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Precise Size Control and Synchronized Synthesis of Six Colors of CdSe Quantum Dots in a Slow-Increasing Temperature Gradient

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The present study describes a simultaneous and highly reproducible large-scale synthesis of six (and more) colors of size-homogeneous and highly luminescent CdSe quantum dots in a single reaction, controlled by a slow-increasing temperature gradient. The described protocol allows a precise control and a synchronized isolation of aliquots of CdSe nanocrystals with defined sizes, avoiding disturbance of the growth of nanocrystals (existing in the reaction mixture) to the isolation of the next aliquot. The obtained quantum dot fractions are of high quality (in 95% size-homogeneous) and have sharp photoluminescence spectra (fwhm ∼ 30 nm), quantum yields of 45–70% (in organic solvent), and a lack of aggregation in organic solvents. The method is environmentally friendly as it ensures almost complete utilization of the precursors and productive yield ∼95%.

The wide application of semiconductor CdSe quantum dots in electronics and life science research requires their large-scale production.[1−3] The large-scale synthesis has to be precisely controlled and highly reproducible. It has to guarantee a production of quantum dots with high quality (a very narrow size distribution and a high quantum yield) and desired sizes. The present study tries to satisfy all of these requirements to the large-scale production of CdSe (core) quantum dots.

The methods for synthesis of CdSe quantum dots, described in the literature, are too many and too variable. They are dated from ∼1986[4,5] and are based on highly toxic Cd and Se ingredients. The methods describing a synthesis of high quality nearly monodispersed CdSe quantum dots, using the safety "green" chemistry approach, have appeared in the last several years.[6−12] These methods basically include a "hot injection": Se or Cd precursor is added extremely fast (in milliseconds) to the reaction mixture at 280−320 °C; the formation of nanocrystals occurs within 2−3 min, followed by a growth delay and a saturation to plateau after ∼10 min.[6,7] The obtainment of nanocrystals with desired sizes takes place by stopping the reaction in the exact moment, using a fast cooling and a transfer in the organic solvent. The fast rate of the reaction (when it occurs at a constant high temperature) restricts the control of the exact moment of stoppage. A very low possibility exists to isolate nanocrystals with many defined sizes by taking several aliquots from one pot because in any moment of the reaction there are particles with different sizes. The reported size distribution for each quantum dot fraction is usually 5−10%. In the varieties of the method of "hot injection", when after nucleation the temperature of the synthesis decreases and is fixed at 260−290 °C,[13,14] it is possible to isolate several size-homogeneous quantum dot fractions. However, the reaction occurs fast enough to ensure a precise size control and highly reproducible synthesis of several monodispersed quantum dot fractions with desired sizes from one pot. Moreover, the additional decrease of the temperature (below 240−260 °C) results in the stoppage of crystal growth.

It is widely accepted that the extremely fast rate of crystal growth markedly decreases the reproducibility of the simultaneous synthesis of several size-homogeneous CdSe quantum dot fractions in a single reaction.

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In the present study, we describe a simultaneous and highly reproducible synthesis of at least six colors of size-homogeneous and highly luminescent CdSe (core) quantum dots in a single reaction by a controlled slow-increasing temperature gradient. The gradual increase of the temperature allows a continuous growth of quantum dots to complete depletion of the precursors. Usually, if the increase of the temperature is faster than the time of size saturation of the nanocrystals, continuous nucleation takes place and it is impossible to obtain several quantum dot fractions with desired sizes in a single reaction. We found that the slow-increasing temperature gradient keeps a balance between the size of the nanocrystals and the concentration of the nonreacted precursors in the mixture, which gives the possibility of suppressing the continuous nucleation and obtaining several size-homogeneous quantum dot fractions at several steps of the gradient. The reproducibility of the one-pot synthesis in a slow-increasing temperature gradient allows also an easy automation of the process and a shortening of the time, which is preferable to working with carcinogenic and teratogenic compounds such as Cd.

The synthesis was carried out by the following protocol: Se powder (0.7896 g) was added to trioctylphosphine (TOP; 7.4 g), and the mixture was heated (under an argon flow) to 150 °C for the preparation of a TOP−Se stock solution. Separately, CdO (0.450 g) and stearic acid (8 g) were heated to 150 °C in an argon atmosphere in a three-necked flask. After dissolution of CdO, the solution was cooled to room temperature. Trioctylphosphine oxide (TOPO; 8 g) and 1-heptadecyloctadecylamine (HDA; 12 g) were added, and the mixture was heated to 150 °C. At this temperature, 4 mL of a TOP−Se stock solution was rapidly injected into the reaction chamber (containing a Cd precursor) to start nucleation. The temperature of the chamber was fixed at 110 °C for 40 min to avoid additional growth of the CdSe nanocrystals and to obtain the first (blue fluorescence) color. An aliquot of 2 mL was removed from the reaction mixture by syringe and placed in 20 mL of chloroform. Next, five size-homogeneous fractions of CdSe quantum dots were obtained in the following steps:

(a) Second (dark-green fluorescence) color: the temperature was increased in a uniform gradient up to 120 °C for 50 min (0.2 °C/min).

(b) Third (yellow-green fluorescence) color: the temperature was increased in a uniform gradient up to 150 °C for an additional 60 min (0.5 °C/min).

(c) Fourth (yellow fluorescence) color: the temperature was increased in a uniform gradient up to 190 °C for an additional 80 min (0.5 °C/min).

(d) Fifth (orange fluorescence) color: the temperature was increased in a uniform gradient up to 220 °C for an additional 100 min (0.3 °C/min).

(e) Sixth (red fluorescence) color: the temperature was increased in a uniform gradient up to 250 °C for an additional 120 min (0.25 °C/min).

The obtained quantum dot fractions were characterized with high-resolution transmission electron microscopy (HR-TEM), spectrophotometry, and spectrofluorimetry. UV/vis absorption spectra were recorded using a Shimadzu spectrophotometer. Photoluminescence (PL) spectra were recorded using a Shimadzu spectrofluorimeter. HRTEM images were recorded using a JEOL transmission electron microscope operating at 300 kV.

Using the described protocol, it was possible to obtain six (and more) size-homogeneous fractions in a single reaction (2.12 ± 0.11, 2.38 ± 0.10, 2.70 ± 0.13, 3.04 ± 0.12, 3.66 ± 0.14, and 4.25 ± 0.11 nm in diameter; the mean $\pm$ standard deviation values were calculated from the absorbance spectra of quantum dot fractions, obtained in three independent synthetic protocols for each value; Figure 1B). The size of each fraction was calculated from the absorbance spectra, according the equation of Yu et al.[15]

It was possible to keep a narrow size distribution of CdSe quantum dots at each time point of the growth. The growth kinetic curve was linear up to 7 h (Figure 1C). This linearity allowed precise control of the growth.

The calculated sizes from HRTEM images (2.1, 2.5, 2.7, 3.1, 3.8, and 4.2 nm in diameter; Figure 1D) were in close proximity to the sizes mentioned above. The number of quantum dots measured for each value was 50. The size distribution of each fraction was within 2.5−5%.

The PL spectra of CdSe quantum dots were very sharp (fwhm $\sim$ 30 nm; Figure 1E), which is also evidence for a narrow size distribution of the obtained fractions. The quantum yield varied from 45 to 70% (in chloroform), depending on the quantum dot size.

It was possible to isolate a fraction with the desired size. Stoppage of the reaction at the 260th minute of the gradient resulted in obtainment of nanocrystals with diameters 3.5 ± 0.12 nm (the mean $\pm$ standard deviation value was calculated from the absorbance spectra of quantum dots, obtained in two independent synthetic protocols; Figure 1C).

There are several details in the synthetic conditions that have to be followed precisely.

First, the ratio of Cd−Se precursors has to be in a narrow range, from 0.9:1 to 1:1. At this ratio, the initiation of new nanocrystals is suppressed. This suppression is stronger than the suppression of the growth of the already formed nanocrystals. The increase of a Cd or Se precursor leads to aggregation of the nanocrystals and/or to an increase of the size distribution of each fraction. Second, the long-chain fatty acids (e.g., stearate, oleate) are preferable in the dissolution of the Cd precursor (CdO). The short-chain fatty acids (especially cadmium acetate) are not appropriate for the proposed synthetic protocol. They do not give the possibility of keeping the size distribution in a narrow range during the time of synthesis. Third, it is necessary to use long-chain aliphatic amines as coordinating ligands (e.g., HDA and ODA). The only use of traditional coordinating ligand TOPO increases the size distribution. Fourth, the rate of increase of the temperature gradient must not exceed 0.5 °C/min. Following these conditions, it is possible to obtain at least six size-homogeneous and highly luminescent CdSe quantum dot fractions in a single reaction.

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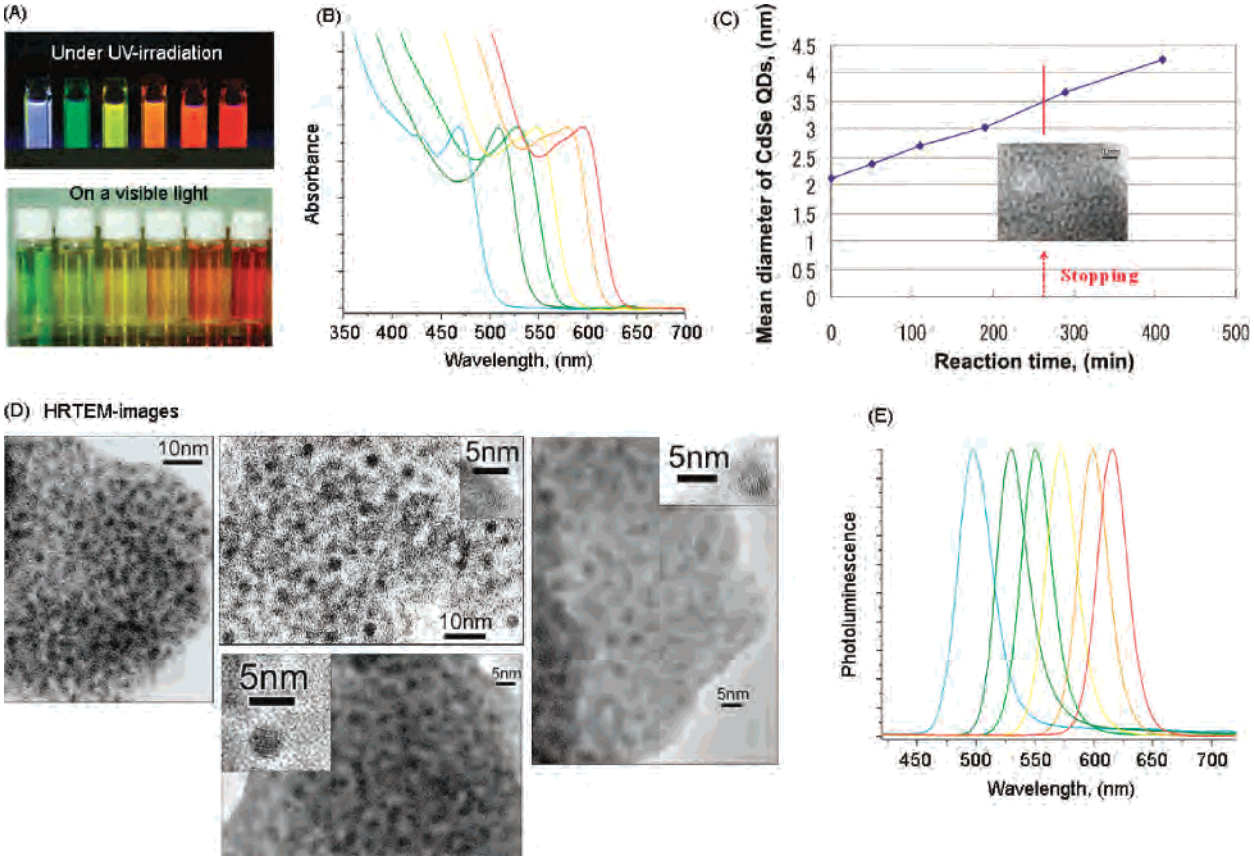

Figure 1. Characteristics of different colors of CdSe quantum dots, synthesized at a slow-increasing temperature gradient: (A) images under UV irradiation and on visible light; (B) normalized absorbance spectra; (C) kinetic curve of crystal growth; (D) HRTEM images; (E) normalized PL spectra ($\lambda_{ex} = 420$ nm).

The described protocol allows precise control and synchronized isolation of aliquots of CdSe nanocrystals with exactly defined sizes, avoiding disturbance of the growth of the nanocrystals (existing in the reaction mixture) to the isolation of the next aliquot. The obtained fractions are with high quality: in 95% size-homogeneous, fwhm of the PL spectra ~ 30 nm, quantum yields of 45−70% (in toluene, hexane, or chloroform), high transparency (lack of aggregation) (Figure 1A). The method is highly reproducible and environmentally friendly, the toxic wastes are low, and the method allows automation of the synthetic process. This ensures almost complete utilization of the precursors and a productive yield ~95%. The described technology has a limitation. It relates only to the synthesis of CdSe core quantum dots and does not relate to the synthesis of CdSe/ZnS core/shell quantum dots (the most widely used in the practice). The CdSe core nanocrystals, obtained in our synthetic protocol, can be coated with an inorganic shell (e.g., ZnS, ZnSe; using standard protocols), which increases their quantum yield and does not reflect significantly on their size distribution. The additional coating with an organic (silica) shell makes them water-soluble, functionalized, and ready for bioconjugation and application in life science research.

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