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Preparation of CdSe nanocrystals in a micro-flow-reactor

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A micro-reactor was utilized for continuous and controlled CdSe nanocrystal preparation. Effects of reaction conditions on optical properties of the nanocrystals were investigated; in this current system, rapid and exact temperature control of the micro-reactor was beneficial for controlling particle diameter and reproducible preparation of particles; additional effort was made towards narrower particle-size distributions.

CdSe nanocrystals increasingly attract attention for applications such as fluorescence tags for biological molecules, raw materials for tuneable LEDs, optical memory, and so on.[1,2] When the CeSe semiconductor size is smaller than the exciton Bohr radius ($<$ *ca.* 7 nm),[3] the band gap widens for smaller particles and fluorescence from CdSe particles shifts to a shorter wavelength. Therefore, it is possible to adjust fluorescence colour by adjusting particle size. For CdSe nanocrystals, preparation in a surfactant, like trioctyl phosphine (TOP) and its oxide (TOPO), at high temperature (250–350 °C) is often utilized. Although this method can provide high quality CdSe nanocrystals and also has a wide applicability for many materials as well as CdSe nanocrystals, a large batch preparation of CdSe nanocrystals has not been reported yet. For example, in reported papers, particles are usually prepared in a small batch (about 5 to 50 mL)[4–11] in order to control reaction conditions properly.

Generally, as vessel size becomes larger, temperature control and homogeneous mixing becomes harder to accomplish and thus a scaling up of reaction vessel often becomes a serious problem, especially for performing a rapid reaction. CdSe nanocrystal preparation utilizing TOPO and TOP requires a high temperature and rapid nucleation to generate a large number of nuclei at one time. Therefore, scaling up of CdSe nanocrystal preparation is considered not so straightforward in spite of the rapidly increasing demand for the material. From this point of view, a new method which can be easily controlled and scaled-up is desired for industrial production of CdSe nanocrystals.

Recently, a micro-reactor, whose representative length is of micron-order, has been developed and has attracted increasing interest.[12] Its short representative length facilitates accurate control in reaction conditions (especially temperature).[13] For example, a simulation based on heat conduction showed that only 0.4 s was necessary for a 0.2 mm diameter channel to heat a liquid inside from 20 to 300 °C (specific heat = 1 cal/(g. °C)), thus demonstrating its absolute advantage in temperature control over a batch reactor. This rapid temperature control also allows exact control of reaction time; especially for a short reaction time.[14] A micro-reactor is usually designed as a flow-type reactor; integrating them can realize industrial applications of a micro-reactor. Scaling-up through integration of reactors can free production from common problems ascribable to conventional up-scaling of reactor vessels, such as heterogeneity in mixing and temperature control. A simple calculation shows that seventy reactors with a flow rate of 0.25 mL min^{-1} can treat 10 L of reaction solution in 10 h. Owing to the small reactor size the parallel operation is quite realistic. These advantages demonstrate the potential of a micro-reactor as an industrial reactor for well-controlled reactions. In addition, the small vessel size of the reactor must be suitable as a rapid checker of reaction parameters.

Recently, some researchers have utilized a micro-reactor for nanocrystalline preparations. Edel *et al.* reported CdS nanocrystal preparation in an aqueous method utilizing a micromixer.[15] Also, Wang *et al.* utilized a liquid interface in a micro-reactor for TiO_2 nanocrystal particle preparation.[16] However, there are no reports utilizing one salient micro-reactor feature: rapid and exact temperature control of nano-particles; also, few discussions have been made on controllability and reproducibility of the method, which would be crucial for industrial application. Also, if it is possible to utilize a micro-reactor for continuous preparation of nano-particles in a hot surfactant, the same strategy would be applicable for many other kinds of materials which are currently prepared by precipitation in a similar manner.[17–20] Therefore, the authors used the micro-reactor for CdSe preparation for a nanocrystal preparation using a hot surfactant, TOPO, and TOP; particle size controllability, fluorescence peak controllability, and particle reproducibility were investigated. Also, the effects of some operation conditions on particle size distributions were also explored.

The CdSe nanocrystal preparation method reported by Qu *et al.*[1] was modified for this reaction system. Typically, Se powder was added to trioctyl phosphine (TOP) to prepare a TOP-Se stock solution. Meanwhile, $Cd(CH_3COO)_2$ was added to stearic acid and heated at 130 °C. Then, trioctyl phosphine oxide (TOPO) was added under a nitrogen flow. After the solution was cooled to below 100 °C, it was mixed with TOP-Se to make a raw material solution. The raw material solution was loaded into a glass syringe, which is connected to a glass capillary. Residence time of the reaction solution in the heating portion of the reactor was determined by flow rate and capillary length. A schematic representation of the reaction system is shown in Fig. 1. The product was collected in a test tube and a portion was diluted 20 times with chloroform for UV-VIS spectroscopy and fluorescence spectroscopy. The average particle diameter was estimated from UV-VIS absorption peaks on the basis of the literature reported by Dushkin *et al.*[12]

The micro-reactor was able to produce CdSe nanoparticles continuously at temperatures from 230 to 300 °C with reaction times of 7 to 150 s. Effects of these parameters on the absorption peak location are shown in Fig. 2, where absorption peaks red-shift with reaction time. Among similar reaction times, higher temperatures yield longer absorption-peak wavelengths. Ab-

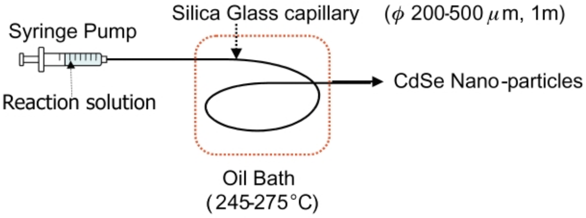

Fig. 1 Diagram of the flow reactor for CdSe nano-particles.

sorption peak location corresponds to particle size of CdSe nanoparticles; estimated particle size was varied from around 2 nm to 4.5 nm. The particle size development curve was similar to the one reported for a batch system.[12] Fluorescence peak location of the products corresponded to the absorption peak; it was found to vary from *ca.* 450 to 600 nm with particle size. The quantum yield of 560 nm fluorescence was about 1.5%. However, the relative intensity of fluorescence was weak for smaller particles; in our tests, photoluminescence with a peak less than 500 nm often accompanied emission peaks.

To assess reproducibility of particle size distribution, 10 mL of reaction solution was continuously flowed into a capillary with residence time of 10 min; thereafter, the product was sampled every 2 h to examine reaction stability. The result is shown in Fig. 3. Absorbance spectra corresponding to the particle-size distribution of the products are well matched, indicating a high reproducibility of CdSe nano-particle size distribution achieved by this method. This high reproducibility can be attributed to accuracy in temperature and reaction time control; it shows the high potential of this method for mass production of CdSe nano-particles.

Narrow particle diameter distribution is required to obtain a sharp fluorescence peak. Particle diameter distribution is shown by absorption-peak sharpness. Therefore, effect of operation conditions on the absorption-peak width was investigated. When a 500 μm capillary was used instead of the 200 μm capillary, the absorption peak greatly widened. Calculations based on heat conduction showed that about 4 s is required to reach reaction temperature for a 500 μm capillary, whereas only 0.4 s is required for a 200 μm capillary. As heat conducts away from the capillary wall, the slower heating rate yields more heterogeneous heating in the capillary and might affect nucleation and growth to give wide particle size distribution. This result shows one advantage of a micro-reactor for controlling particle size.

When a fluid flows in a capillary there is a velocity distribution which induces a residence time distribution. Therefore, a small (0.5μL) N_2 bubble was introduced into the capillary every 3 s to avoid distribution. Fig. 4 shows the result; segmentation of the reaction solution by the N_2 bubble was found to be effective for narrowing the particle diameter. The bubble prevents mixing between segments of raw materials and reduces the residential time distribution and consequently reduces particle size distribution.

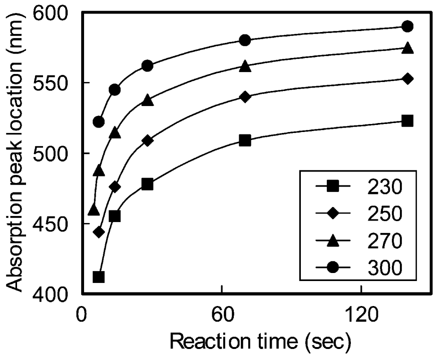

Fig. 2 Effect of reaction time and temperature on average CdSe nano-particle size.

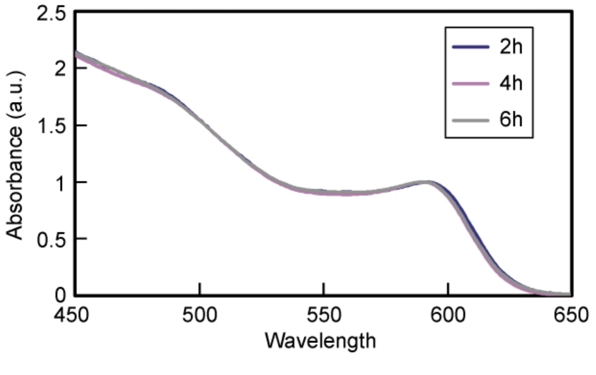

Fig. 3 Reproducibility of CdSe nanocrystal preparation. Preparation conditions: 270 °C, 10 min.

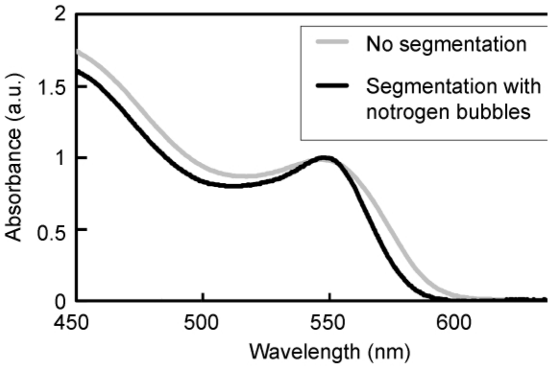

Fig. 4 Effect of segmentation of reaction solution flow on particle size distributions (275 °C, 60 s).

In conclusion, a micro-reactor was utilized in order to produce CdSe nano-particles continuously. It was possible to produce CdSe nanoparticles continuously by continuous injection of the raw-material solution for CdSe into a pre-heated glass capillary type micro-reactor. Absorbance peaks of products were varied from about 450 to 600 nm, which corresponds to a particle size of about 2 to 4.5 nm, respectively. Longer reaction time and higher reaction temperature yielded larger particles. Fluorescence peak location was also controlled by reaction time and temperature. Reproducibility of particle size distribution was high. This high reproducibility was considered to be caused by increased accuracy in temperature and reaction time control. For narrower particle size distribution, thinner capillary diameter and segmentation of a reaction solution by inert gas was effective.

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