Micro-Space Synthesis of Core–Shell-Type Semiconductor Nanocrystals for Thermosensing

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Optical properties of semiconductor nanocrystals possess characteristic dependence on temperature, thus making them good candidates for temperature sensors. We synthesized CdSe and CdSe/ZnSe/ZnS core/shell-type semiconductor nanocrystals using a microreactor and optimized the structure of composite semiconductor nanocrystals to obtain high quantum yield with high stability for thermosensing.

Microreactors are attracting attention as high-performance reactors with the ability to control precisely reaction conditions and serve as high-mix and low-volume production reactors suitable for biochemical, fine chemical, and pharmaceutical industries.[1] However, because they are miniaturized, and thus, have smaller channel dimensions, measurement of "real" temperature of the micro-space is difficult. Moreover, the laminar flow nature of microfluids increases the temperature distribution, although microreactors are considered to control temperature much easier than the conventional reactors. If it is possible to measure the temperature distribution of the micro-space to access the reactor, it would be possible to design much higher-performance reactors for individual reactions. Especially at high reaction temperatures, highly efficient heat transfer can cause perturbations in the reaction temperature.

Recently, temperature measurements of microchannels have been studied using an organic dye for temperatures up to about 60 °C.[2] However, at higher temperatures, where a higher temperature perturbation is expected, an inorganic fluorescent dye would be preferable for its high thermal and photo-stability. In addition, development of colloid technology provides high-quality semiconductor nanocrystals with a high monochromic fluorescence quantum yield. The composite structure of a nanocrystal can be designed to provide high quantum yield. Furthermore, surface modification can afford a stable dispersion in various solutions ranging from water to oil phase.[3,4]

Among the semiconductor nanocrystals, CdSe nanocrystals have the widest application because of excellent luminescent properties and higher photostability compared to organic dyes. Furthermore, it is possible to improve the luminescence intensity by coating on their surface adding a shell of a larger band gap semiconductor, such as ZnSe or ZnS, which also improves the luminescence efficiency. The coating layer can confine the electrons and holes at the interface leading to a larger offset band and can efficiently eliminate surface defects by epitaxial growth of the shell. On the other hand, it is clear that the most widely used CdSe/ZnS system assures better exciton confinement than CdSe/ZnSe. The rather large value of the lattice mismatch parameter of CdSe/ZnS may, however, give rise to structural defects at the core/shell interface, which can cause photoluminescence quenching. Whereas, the CdSe/ZnSe and ZnSe/ZnS system offers better lattice matching. Moreover, deposition of ZnS outer shell onto CdSe nanocrystals, which are already covered with relatively thin ZnSe layer, significantly improves the fluorescence efficiency as reported by Reiss et al.[5–7] Except for some reports on temperature dependence of optical properties of semiconductor nanocrystals,[5,7] as far as the authors know, there is no report yet on CdSe nanocrystals and their composite particles as a thermosensor solution, that can be used for measurements in the temperature region of 50–200 °C in the microchannel.

Therefore, in this study, we evaluated the application of nanocrystals as thermosensors at high temperatures. The structure of composite semiconductor nanocrystals was optimized to obtain high quantum yield with high stability. If their optical properties depend largely on temperature, it should be possible to utilize them as thermosensors that can indicate temperature distribution in a microchannel, which would contribute to practical temperature control of the microreactor.

In our study, CdSe,[8] CdSe/ZnSe, and CdSe/ZnSe/ZnS core/shell/shell semiconductor nanocrystals were synthesized via a colloid growth method by using a microreactor. Microreactor technology has been demonstrated as superior in producing nanocrystals with well-controlled sizes and shell thicknesses because of the precise control of temperature and reaction time.[9] Therefore, microreactors are expected to control the nanocrystal structure by maintaining homogeneity, afford an optimized quantum yield with higher stability, and provide an easier approach than the general batch reaction systems.

Results of the STEM observation of nanocrystals as shown in Fig. 1 revealed that the particle size increased due to coating process, and coating layer thickness increased with an increase in the reaction time. The particle size of the CdSe/ZnSe (3.9 nm) and CdSe/ZnSe/ZnS (6 nm) nanocrystals was con-

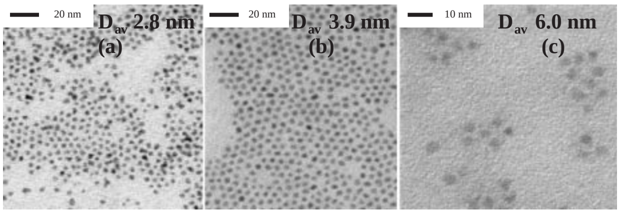

Fig. 1. STEM image of CdSe (a), CdSe/ZnSe (b), and CdSe/ZnSe/ZnS (c).

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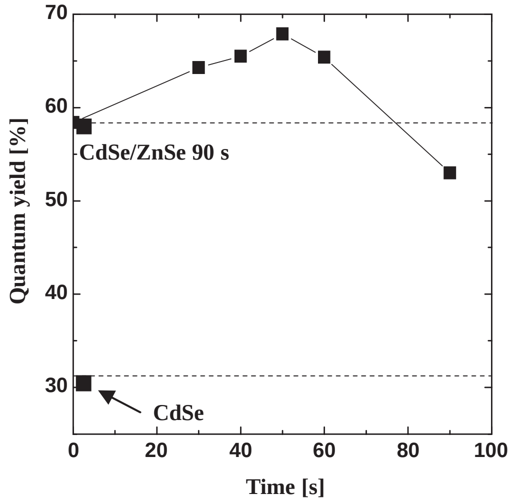

Fig. 2. QY of CdSe and CdSe/ZnSe/ZnS.

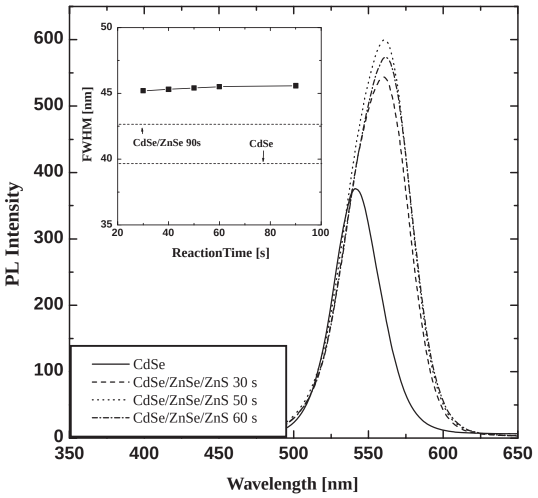

Fig. 3. Photoluminescence spectra and plot of corresponding FWHM values of CdSe and CdSe/ZnSe/ZnS nanocrystals.

firmed by STEM image from CdSe (2.8 nm). The layer thickness was about 0.6 nm for ZnSe, and 1.1 nm for ZnS. In addition, Figure 2 shows the effect of reaction time (ZnS) on quantum yield (QY) of CdSe/ZnSe/ZnS. When the QY of CdSe and CdSe/ZnSe/ZnS nanocrystals were compared with increasing reaction time, it was found out that the QY of CdSe/ZnSe/ZnS (55–65%) was double that of CdSe (about 30%). However, the QY of CdSe/ZnSe/ZnS decreased with an increase in reaction time because of increasing ZnS-layer thickness and consequent strains at the interface with reaction times over 50 s reaction time. In Fig. 3, the red-shifts were observed in photoluminescence spectra which are consistent with the report by Chen et al.,[10] and indicated successful passivation by epitaxial overgrowth. In addition, Chen et al. have reported that the red-shift of emission spectra of core/shell nanocrystals can be explained by quantum confinement and coherency strain effects. Moreover, a constant full width at half maximum (FWHM) of fluorescence spectra (Fig. 3) indicates that it is possible to prepare homogeneous double coated core–shell nanocrystals by using a microreactor. Therefore, CdSe and CdSe/ZnSe/ZnS composite nanocrystals were successfully formed in a microreactor, and their quantum yields were improved by coating with wide-bandgap materials. Thus, microreaction technology was proven to be effective for the formation of homogenous nanocomposite particles. The structure of composite semiconductor nanocrystals was optimized to obtain a high QY with high stability for thermosensing.

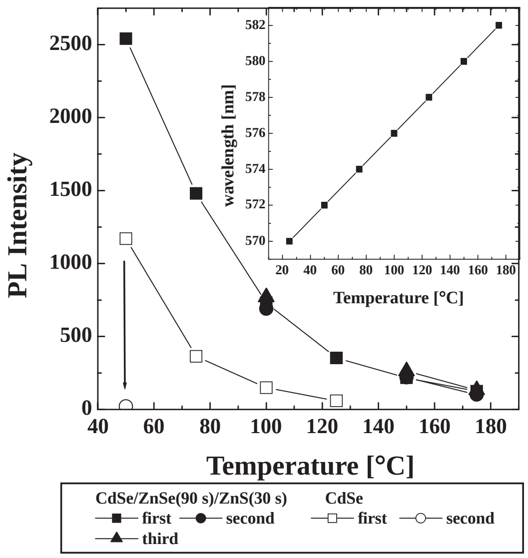

Fig. 4. Fluorescence intensity and wavelength of CdSe and CdSe/ZnSe/ZnS nanocrystals versus temperature.

The applicable temperature range, thermo-stability and error bound for the CdSe/ZnSe/ZnS and CdSe nanocrystals were determined. Figure 4 shows temperature dependence of optical properties (maximum photoluminescence (PL) wavelength and intensity) and the heat stability of CdSe and CdSe/ZnSe/ZnS nanocrystals in a microreactor (300 µm in width, 200 µm in depth). In both cases, the photoluminescence intensity decreased with increasing temperature from 50 to 175 °C (1/15 for CdSe and 1/25 for CdSe/ZnSe/ZnS). However, PL from CdSe was not observed for the second heat application, whereas it was reproducible for CdSe/ZnSe/ZnS. This result showed that the coating layer was effective in reducing the thermal degradation of nanocrystals. In addition to PL enhancement, reversible temperature dependency of PL intensity in CdSe/ZnSe/ZnS can be explained by phonon scattering of CdSe lattice,[3,4] and our results also on fit well with the reported equation.[10] Generally, PL intensity is also reduced by surface defects generated in nanocrystals, and is often irreversible.[3,4] Also, in the current case, irreversible luminescence of CdSe nanocrystals was attributed to the surface defects generated by some surface reaction under high temperature and light irradiation. The disparity in PL intensity of different nanocrystals measured for CdSe/ZnSe/ZnS at a fixed measuring point for each measurement (ie, first, second, and third measurement per se) was ≈2% and was found to be extremely reproducible, that was, 0.94 °C (at 50 °C), 0.73 °C (at 75 °C), 0.79 °C (at 100 °C), 0.84 °C (at 125 °C), 1.2 °C (at 150 °C), and 2.2 °C (at 175 °C), respectively. However, the absorbed minimal disparity (12%) in PL intensity after the second and third measurements as in the case of 100, 150, and 175 °C (Fig. 4) may be attributed to measurement deviation due to equipment error. Similarly, minimized disparity was found when the measuring point was changed in a reactor where the temperature was uniform.

Temperature difference in flow direction of a microreactor is sometimes expected to be very large reaching up to several ten degree centigrade.[11] Even perpendicular to the flow, a 5 °C difference was observed within 40 µm at 70 °C.[11] These results show that it is possible to utilize CdSe/ZnSe/ZnS nanocrystals as thermosensors, at least from 50 to 175 °C range. It should be possible to measure reproducibly a temperature distribution in a microchannel after optimization of the measurement method.

Figure 4 also shows that the wavelengths of maximum point of intensity are linearly dependent on temperature. In CdSe/ZnSe/ZnS core/shell nanocrystals, the red-shift was 12 nm at 150 °C and was reproducible. In fact, the wavelength shifted 2 nm for every 25 °C increase in temperature. Moreover, CdSe and CdSe/ZnSe/ZnS nanocrystals showed red-shifted emission spectra. These results mean that the energy shifted to low-energy side due to temperature dependent band gap shrinkage in the nanocrystals. This temperature dependence of wavelength can be used for their application as thermosensors.

In conclusion, CdSe and CdSe/ZnSe/ZnS nanocrystals were prepared using a microreactor, and the temperature dependence of their optical properties were determined. It was shown that their photoluminescence intensity and wavelength depended on temperature. Furthermore, microreactor-based optimization of CdSe/ZnSe/ZnS composite particle structure was shown to produce a high quantum yield and provide stability required for reversible temperature measurements. In addition, the nanocrystals could be used to measure temperature distribution.

Experimental

Micro-Space Synthesis of Semiconductor Nanocrystals. $Cd(CH_3COO)_2\cdot H_2O$ was dissolved by oleic acid and octadecene (ODE) mixture at 180 °C under argon flow. Se powder was dissolved in trioctylphosphine (TOP). These solutions were mixed and used as raw material for CdSe.

The solution was injected in microreactor heated at 240 °C, affording CdSe nanocrystals. The heating time was controlled by using a specific flow rate and specific length of the heated microchannel.

The ZnSe raw material was prepared as follows. $Zn(CH_3COO)_2\cdot 2H_2O$ was dissolved in oleylamine and ODE. This solution was mixed with Se TOP solution. For the CdSe/ZnSe core/shell nanocrystals, the raw material was mixed with the washed CdSe nanocrystals solution. The mixture was injected into microcapillary reactor heated at 200 °C. The ZnS raw material was made from zinc diethyldithiocarbamate acid salt dissolved in TOP solution forming a CdSe/ZnSe solution. The mixture was injected into microcapillary reactor heated at 150 °C. The absorption and PL emission spectra (Jasco V-570, FP-6600, Japan) of CdSe and CdSe/ZnSe/ZnS were measured, and the QYs were determined by comparison with rhodamine B solution.

Temperature Measurement. Temperature dependence of optical properties and reproducibility of CdSe, CdSe/ZnS, and CdSe/ZnSe/ZnS nanocrystals in a microreactor (300 µm in width, 200 µm in depth) were investigated. The microreactor was fabricated on a silicon plate by dry-etching and covered with glass plates. Nanocrystals were dispersed using octadecene, and their solutions were fed into microreactor by a syringe pump. Experiments were operated under isothermal condition, such as 50–200 °C at a flow rate of $1\,\mathrm{mm\,s^{-1}}$. As a result of heat conduction simulation in microreactor, temperature of the solution (specific heat $= 1\,\mathrm{cal\,g^{-1}\,{}^{\circ}C^{-1}}$) was uniformly kept at 5 cm point from the inlet; therefore, we determined the measuring point as 30 cm from the inlet. Fluorescence intensity was determined on a fluorescence microscope equipped with a fluorometer (C7473; Hamamatsu Photonics, Japan), Ar gas laser (Stabilite 2017; Spectra-Physics, Japan, 488 nm) and a longpass filter (OG515; Edmund Industrial Optics, NJ, U.S.A.) and as shown in Fig. 5. The typical example of PL spectra from CdSe/ZnSe/ZnS NCs by the current method is also shown in Fig. 5.

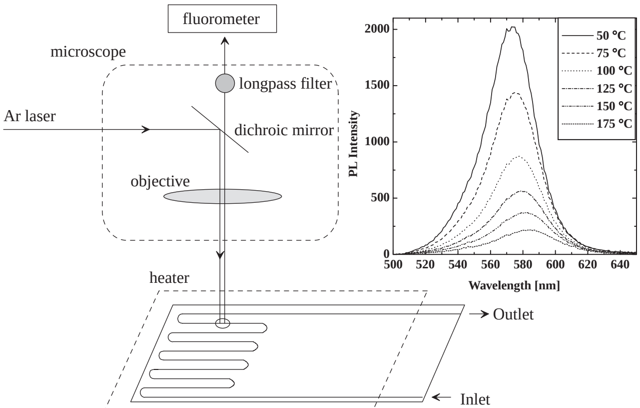

Fig. 5. Schematic illustration of microscope fluorometer for temperature measurement.

References

1 K. F. Jensen, *Chem. Eng. Sci.* **2001**, *56*, 293.

2 Y. Sato, G. Irisawa, M. Ishizuka, K. Hishida, M. Maeda, *Measurement Science Technology* **2003**, *14*, 114.

3 G. W. Walker, V. C. Sundar, C. M. Rudzinski, A. W. Wun, M. G. Bawendi, D. G. Nocera, *Appl. Phys. Lett.* **2003**, *83*, 3555.

4 D. Valerini, A. Creti, M. Lomascolo, L. Manna, R. Cingolani, M. Anni, *Phys. Rev. B* **2005**, *71*, 235409.

5 P. Reiss, J. Bleuse, A. Pron, *Nano Lett.* **2002**, *2*, 781.

6 Y. Ebenstein, T. Mokari, U. Banin, *Appl. Phys. Lett.* **2002**, *80*, 4033.

7 P. Reiss, S. Carayon, J. Bleuse, A. Pron, *Synth. Met.* **2003**, *139*, 649.

8 H. Nakamura, Y. Yamaguchi, M. Miyazaki, M. Uehara, H. Maeda, P. Mulvaney, *Chem. Lett.* **2002**, 1072.

9 H. Wang, H. Nakamura, M. Uehara, Y. Yamaguchi, M. Miyazaki, H. Maeda, *Adv. Funct. Mater.* **2005**, *15*, 603.

10 X. Chen, Y. Lou, A. C. Samia, C. Burda, *Nano Lett.* **2003**, *3*, 799.

11 R. K. P. Benninger, Y. Koc, O. Hofmann, J. Requejo-Isidro, P. M. W. French, A. J. deMello, *Anal. Chem.* **2006**, *78*, 2272.