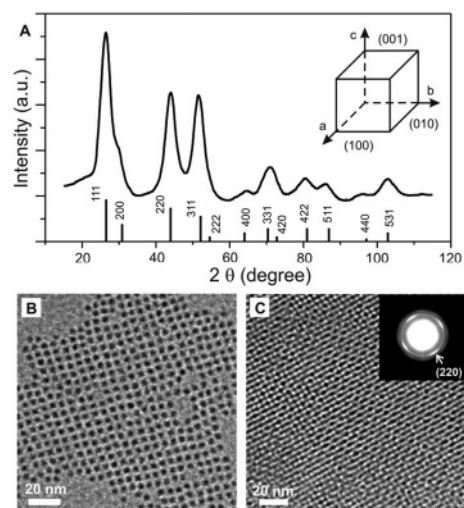

Figure 3. (A) XRD pattern of the CdS crystals with a first absorption peak at 456 nm. The standard diffraction peak positions and relative intensities of bulk zinc blende CdS are indicated. TEM images of (B) monolayers and (C) superlattices of the CdS nanocrystals. The inset in C illustrates an ED pattern taken in the same area.

that the nanocrystal nucleation and growth stages can be automatically separated in a homogeneous system with the presence of nucleation initiators. This concept, using initiators to control the thermodynamics and kinetics of nucleation and growth, could be readily generalized for making other metal-sulfide nanocrystals via a one-pot synthesis. Such synthesis, without precursor injection, is easy for small-scale laboratory synthesis, and more importantly, it is suitable for the industrial preparation of high-quality nanocrystals.

Supporting Information Available: Details regarding measurement of the number of stable nuclei in the CdS nanocrystal synthesis, as well as sample preparation for XRD measurements (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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