VIP CdSe Nanocrystals

DOI: 10.1002/ange.200804266

Synthesis of Metal–Selenide Nanocrystals Using Selenium Dioxide as the Selenium Precursor**

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Colloidal metal–selenide nanocrystals (e.g., CdSe and PbSe) are a class of semiconductor nanocrystals that are important in both fundamental science and technological applications.[1–3] In the area of fundamental science, the synthesis of high-quality metal–selenide nanocrystals with well-controlled size, shape, and surface passivation has led to the systematic elucidation of size-dependent scaling laws and photophysical processes in quantum-confined systems.[1,2] In the area of technological applications, metal–selenide nanocrystals have been used as major building blocks for applications such as biomedical diagnosis, solar cells, and light-emitting diodes (LEDs).[3]

To date, two general approaches have been developed for producing high-quality metal–selenide nanocrystals.[1,4,5] The first approach relies on rapid precursor injection to achieve a separation of the nanocrystal nucleation and growth stages.[1,4] This injection-based synthesis has led to the preparation of nearly all types of high-quality metal–selenide nanocrystals.[1,4] However, the injection-based synthesis is not suitable for the large-scale industrial preparation of high-quality nanocrystals (that is, tens to hundreds of kilograms) because the rates of precursor injection and mass transfer are limited in the apparatus for industrial synthesis.[5,6] The second approach is a non-injection synthesis (NIS), which is based on the concept of controlling the thermodynamics and kinetics in the nanocrystal nucleation stage.[5,6] We have previously demonstrated that the separation between nucleation and growth can be automatically achieved in a homogeneous reaction system by controlling the chemical reactivity of the precursors.[5] The quality of the nanocrystals made by the NIS method is at least comparable to the best particles made by injection-based methods.[5,6] In addition, the NIS method is suitable for the industrial preparation of high-quality nanocrystals.[5,6]

However, to synthesize high-quality nanocrystals, both approaches normally require air-free manipulations using a glove box because of the use of the following air-sensitive compounds as selenium precursors: bis(trimethylsilyl)selenium, organophosphine selenide, and selenium powder.[4,5] Such air-free manipulations substantially increase the complexity as well as the cost of the synthesis of metal–selenide nanocrystals. Herein, we report a simple NIS method for making high-quality CdSe nanocrystals using SeO_2 as the selenium precursor. Because of the high chemical stability of SeO_2, this new synthesis does not require the use of a glove box. In addition, the synthesis can be conducted in air, without using a Schlenk line. Moreover, this new approach can be generalized for the formation of high-quality metal–selenide nanocrystals with different compositions such as PbSe and PdSe.

In a typical CdSe nanocrystal synthesis, SeO_2 (0.1 mmol) and cadmium myristate (0.1 mmol) were added to a three-neck flask with 1-octadecene (ODE, 6.3 mL).[8] The resulting mixture was heated, with stirring, to 240 °C at a rate of 25 °C min^{-1}. After the temperature reached 240 °C, serial aliquots were removed for kinetic studies. No nucleation occurred as the temperature reached 240 °C (Figure 1a). After 30 s at this temperature, small nanocrystals appeared. As the nanocrystals grew, their size distribution continued to decrease. After the size of nanocrystals had reached 3.0 nm, oleic acid (0.1 mL) was added dropwise (1 drop per 10 s) into the reaction solution with the aim of providing extra ligands for stabilizing the nanocrystals during a period of further growth; this was indeed the case, as the kinetics of nanocrystal growth became very stable. The size distribution of nanocrystals further narrowed with particle growth until a final size of about 4.0 nm in diameter was reached (Figure 1a). With further annealing at the reaction temperature, the narrow size distribution of the resulting particles was maintained, at least for one night. Neither Ostwald ripening nor secondary nucleation were detected during the synthesis. In addition, this SeO_2-based synthesis exhibits more stable nanocrystal nucleation kinetics than the synthesis using selenium powder as a precursor.

Without size sorting, typical CdSe nanocrystals from this synthesis are of sizes that have a standard deviation of about 5% (Figure 1b). According to the X-ray powder diffraction (XRD) pattern, the resulting CdSe nanocrystals have a zinc blende structure (Figure 1c). This result is consistent with the absorption spectra of these nanocrystals. The gap between the first ($1S_{3/2}1S_e$) and second ($2S_{3/2}1S_e$) exciton peaks for the CdSe nanocrystals is wider than that for a typical wurtzite particle, but is identical to that for those zinc blende CdSe nanocrystals produced using selenium powders.[5]

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[**] We thank Dr. Kathryn R. Williams and Kerry Siebein for technical support. Y.C.C. acknowledges the NSF (DMR-0645520 Career Award), ONR (N00014-06-1-0911) and the American Chemical Society Petroleum Research Fund (42542-G10) for support of this research.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200804266.

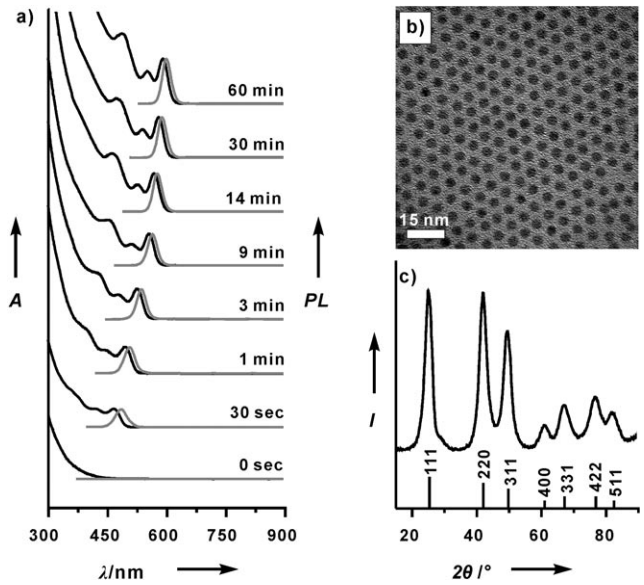

Figure 1. a) Temporal evolution of the absorption (black) and photoluminescence (PL) spectra (gray) of the reaction mixture after reaching 240°C. b) TEM image of CdSe nanocrystals with a diameter of 4.0 nm and a standard deviation of ca. 5%. c) XRD pattern of CdSe nanocrystals measured from the same sample shown in panel (b). The stick pattern shows the positions of standard XRD peaks for bulk zinc blende CdSe.[7]

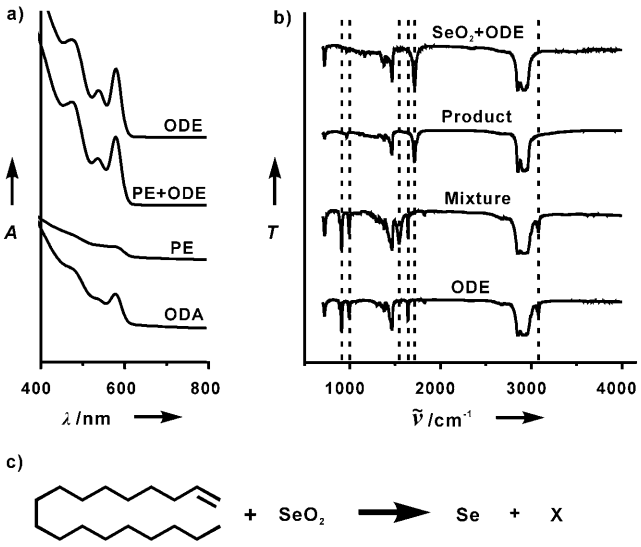

Figure 2. a) Absorption spectra of CdSe nanocrystals synthesized in various solvents: ODA, PE, PE mixed with ODE, and ODE. b) FT-IR transmittance (*T*) spectra of ODE, a reaction mixture of $Cd(My)_2$, SeO_2 and ODE (before reaction, mixture), after reaction at 240°C (product); and of the product of the reaction of SeO_2 and ODE at 240°C. c) The reaction between ODE and SeO_2. X represents the mixture of organic by-products.[8]

To explore the effect of oxygen on the formation of CdSe nanocrystals, we conducted a control synthesis under air-free conditions using a Schlenk line.[8] In this synthesis, small particles appeared when the temperature reached 230°C (Figure S1 in the Supporting Information). The subsequent kinetics are similar to those of the synthesis conducted in air.[8] The nanocrystals resulting from this air-free synthesis are of nearly identical quality to those made from the synthesis in air.[8] These results show that, compared to the air-free synthesis, the existence of oxygen in the reaction system affects the early nucleation stage in CdSe nanocrystal synthesis and delays CdSe nanocrystal nucleation. However, the presence of oxygen does not substantially affect the quality of the resulting CdSe nanocrystals. These results most likely occur for the following reasons: 1) oxygen has an extremely low solubility in ODE, and 2) the trace amount of oxygen in the reaction solution is consumed at a very early stage of the synthesis. These results further confirm that this new synthesis does not have to be conducted under air-free conditions.

In this new synthesis, the selenium precursor (SeO_2) needs to be reduced to an active form, such as Se^0, for the formation of CdSe nanocrystals; it seems likely that ODE is the reducing agent. To test this hypothesis, we conducted three experiments in which ODE was replaced by other solvents while the amount of cadmium myristate and SeO_2 were kept unchanged, as in the typical synthesis described above. In the first experiment, ODE was replaced by its saturated counterpart—octadecane (ODA). The number of CdSe nuclei formed in this ODA-based synthesis is approximately about half of that formed in the synthesis with ODE as solvent (Figure 2a). In addition, according to the half-width of their first absorbance peaks, the quality of the resulting particles formed in ODA is much lower than that of particles formed in ODE. These results indicate that the vinyl group of ODE is critical for the synthesis of high-quality CdSe nanocrystals, but the saturated alkyl chain can also reduce SeO_2 to Se^0 by a reaction such as dehydrogenation.[9] In the second experiment, phenyl ether (PE) was chosen as a solvent to replace ODE, because PE molecules have only aromatic rings and are not easily oxidized by SeO_2. Only trace amounts of CdSe particles were formed in this reaction, and the quality of the resulting particles was poor (Figure 2a). Moreover, unreacted SeO_2 was observed as a white powder in the reaction flask, whereas this phenomenon was not observed in syntheses with either ODE or ODA as solvent. To further explore the role of ODE in the CdSe nanocrystal synthesis, we carried out the third experiment with PE as solvent and a small amount of ODE (85 μL) at a molar ratio of ODE and SeO_2 of 3:1. Amazingly, UV/Vis spectra show that the CdSe nanocrystals resulting from this synthesis are of nearly identical quality to those nanocrystals from the typical synthesis with ODE as solvent (Figure 2a). These results show that ODE is not only a solvent but also a reactant in this SeO_2-based CdSe nanocrystal synthesis.

To investigate the molecular mechanism of precursor evolution in this synthesis, we studied a reaction of cadmium myristate (2 mmol), SeO_2 (2 mmol), and ODE (4 mmol), which was conducted at 240°C. The FTIR spectrum of the reagent mixture before the reaction shows the characteristic peaks of the ODE vinyl group (out-of-plane C–H bend: 909.7 cm^{-1} and 991.2 cm^{-1}; C=C stretch: 1641.4 cm^{-1}; and C–H stretch: 3077.6 cm^{-1}, Figure 2b).[10] The peak of the carbonyl group of cadmium myristate appears at 1542.0 cm^{-1} (Figure 2b). The FTIR spectrum of the reaction

product mixture shows that all the characteristic peaks of ODE and cadmium myristate disappear, while a new peak appears at 1713.2 cm^{-1} (Figure 2b). This result shows both ODE and cadmium myristate are consumed during the reaction, and further confirms that ODE is indeed a reactant in the CdSe nanocrystal synthesis. Moreover, the new peak at 1713.2 cm^{-1} is in the typical frequency range for a carbonyl group. ^{13}C NMR spectroscopy showed that the organic by-product mixture contains both carboxylic acid and ketone groups.[8] The carboxylic acid group is assigned to a by-product from cadmium myristate, while the ketone is possibly a by-product of the reaction between ODE and SeO_2.

To examine this possibility, we further studied a control reaction ((SeO_2 (2 mmol) and ODE (4 mmol)) without cadmium myristate. The FTIR spectrum of the product mixture from this reaction is very similar to the spectrum of the products from the reaction with cadmium myristate (Figure 2b). This result indicates that the ketone is indeed a product of the reaction of ODE and SeO_2. However, thin-layer chromatography showed that the product from this reaction was a complicated mixture. ^1H NMR and ^{13}C NMR spectroscopy showed that the product mixture is composed of methyl ketones, a small amount of alkenes with a C=C double bond at the centre of their chains, and a trace amount of aldehydes (Figures S3 and S4 in the Supporting Information). Methyl ketones and aldehydes are assigned to the products of SeO_2-mediated oxidation of the vinyl group of ODE, while the alkenes are the products of SeO_2-mediated dehydrogenation of the hydrocarbon chain of ODE.[9]

In addition, the reaction of SeO_2 and ODE also yielded dark-gray precipitates. Differential scanning calorimetric measurements showed that the precipitates have a melting point of 221 °C (Figure S5 in the Supporting Information), which indicates that they are selenium crystals.[9] The results from these mechanistic studies suggest that the reduction of Se^{IV} to Se^0 is an important step in this SeO_2-based, non-injection synthesis of CdSe nanocrystals (Figure 2c). The formation of Se^0 requires a high temperature, which thus reduces the chances of multiple nucleation during the formation of CdSe nanocrystals.[5] This can, in part, explain why the SeO_2-based synthesis exhibits more stable nucleation kinetics than the non-injection synthesis directly using Se^0 as the selenium precursor.

Because of its stable nucleation kinetics, this SeO_2-based synthesis allows the control of the number of nuclei and thus the final size of the resulting nanocrystals, while the high quality of the resulting nanocrystals remains unchanged. We have previously demonstrated the relationship between nanocrystal growth rate and the number of nuclei in a synthesis of CdS nanocrystals, that is, a slower nanocrystal growth rate results in a larger number of nuclei and thus the final particles are smaller, and vice versa.[6] We found that this relationship is also valid in the SeO_2-based synthesis reported herein.

In this study, control of the nanocrystal growth rate at the nucleation stage of the formation of CdSe nanocrystals was achieved by various methods for tuning the reactivity of cadmium precursors. In one method, we used two approaches to decrease the nanocrystal growth rate. Firstly, because of its relatively low reactivity, cadmium docosanate was used to replace cadmium myristate as the cadmium precursor in the synthesis.[8] Secondly, 1,2-hexadecanediol was introduced into the reaction system because cadmium myristate (or docosanate) can be further stabilized by 1,2-hexadecanediol through chelation.[8] Indeed, these two approaches led to slower nanocrystal growth rates, larger numbers of nuclei and smaller resulting particles (Figure S6 in the Supporting Information). In another method, we introduced a small amount of cadmium acetate into the reaction mixture to increase the nanocrystal growth rate at the nucleation stage, because cadmium acetate exhibits a higher reactivity than cadmium myristate. Our results show that this method did lead to the synthesis of larger CdSe nanocrystals than the typical synthesis without cadmium acetate.[8] Based on these approaches, we have synthesized high-quality, zinc blende CdSe nanocrystals with an approximate size range of 2.0–6.2 nm (Figure 3). These nanocrystals have a typical photoluminescence quantum yield of about 40%, and have up to four absorption peaks, indicating their narrow size distribution (Figure 3a). Indeed, transmission electron microscopy (TEM) studies show that these nanocrystals have a typical size distribution of approximately 5% (Figure 3b–d).

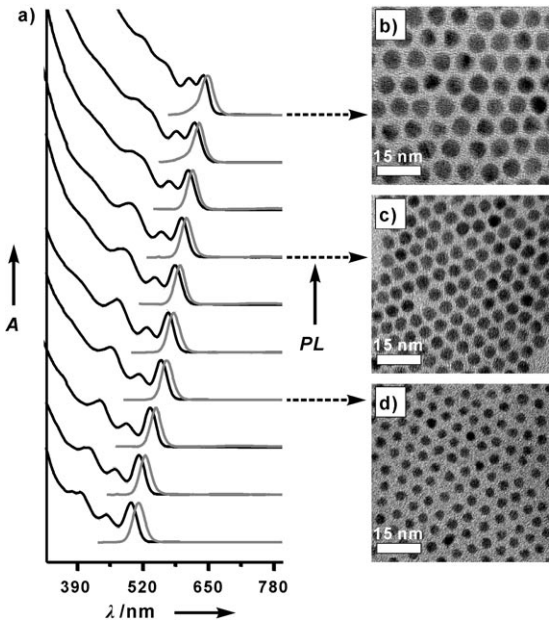

Figure 3. a) Absorption (black) and PL (gray) spectra of the as-prepared CdSe nanocrystals of various sizes. TEM images of CdSe nanocrystals with a diameter of b) 6.2 nm, c) 4.5 nm, and d) 3.0 nm. The relative standard deviations of these sizes are ca. 5%, and the corresponding optical spectra are indicated by dashed arrows.

Furthermore, this SeO_2-based synthesis has been generalized for making PbSe and PdSe nanocrystals. In the synthesis of PbSe nanocrystals, we found that oleic acid alone is insufficient to stabilize the resulting nanocrystals during growth, because the reactions often resulted either in particles with poor size distributions or insoluble products. To overcome this difficulty, we introduced trioctylphosphine

(TOP) into the reaction mixture, because TOP can stabilize PbSe nanocrystals by binding to both the Pb and Se sides on their surfaces. The kinetics of PbSe nanocrystal growth in the presence of TOP were very stable. The resulting nanocrystals from a typical synthesis have a cubic shape with edge length of 15.9 nm and distribution of 7% (Figure 4a). High-resolution TEM studies show that these nanocrystals have (200) faces parallel to two edges of these PbSe nanocubes (Figure 4b), which is consistent with the cubic crystal structure of PbSe. In addition, based on a similar concept for stabilizing nanocrystals in the synthesis, we have successfully prepared PdSe nanocrystals with TOP and oleyamine as ligands. The resulting nanocrystals have a typical diameter of 4.6 nm with a standard deviation of 7% (Figure 4c). Interestingly,

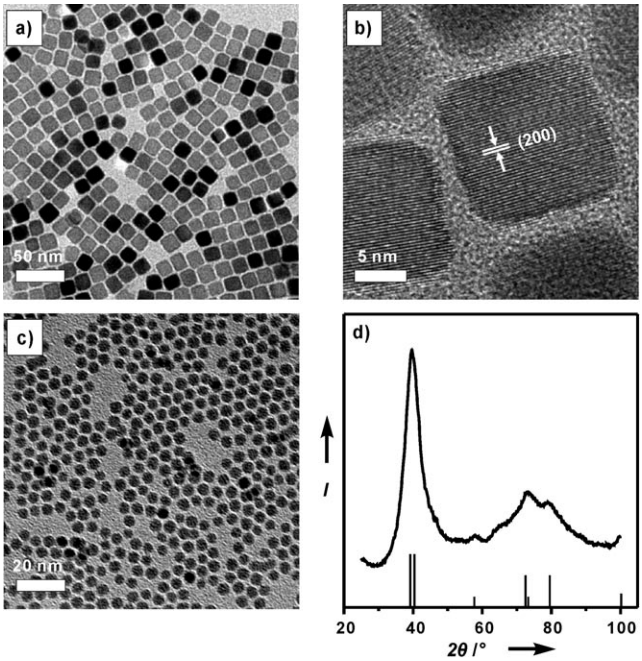

Figure 4. a) TEM image of PbSe nanocubes with a side length of 15.9 nm and a standard deviation of 7%. b) High-resolution TEM image of PbSe nanocubes: the ordered distance of 3.05 Å corresponds to the lattice spacing of the (200) faces in cubic PbSe. c) TEM image of $Pd_{4.5}Se$ nanocrystals. d) XRD pattern of $Pd_{4.5}Se$ nanocrystals measured from the same sample shown in (c). The stick pattern indicates the positions of standard XRD peaks for bulk $Pd_{4.5}Se$.[7]

energy dispersive spectroscopy (EDS) showed that these nanocrystals possess an atomic molar ratio between palladium and selenium of 4.5:1 but not 1:1 (Figure S7 in the Supporting Information). The EDS result is consistent with the XRD measurement, in which the Bragg diffraction peaks of these nanocrystals nearly perfectly match those of bulk $Pd_{4.5}Se$ (Figure 4d).[7]

In summary, we have reported a NIS method for the synthesis of high-quality zinc blende CdSe nanocrystals with SeO_2 as the selenium precursor. Mechanistic studies show that ODE acts as a reducing agent for SeO_2 in this synthesis. The synthesis can be conducted in air, and eliminates the need for air-free manipulations using a glove box or a Schlenk line. Moreover, this synthesis exhibits controllable kinetics in both the nucleation and growth stages, and thus allows detailed control of the numbers of nuclei and final size of the resulting nanocrystals. Importantly, such a synthesis is convenient for small-scale laboratory preparation, and is also suitable for a large-scale industrial synthesis of high-quality nanocrystals at low cost. In addition, we have generalized this SeO_2-based NIS method for making other metal–selenides, such as PbSe and $Pd_{4.5}Se$ nanocrystals.

Received: August 28, 2008
Published online: October 10, 2008

Keywords: cadmium · crystal growth · nanostructures · selenium · semiconductors

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