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Continuous In Situ Synthesis of ZnSe/ZnS Core/Shell Quantum Dots in a Microfluidic Reaction System and its Application for Light-Emitting Diodes

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For the continuous production of quantum dots (QDs), continuous-flow microfluidic reaction systems have been recognized as an effective and alternative strategy to the conventional batch systems due to precise controllability of reaction conditions, including high heat and mass transfer, temperature control, high surface-to-volume ratio, efficient mixing, low reagent consumption, and continuous production.[1,2] In addition, the microfluidic reaction system provides easy scale-up and reduces the reaction time, which is highly suitable for the large quantity production of monodisperse QDs for industrial applications in electronics and the life sciences.[3] Unfortunately, the most composition of previously synthesized QDs is mainly dedicated to Cd chalcogenide material, which is known to be a hazardous substance and to cause serious health problems and is therefore applied in limited applications.[4] In addition, research on blue-emission QDs has remained elusive because it is difficult to synthesize small sizes (<1.6 nm) of CdSe-based QDs that have a narrow size distribution and high quantum efficiency.[5] Furthermore, several reported continuous reaction systems required more than two reactors or complex synthetic procedures, which may limit to produce core/shell QDs.[6]

In order to overcome these present issues in the synthesis of QDs, several aspects should be considered and improved as follows: 1) selection of heavy-metal-free QDs emitting in a visible emission range; 2) continuous and single reaction system for the synthesis of both core QD or core/shell QDs; and 3) selection of materials for easy fabrication, cheap, and highly transparent reactors. For the selection of heavy-metal-free component in QDs, zinc selenide (ZnSe) QDs are

considered as a promising candidate materials due to their high fluorescence emission in UV to blue range among several candidates materials.[7] In addition, the emission wavelength of ZnSe QDs is easily controllable in the ranges of green, red, and white light through impurity doping or surface functionalization.[7,8]

In the aspects of materials selection for the fabrication of reactors, previous research on QDs synthesized by microfluidic reaction systems were mainly fabricated using metals.[9] Unfortunately, homogeneous mixing of reagents, which is a major limitation of batch reactor system, is impossible to monitor in the inner space of the opaque reactors and it is also difficult for the mass production of reactors.[6] To overcome these issues, we presented a microstructure-embedded cyclic olefin copolymer (COC)-based microfluidic devices using a microinjection technique, which is highly suitable for the rapid replication and mass production of the microfluidic reactors or devices recently.[10] In addition, the COC, which is a class of polymers based on cyclic olefin monomer and ethane, is a highly transparent and the most stable polymer in acid, base, and organic solvents, which are commonly used in the synthesis of various types of nanomaterials.[11] Because of the unique properties of COC, it is suitable for the fabrication of reactors which are easy to monitor both homogeneous mixing and reactions.

Herein, we report a continuous in situ synthesis of ZnSe/ZnS core/shell QDs in a microfluidic reaction system. To the best of our knowledge, this is the first research on the synthesis of QDs using thermoplastic-based microfluidic reaction system and continuous one-step production of ZnSe QD core itself and in situ synthesis of ZnSe/ZnS QD core/shell simultaneously. Furthermore, we investigated the effects on the flow rates of precursor solutions of Zn, Se, and S to the size and optical properties of QDs in the microfluidic reaction system. Finally, we fabricated light-emitting diodes (LEDs) using the produced ZnSe/ZnS core/shell QDs as a wavelength converter to demonstrate the potential application of synthesized QDs.

The schematic illustrations for the whole synthetic processes of ZnSe/ZnS core/shell QDs using the continuous microfluidic reaction system were shown in **Figure 1**a and Figure S1 (see Supporting Information). In the microfluidic reaction system, the system is mainly composed of three major sections as follows: 1) mixing of precursors, 2)

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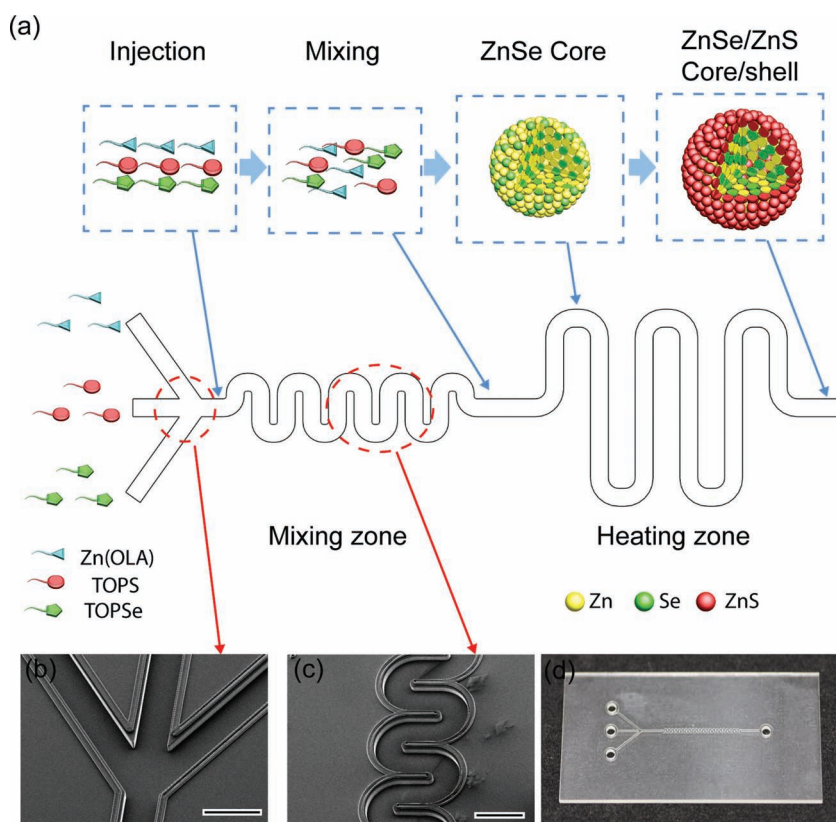E-mail: sjlee@nnfc.re.kr

(a)

Figure 1. a) Schematic illustration of ZnSe/ZnS core/shell synthetic process using a continuous-flow thermoplastic-based microfluidic reaction system. SEM images of b) inlet and c) mixing zone in the microfluidic device. d) A photograph of the microfluidic device.

formation of ZnSe core QDs, and 3) coating of ZnSe cores with ZnS shells. The detailed role of the major sections and formation mechanisms of ZnSe/ZnS core/shell QDs will be further discussed in the next sections. In the microfluidic reaction system, the reactor is an important component for the synthesis of QDs. For the precise fabrication of the reactors and easy monitoring of reactions, the microfluidic reactor was made of plastic and they were fabricated using a nickel master stamp and microinjection molding method as previous reported.[10] The detailed dimension of microfluidic reactor, fabrication process of the Ni stamp, a schematic illustration of overall experimental work, and a photographic image of microinjection molding machine were demonstrated as shown in Figure S1–4 (see in Supporting Information). The thermoplastic-based microreactor is composed of three inlet channels and one outlet channel as shown in Figure 1a and Figure S5 (see in Supporting Information). The employed microstructures in the microreactor were analyzed by scanning electron microscopy (SEM) as shown in Figure 1b, c and Figure S6 (see in Supporting Information). The inlet channels were connected to the syringe pumps that contained three different precursor solutions. The precursor solutions were composed of Zn, Se, and sulfur (S) sources. The Zn stearate powder dissolved in oleylamine (Zn(OLA)) and both Se and S were dissolved in trioctylphosphine (TOP) and refered as TOPSe and TOPS for the each cases. Three different precursor solutions were injected to the inlet channels and the precursors were mixed efficiently as passing through

the mixing zone of microfluidic reactor (Figure 1a). Once the precursors were mixed, the mixture solution was moved to the heating zone for the further nucleation and growth of QD cores and shells.

In the microfluidic reaction system, perfect mixing of precursor solutions is critically important for the successful synthesis of QDs. For the confirmation of perfect mixing of precursors in the reactor, the mixing behavior of precursors inside of microfluidic reactor was investigated by measuring the fluorescent intentisty changes in the channel with fluorescent solutions and a confocal microscopy. At the beginning, fluorescent solution was only injected through the middle inlet channel while other soultions have no fluorescence. After injection, there was no mixing or fluorescent intensity changes as soon as the dye solution reaching to the mixing zone. However, the fluorescent solution began to mix as passing through the curved microfluidic channels, which is refered as a mixing zone, and the outlet channel was subsequently fully filled with dye solution. This result indicated the perfect mixing of solutions in the microfluidic reactor (see Supporting Information, Figure S7). Based on the simple experiment, it is concluded that the three precursors were injected into the microfluidic device and all the reagents were properly mixed as passing through the mixing zone.

For the successful synthesis of ZnSe/ZnS core/shell QDs using a microfluidic reaction system, the optimized synthetic condition of ZnSe QDs should be confirmed before the shell coating for further comparison between ZnSe and ZnSe/ZnS QDs. For this reason, Zn(OLA) and TOPSe precursor solutions were only injected to the microfluidic reactor to synthesize ZnSe QDs. Moreover, the temperature in the heating zone was set at 220 °C. This reaction temperature was much lower than that in batch systems ($\approx$280 to 310 °C) because of high heat and mass transfer in the microchannels compared to the bulk system.[8,12] In addition, the different precursor flow rates were applied to the reaction systems to investigate the effects of the flow rate to the ZnSe QDs. For this reason, the flow rate of Zn(OLA), refered as F_{Zn}, were changed to 10, 13, 17, and 20 μL min^{-1} (sample 1–4) while the flow rate of TOPSe (F_{Se}) was fixed at 30 μL min^{-1}. The differential injection rate ($\gamma = F_{Zn}/F_{Se}$) and the ratio of the molar concentrations of precursor solutions ($k = [Zn]/[Se] = 0.93$) determine the molar ratio (R) of Zn to Se in the reaction mixture.[4] Therefore, R values increase from 0.31 to 0.62 in a step of 0.1 (sample 1–4), respectively.[4] After the reaction is over, ZnSe QDs were obtained and the UV/vis absorption and photoluminescence (PL) spectra of the ZnSe QDs (aliquots) were shown in **Figure 2**a,b. As the flow rate of the Zn solution was increased as 10, 13, and 17 μL min^{-1}, the absorption shoulders were blue-shifted. It was due to quantum confinement effect

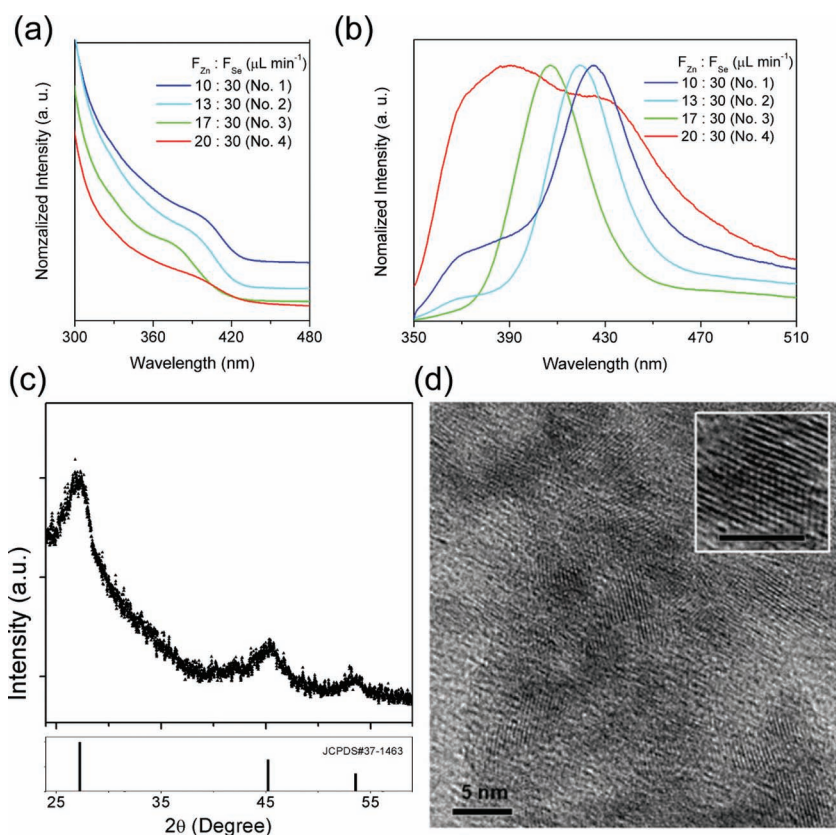© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Figure 2. a) UV/vis absorption and b) PL spectra of ZnSe QDs with different flow rate of Zn and fixed flow rate of Se precursor solutions (excitation: 330 nm and sample 1–4). c) XRD pattern and d) TEM images (sample 3) of pristine ZnSe QDs. Scale bar of the inseted image is 5 nm.

image. The high-resolution image (upper inset) confirmed that the interplanar spacing of 3.22 Å was ascribed to the (111) plane of the ZnSe phase. These obtained results indicate that the ZnSe QDs could be controlled using a microfluidic reaction system.

The adopting of shell to the synthesized QDs is important to improve the stability and emission enhancement.[14] The previous researches generally demonstrated some additional steps used for the formation of inorganic shells after synthesis of core QDs.[6] However, in this study, the S precursors, unlike the previous researches, were introduced with Zn and Se precursors at the same time. Precursor solutions of Zn, Se, and S sources were injected through the three inlets simultaneously, and then transferred to the heating zone (220 °C) after passing through the mixing zone. The detailed flow rate and other conditions were shown in **Table 1**. Optical characteristics of the products were analyzed by UV/vis absorption and PL spectroscopy, and their spectra were shown in **Figure 3**a,b, respectively. The control sample, ZnSe QDs, was used as a reference, which was made using 1-octadecene (ODE) solvent instead of TOPS solution. It exhibited absorption shoulder around 390 nm and emission peak at 421.2 nm from ZnSe QDs. Instead of ODE, an S precursor solution (F_s, sample 10) was applied to the synthesis of ZnSe/ZnS QDs under the same experimental conditions, which showed more distinct emission

(QCE) ascribed to the reduced retention time in the heating zone, and it means that the particle sizes become smaller. Similarly, their emissions from ZnSe QDs moved to 425.2, 419.2, and 407.0 nm, respectively. For sample 2 and 3, they had strong emissions from ZnSe QDs without the emission from impurities. In addition, they had narrow emission peaks: the full width at half maximum (FWHM) were 35.4 nm and 35.6 nm. On the other hand, for sample 1 and 4, the emission from unreacted monomers such as Zn complexes (≈390 nm) appeared strongly, which was ascribed to Zn complexes.[8] We also investigated the synthesis of ZnSe QDs in higher R value (0.93) by changing the F_{Zn} and F_{Se} at the same time (see Supporting Information, Figure S8). Although the growth of QDs was confirmed by absorption and emission spectra, the impurity emission was dominant and the QDs had a broad distribution of particle size. Therefore, optimized synthetic conditions such as the flow rate and molar ratio of precursors should be selected for the synthesis of high quality and monodisperse ZnSe QDs (see Supporting Information, Figure S9). The structure of pristine ZnSe QDs was verified by X-ray diffraction (XRD) pattern and field-emission transmission electron microscopy (FE-TEM) images (Figure 2c,d). The main diffraction peaks appeared at around 27.2°, 45.2°, and 53.6°, respectively, and they were matched with those of zinc blende type ZnSe.[13] The broadening of the peaks was due to the nano-sized crystalline domains. The particle size of the ZnSe QDs was 3.17 ± 0.45 nm as shown in the TEM

Table 1. Microfluidic experiment conditions and their fluorescent properties.

Sample Number	F_{Zn} [μL min^{-1}]	F_{Se} [μL min^{-1}]	F_S [μL min^{-1}]	R[a]	$\lambda^{0,b}$ [nm]	FWHM [nm]
1	10	30	–	0.31	425.2	43.2
2	13	30	–	0.40	419.2	35.4
3	17	30	–	0.53	407.0	35.6
4	20	30	–	0.62	–	–
5	30	30	–	0.93	–	–
6	20	20	–	0.93	421.8	–
7	15	15	–	0.93	421.8	–
8	10	10	–	0.93	430.0	–
9	15	30	30 (ODE)	0.47/0	421.2	–
10	15	30	30	0.47/0.93	424.2	–
11	10	20	20	0.47/0.93	420.2	43.8
12	5	15	15	0.31/0.62	409.8	33.2
13	5	10	10	0.47/0.93	421.2	47.4

[a]Molar ratio of Zn to Se (sample 1 to 9) and Zn to Se/Zn to S (sample 10 to 13) in the mixture;
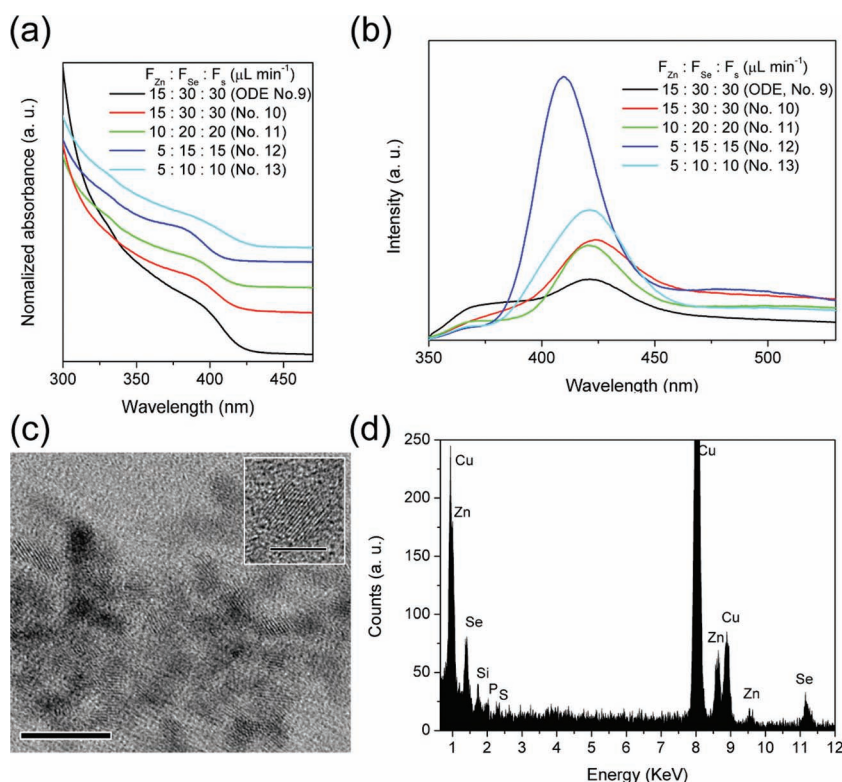[b]Emission peak of QDs.

Figure 3. a) UV/vis absorption and b) PL spectra of ZnSe/ZnS core/shell QDs with different flow rate of Zn, Se, and S solution (excitation: 330 nm and sample 9–13). c) TEM images. Scale bars are 10 nm for the main image and 5 nm for the inset image. d) EDS data of ZnSe/ZnS core/shell QDs (sample 12).

than that of other ZnSe/ZnS QDs. Figure 3c is the TEM images of ZnSe/ZnS core/shell QDs. The spherical nanoparticles with a size of 3.88 ± 0.62 nm were dispersed. In short, the emission intensity of QDs was dramatically increased as the S solution was injected with Zn and Se solutions. In addition, the emission wavelength was blue-shifted, which indicated that ZnS could be formed at the surface of ZnSe QDs. It was confirmed through the energy dispersive X-ray spectroscopy (EDS) spectrum exhibited in Figure 3d. Not only Zn and Se but also S elements were detected. Considering the reactivity difference of precursors (cleavage rates of phosphine chalcogenides increases in the order S < Se), a large amount of the Zn and Se precursors are consumed in the early stage of the synthesis and they produce ZnSe core, then Zn and S precursors react dominantly on the surface of ZnSe QDs to form ZnS shell.[16] In addition, there is low possibility of secondary nucleation of ZnS nanoparticles because the synthesis temperature of ZnS NCs (organometallic method) is higher by 40 °C than that of ZnSe NCs.[12] Through the sequence of experimental results, we achieved two important improvements on both material (colloidal nanoparticle) and microfluidic device system: 1) one-step synthesis of blue-emitting ZnSe/ZnS core/shell QDs, 2) materialization of thermoplastic-based microfluidic reaction system for the continuous synthesis of core/shell QDs with improvement of mass and heat transfer compared to the bulk reaction system.

To demonstrate the usefulness of this ZnSe/ZnS core/shell in LED applications, we fabricated a light-emitting QD-LED under a forward bias current. **Figure 4**a,b are

at 424.2 nm. Their emission became stronger (190%) than that from ZnSe QDs when the integrated PL intensity of ZnSe QDs (sample 9) was set at 100. Although the flow rate of each precursor became slower (sample 11 and 12), the absorption peaks did not move to a longer wavelength, and the emission intensity of samples increased. It is due to effective ZnS shell passivation in growing cores of the QDs that removes surface dangling bonds or defects acting as PL quenching sites.[14] However, in the case of the slowest flow rate (sample 13), the emission efficiency was reduced by defects induced by interfacial strain within the thicker ZnS shell above 2–3 monolayers.[15] Sample 11 and 13 had the same R value because they had reduced flow rate of precursor solutions by 33% and 66% comparing with that of sample 10. Their emission wavelength was blue-shifted by around 1 nm, and emission intensity increased by 150–180%. In the case of sample 12, the R value was adjusted as the flow rate of Zn, Se, and S solution decreased by 5, 10, and 10 μL min⁻¹, respectively. The emission wavelength was blue-shifted (409.8 nm) by 11 nm, and the intensity was dramatically increased up to 270%. Moreover, it had narrower size distribution (full-width at half maximum (FWHM) ≈ 33.2 nm)
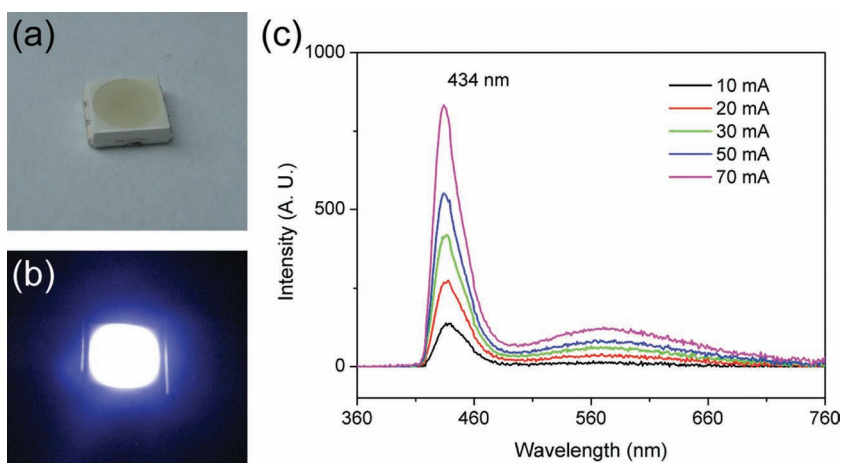

Figure 4. Photographs of a) an as-prepared ZnSe/ZnS QD-LED and b) a blue light-emitting QD-LED under a forward bias current of 70 mA. c) EL spectra of QD-LEDs (sample 12) operating at various forward currents (direct currents: 10, 20, 30, 50, and 70 mA).

photographs of an as-prepared QD-LED and a light-emitting QD-LED under a forward bias current of 70 mA. ZnSe/ZnS QDs as a wavelength converter were loaded on a 396 nm UV LED. Details of the preparation procedure are given in the method section. The blue-light emitting QD-LED is shown in Figure 4b and the electroluminescence (EL) spectra under various forward bias currents of 10, 20, 30, 50, and 70 mA are shown in Figure 4c. As the forward current was increased from 10 to 70 mA, the sharp emission from ZnSe/ZnS QDs (434 nm) was enhanced without any change of the emission wavelength. The broad emission at around 571 nm was ascribed to the radiative deep levels generated by strained lattices or crystal imperfections at the surface such as dislocations and vacancies.[8] The UV emission (396 nm) from the underlying UV LED was not observed because the amount of QDs coated on top of the LED was very large. The emission wavelength of the QD-LEDs was red-shifted by 10 nm comparing with that of the QDs' solution. It could be explained by aggregation of QDs which made a new energy band through overlapping of quantized discrete energy levels.[17]

We demonstrated a successful one-step synthesis of ZnSe/ZnS core/shell QDs using a thermoplastic-based microfluidic reaction system. The use of thermoplastic-based microreactor could overcome the limitations of synthesis of nanomaterials in a microreactor. In addition, the size of QDs can be easily controlled by simply changing the flow rate of precursor solutions and no additional step is required for the formation of shell around core QDs. In addition, the prepared ZnSe/ZnS QDs were applied to the fabrication of QD-LED. It exhibited blue emission at 434 nm excited by a 396 nm UV LED chip. The utilization of microfluidic reaction system for nanomaterials synthesis provides with the uniformity and reproducibility. This thermoplastic-based microfluidic system opens a new route for synthesis of various types of nanomaterials and their applications.

Experimental Section

Reagents and Materials: Zinc acetate (99.99%), selenium (100 mesh, 99.999%), sulfur (99.98%), 1-octadecene (ODE, 95%), OLA (technical grade), TOP (90%), and poly(methyl methacrylate) (PMMA, average $M_w \approx 350\,000$) were purchased from Aldrich. Tributylphosphine (TBP, technical grade) was purchased from TCI. All chemicals were used without further purification steps. COC was purchased from TOPAS.

Design and Fabrication of the Microreactor: The COC-based microreactor is fabricated by microinjection molding method with Ni stamp. The detail design specifications are demonstrated in Figure S1 (Supporting Information). The Ni stamp was fabricated by using the micro-electromechanical systems (MEMS) process and electroplating. The size and thickness of the Ni stamp were 95 mm × 95 mm and 1.2 mm, respectively. Figure S1 (Supporting Information) shows the Ni-stamp fabrication process. First, THB 110N photoresist was coated with 10 μm thick on a bare Si wafer of 8 in. in diameter to make the microchannel. Then, the microfluidic channel was made using UV patterning with channel mask. After developing the micropattern, titanium (Ti)/chromium (Cr) (200 Å/2000 Å) were coated over the micropatterned silicon wafer. In

this case, Ti layers to enhance the adhesion to the silicon wafer and Cr layers play as a seed layer for further Ni electroplating process. The seed metal was deposited using multi-target sputter. The Ni electroforming was performed by electroplating system because the quality of the Ni stamp depended on the shape of COC chip. Also, the Ni stamp with the height of 1.5 mm was included to prevent bending problems during chemical and mechanical polishing. After finishing the Ni plating, photoresist was removed and chemical mechanical polishing was performed to flat the surface of Ni stamp. The final Ni stamp is shown in Figure S3 (Supporting Information).

A plastic microinjection mold machine (A270C 400-100, ARBURG) and Ni stamp was used to produce the microreactor in order to achieve its cost-effectiveness and mass production as shown in Figure S4 (Supporting Information). Polymer-based microreactor was fabricated using the conventional injection molding machine with the nickel template inserts. In this case, COC was chosen as the substrate material of the chip due to its great advantages over the other thermoplastic polymers in terms of optical, physical and chemical properties. The total time of the microinjection molding process was less than 1 min to replicate the COC substrate. In this paper, the two COC substrates bonded by ultrasonic bonder (2000X, Branson) in short period time. In order to bond COC chips, the melting line with the height of 20 μm was fabricated on the top side of the channel mold. Furthermore, the melting line was a sharp form as like a triangle which could be easily melted by sonic energy.

Synthesis of ZnSe QDs and ZnSe/ZnS Core/Shell QDs using a Microfluidic System: The Zn precursor solution was prepared by heating Zn acetate (0.73 g, 4 mmol) with OLA (4 mL, 12 mmol) at 170 °C until the solution turned clear and yellowish, and then 2.0 mL of ODE was added. Se stock solution was prepared by dissolving Se powder (0.29 g, 3.6 mmol) in 1.0 mL of TOP (or TBP) and 4.0 mL of ODE. Then, the solutions of the Zn and the Se precursors were delivered in two continuous-flow microtubes with a syringe pump. The flow rate was changed from 5 to 30 μL min^{-1}. A COC microreactor was connected to the heating zone which was made of the combination of stainless steel tube and aluminum plate to increase the heat transfer and stabilize in high temperature for the further reaction. In the heating zone, the precursor solutions were heated for synthesis of QDs by an induction heater at 220 °C, and the length of heating zone was around 20 cm. After the precursor solutions passed through the mixing zone, they are transferred to the heating zone. The prepared QDs were collected and dispersed in hexane or chloroform. The synthesized ZnSe QDs solution was purified by precipitation with addition of methanol and acetone.[8]

In the case of ZnSe/ZnS core/shell QDs, S stock solution was prepared additionally. The Zn and the Se solutions are the same for synthesis of ZnSe QDs. The S stock solution was prepared by dissolving S powder (0.08 g, 2.5 mmol) in 3.0 mL of TOP and 4.0 mL of ODE. The three microchannels were used for the injection of Zn, Se, and S precursors, respectively. The mixing and heating zones in the microfluidic system are identical to those used for the synthesis of ZnSe QDs.

Preparation and Characterization of ZnSe/ZnS QD-LEDs: PMMA powder (0.10 g) was dissolved in chloroform. Then, 0.8 mL of ZnSe/ZnS QDs in chloroform was mixed with the PMMA solution and put in a vacuum chamber to remove chloroform present in the mixture. A few drops of the QD/PMMA mixture were dispensed

on UV LED chips and cured at room temperature. The emission wavelength of LED chip (non-epoxy molding packages) was 396 nm. Optical characteristics, such as spectra of the reference UV LED and QD-LED, were measured under various forward currents at room temperature.

Instruments: UV/vis absorption spectra of ZnSe QDs and ZnSe/ZnS core/shell QDs were obtained using a Shimadzu UV-3101 PC spectrometer. PL excitation and PL were recorded by an F-7000 Hitachi fluorescence spectrometer PL System equipped with a xenon lamp (500 W) excitation source operated at room temperature. The crystalline phases were analyzed by using a Rigaku D/max-RC X-ray diffractometer (XRD) with Cu Ka (λ = 1.542 Å) radiation operating at 40 kV and 45 mA. The scan rate was 1° min^{-1} and the measurement range was from 25 to 60°. The morphology and size of as-obtained samples were observed using a field-emission transmission electron microscope (FE-TEM, Jeol JEM2100-F) operating at 200 kV.

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