We report a continuous-flow microreaction synthesis of ZnSe quantum dots (QDs) which are controllable in their emission from blue to white light. The emission of ZnSe QDs exhibits quantum confinement effect, which is adjusted by the flow rate of precursor solution. The ZnSe QDs’ high concentration solution shows red-shifted emission in the blue region and strongly enhanced green-yellow emission from deep levels due to the inter-QD energy transfer, thereby exhibiting white color with CIE color coordinates of (0.33, 0.33). The red-shifted band-edge emission with longer decay time in the dense solution confirms that the energy is transferred efficiently between QDs.

© 2013 The Electrochemical Society. [DOI: 10.1149/2.005308ssl] All rights reserved.

Manuscript submitted March 25, 2013; revised manuscript received April 29, 2013. Published June 4, 2013.
Figure 1. (a) Schematic illustration of a continuous-flow microreactor system for the synthesis of ZnSe QDs, (b) UV/VIS absorption and (c) PL spectra of ZnSe QDs (aliquots) with different flow rate.

Figure 2a shows X-ray diffraction (XRD) patterns of ZnSe QDs. The main diffraction peaks appeared at around 27.2°, 45.2°, 53.6° corresponding to (111), (220), and (311) planes of ZB phase of ZnSe (JCPDS Card No. 65–9602). More specifically, the (111) peak of ZB ZnSe was asymmetrically broadened by the convolution of the (100), (002), and (101) peaks of WZ phase of ZnSe (JCPDS Card No. 15–0105). In addition, the suppression of the (102) and (103) planes of WZ ZnSe can be explained by the presence of stacking faults along the (002) direction. The broadening of the peaks is due to the nanosized crystalline domains. Figure 2b and 2c show transmission electron microscopy (TEM) images of ZnSe nanoparticles. They revealed highly crystalline nanostructure with both spherical and rod-shape morphology. In the case of nearly spherical ZnSe QDs (Figure 2b), the size was around 2–3 nm and the measured interplanar spacing (3.28 Å) matched the (111) plane of ZB ZnSe phase. In anisotropic nanostructures (Figure 2c), the diameter was similar to that of the spherical particles but the length was elongated to 5–6 nm. Their interplanar spacing was around 3.53 Å, which was matched with the (100) plane of WZ ZnSe phase. In our continuous microfluidic reaction system, the monomer concentration was fixed and reaction time was long enough due to slow flow rate of precursor solutions. In the initial part of the reaction, high monomer supersaturation kinetically favored both nucleation and growth of the ZB phase, which was more symmetrical than the WZ phase. As the amount of ZnSe QDs synthesized in the microreactor increased, the monomer concentration became extremely low. In the very low supersaturation condition promoting thermodynamic control of the growth, it is expected that the secondary WZ phase growth onto the QDs’ surface become dominant. Due to that, stacking faults were observed in these structurally heterogeneous nanostructures (Figure 2c). Therefore, ZB ZnSe QDs and rod-shape nanocrystals with both the WZ and ZB structure coexisted.

The selective area electron diffraction (SAED) pattern (Figure 2d) of Figure 2. (a) XRD patterns of ZnSe QDs, (b) Low magnification TEM image of ZnSe NPs, (c) High magnification TEM image of rod shape ZnSe nanostructures, (d) SAED pattern of ZnSe QDs. Scale bar of inset is 5 nm.
Figure 3. (a) PL spectra of dilute and dense QDs’ solution excited at 330 nm, (b) CIE color coordinates and the photos of samples.

Figure 3a shows the PL spectra of ZnSe QDs’ solution with the same flow rate (10 μL min⁻¹) and different concentration (dilute and dense QDs’ solution). Aliquots of ZnSe QDs were dispersed in 8.0 mL (dilute solution) and 0.5 mL (dense solution) of chloroform. In the dilute solution, the emission was composed of both strong band-edge emission (426.4 nm) and weak defect emission (~522.0 nm). The greenish emission band was ascribed to radiative deep levels generated by strained lattices or crystal imperfections at the surface such as dislocations and vacancies. As shown in the TEM image (Figure 2c), it is confirmed that elongated particles have the highly defective crystalline nanostructures. On the other hand, in the dense solution, the band-edge emission exhibited at 440.0 nm, which was red-shifted by 13.6 nm compared to the dilute solution. In addition, the greenish-yellowish emission band from deep levels (~565.0 nm) increased significantly. Figure 3b shows the Commission Internationale de l’Eclairage (CIE) color coordinates and camera images of ZnSe QDs’ solution with different concentration. Sample No. 1 is dilute solution emitting blue light with the CIE value of (0.21, 0.17). Sample No. 2 is dense solution emitting white light with the CIE value of (0.33, 0.33).

Figure 4a shows time-dependent photoluminescence (TDPL) decay measurements for the samples (used in Figure 3) measured at the exciton peak maximum (426.0 nm and 440.0 nm of the dilute and dense QDs’ solution). The decay curves of the ZnSe QDs’ solution with both low and high concentration were not mono-exponential, and they were fitted by two exponentials: the dilute solution (τ₁ = 0.52 ns, τ₂ = 3.16 ns) and the dense solution (τ₁ = 0.99 ns, τ₂ = 4.43 ns). The longer decay times (τ₂) are interpreted as the intrinsic transition of the QDs or “excitonic transition”. The shorter decay times (τ₁) could be partial quenching of the exciton luminescence by surface and lattice defects such as unsaturated surface bonds of Zn or Se, and/or Se vacancies inside the QD, providing additional decay channel. The decay curve of the dense solution shows a slower decrease in normalized emission intensity than that of the dilute QDs’ solution. This is attributed to Förster resonance energy transfer (FRET) that relates the efficiency of ET from donor-acceptor dipole-dipole interactions to the spectral overlap of donor emission and acceptor absorption. Figure 4b exhibits schematic diagram of resonant ET process from small (donor) to large (acceptor) ZnSe QDs. Assuming the ET via a dipole-dipole interaction within a donor-acceptor distance (R), the ET rate scales with R⁻⁶ dependence. In the case of dense QDs’ solution, the spatial distance between the individual particles is sufficiently short, so the inter-QD ET occurs efficiently. Furthermore, there was spectral overlap of the donor emission and the acceptor absorption, which increased the ET. Although the energy of excitonic emission transferred sequentially from the small QDs to the large QDs, the energy of defected-related emission does not migrate because the defect in QDs acts as a trap. Therefore, the red-shifted excitonic emission, increased intensity of defect emission, and prolonged decay time in the dense QDs’ solution confirms that the energy is transferred efficiently between QDs.

In summary, we first demonstrated white-emitting ZnSe QDs by a continuous-flow microreaction method. The emission from the QDs moved from 413 nm to 432 nm when its flow rate was changed from...
25 μLmin⁻¹ to 5 μLmin⁻¹. The ZnSe QDs had strong band-edge emission and weak defect emission. In dense solution of ZnSe QDs, it showed red-shifted (14.6 nm) band-edge emission and enhanced green-yellow emission from deep levels due to the inter-QD energy transfer comparing with dilute solution, thereby it exhibited white color with CIE color coordinates of (0.33, 0.33). This work related to the ET between individual QDs will become the foundation for advanced QD-based application.

Acknowledgment

This research was supported by WCU (World Class University) program through the Korea Science and Engineering Foundation funded by the Ministry of Education, Science, and Technology.

References