Continuous Preparation of CdSe Nanocrystals by a Microreactor

Hiroyuki Nakamura, Yoshiko Yamaguchi, Masaya Miyazaki, Masato Uehara,† Hideaki Maeda,* and Paul Mulvaney††
Micro-space Chemistry Laboratory, National Institute of Advanced Industrial Science and Technology (AIST), 807-1 Shuku, Tosu, Saga 841-0052
†*Department of Applied Chemistry, Kyushu University, Hakozaki, Higashi-ku, Fukuoka, 812-8581*
††*School of Chemistry, University of Melbourne, Parkville, VIC, 3010 Australia*

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In order to provide a continuous preparation method of CdSe nanocrystals, a microreactor was utilized. Particle size of a CdSe was controlled easily by a second order controlling of reaction time. The fluorescence color was also possible to be controlled by the reaction time.

A microreactor, whose representative length is micron order (i.e., less than 1 mm), has been developed and is attracting increasing interest.[1] In a microfluidic reactor, because of this short representative length, accurate control of reaction conditions is easy to be accomplished.[2] For an example, a heat conduction simulation showed that liquid (specific heat = 1 cal/(g·°C)) inside a 0.2 mm diameter channel can be heated from 20 to 300 °C in 0.2 s, thus showing its absolute advantage in temperature control over a batch reactor. This rapid temperature control is considered to allow an exact control of the reaction time; especially for a short reaction time.

A microreactor is usually designed as a flow type reactor. The reactor is said to be easily integrated for mass production without intrinsic scaling up. A simple calculation shows 100 L/day of product is possible when 700 reactors are operated in parallel at a flow rate of 0.1 mL/min. As the unit size of the reactor is very small, it is reasonably possible to run that number of reactor parallel. The scaling-up by the integration of reactors can make the production free from the common problems ascribable to the conventional scale up of reactor vessels, such as heterogeneity in mixing and temperature control. These advantages show the potential of a microfluidic reactor as an industrial reactor for a well-controlled reaction.

Recently, CdSe nanocrystals are attracting an increasing attention, mainly because it can be an ideal fluorescent tags for biotips for diagnosis and basic biological research.[3] When the particle size is smaller than the exciton Bohr radius (<ca. 7 nm),[4] one can vary the fluorescent color by varying particle size. Therefore, it is possible to obtain a various colors of fluorescent tags of CdSe. Many preparation methods for nanocrystals are reported, however, the difficulties in mass production of nanocrystals are often alleged.[5] The reason for this difficulty is again due to scale-up. For particle preparation, it is important to control the nucleation and growth. Especially, for the case of nanocrystal preparation, it is common to use a high nucleation rate to obtain small size particles. However, in this case, the temperature and chemical composition in the reaction solution are easy to be heterogeneous by a scale up thus making accurate and reproducible control harder to accomplish. For examples, many kinds of nanocrystals of a semiconductor including CdSe is often prepared by the reaction in hot surfactants like torioctylphosphineoxide(TOPO) and trioctylphosphine(TOP) at high temperature (≈250–350 °C). In most cases, the particle preparation is done using a small batch (about 5 to 50 mL)[6–13] to avoid the heterogeneity in the reactor. In addition, to control the nucleation and growth of particles, a raw material solution at room temperature is often injected into a high temperature solution for a rapid temperature drop. In spite of these efforts, it is not easy to obtain a particle diameter of nanocrystals reproducibly.[14]

Therefore, the authors tried to use a simple microfluidic system. In the system, a capillary was connected with a syringe to make a micro-fluidic system and part of the capillary was heated by oil bath.

In this study, a hot surfactant method using TOPO-TOP-stearic acid[8] was modified for the CdSe nanoparticle preparation. Typically, 10 mmol of Se was added to 25 g of TOP to prepare a TOP-Se stock solution. Meanwhile, 266.6 mg of $Cd(CH_3COO)_2$ was added to 20 g of stearic acid and heated at 130 °C for 15 min. Then 20 g of TOPO was added under a nitrogen flow. After the solution was cooled to below 100 °C, it was mixed with 12.5 g of TOP-Se and 7.5 g of TOP to make a raw material solution. The raw material solution was loaded into a glass syringe connected to a glass capillary. The syringe was set to a syringe pump and the raw material solution was pushed into the capillary in a constant rate (5 to 100 L/min). The inner and outer diameters of the capillary were 0.2 mm and 0.36 mm, respectively, and 100 cm of it was dipped in a 275 °C oil bath. The reaction time can be calculated from the volume of the heating part of the reactor and the flow rate. In this study, reaction time was varied from 30 s to 600 s.

The resulting product was collected in a test tube and part of it was diluted by 100 times by chloroform for UV-VIS spectroscopy and fluorescence spectroscopy. The band gap was calculated from the average particle diameter estimated from UV-VIS absorption peak on the basis of the procedure reported by Alve et al.[4] TEM observation was also performed.

When the raw material solution mixture was carried into the heating part of reaction capillary, the solution is considered to be heated immediately and cooled down when it came out from it. In the present reaction system, the reaction starts by heating and stops by cooling down. Therefore, the reaction time can be determined by flow rate and the capillary length.

By the present method, CdSe nanocrystals were easily obtained with a continuous manner. The fluorescence spectra of the products are shown in Figure. 1, and the preparation conditions and diameter estimated from the absorption peaks[4] are summarized in Table 1. As the reaction time varied from 30 s to 10 min, the fluorescence peak shifted from 545 to 595 nm and the average particle size estimated from the absorbance peak location changed from 2.8 nm to 4.2 nm.

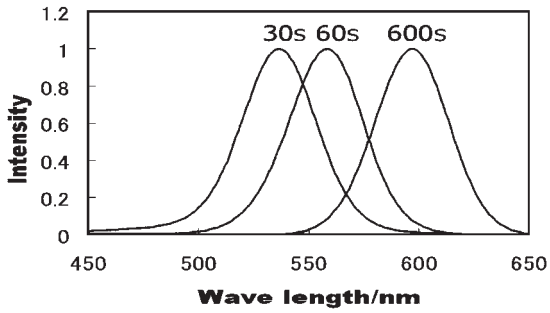

Figure 1. Fluorescence spectra from CdSe nanocrystals. The time on each curve indicates reaction time.

Table 1. Reaction conditions, absorption peak and estimated diameter of CdSe nanocrystals

Run No.	1	2	3
Reaction time/s	30	60	600
Flow rate/μL·min^{-1}	100	50	5
Band gap/eV	2.38	2.25	2.10
Diameter/nm	2.8	3.4	4.2

As shown in Table 1, the second to minutes order reaction time at a temperature as high as 275 °C achievable by changing the flow rate was effective for the control of the average particle size. A TEM picture of the sample 3 is shown in Figure 2. The particle size was about 5 nm and lattice image was clearly seen to show the particle is crystallized.

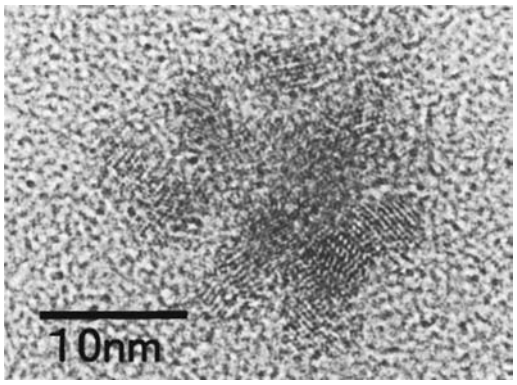

Figure 2. TEM picture of CdSe nanocrystals. Preparation conditions: see Table 1 (No. 3).

In order to check the stability of the CdSe preparation, the product was corrected for five times separately in sample tubes, during reaction. As shown in Figure 3, the absorption spectra of the products were almost identical and a quite high reproducibility in absorption peak was confirmed. It is considered to be caused by the quite high reproducibility of thermal history of the reaction solution.

In conclusion, in order to provide a novel method for a continuous CdSe nanocrystal preparation, a capillary type microreactor was employed. By using the method, quick and accurate control of the reaction temperature was possible and CdSe nanocrystals were able to be prepared continuously. By varying the residence time from 30 s to 600 s, fluorescence peak of the CdSe nanocrystals is shifted from about 545 to 595 nm and particle diameter shifted from 2.8 nm to 4.2 nm. Repeated experiments showed a high reproducibility of absorption spectra. These results show a strong advantage for the controlled mass production of nanoparticles.

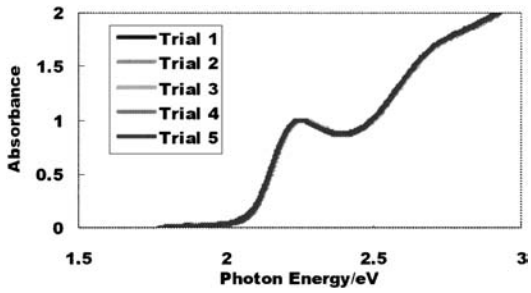

Figure 3. Reproducibility of absorbance spectra of CdSe nanocrystals. Reaction time: 60 s.

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