Organic Liquid Phase Synthesis and Characterization of Core-shell CdSe@ZnS Quantum Dots

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The chalcogenide CdSe quantum dots (QDs) with ZnS nanoshells were obtained by wet chemical synthesis route, which was performed by using cadmium oxide and tetradecylphosphine oxide (TDPO) and tri-n-octyl-phosphine oxide (TOPO) as complexing agents in tri-n-butylphosphine (TBP) solvent in the reactor protected by an argon atmosphere. The photo-luminescence function of CdSe/ZnS QDs leads to potential *in vivo* medical applications. The ZnS nanoshells with various Zn/S Stoichiometric ratios were analyzed by X-ray absorption near-edge structure (XANES) at NSRRC along with other analytical tools such as particle size analyzer, photoluminescence (PL) spectroscopy, FE-SEM, TEM, and XPS. The desired particle size and photoluminescence response of CdSe/ZnS QDs can be achieved nanoshell growth rate as well as synthesis temperature and reaction time through organic liquid phase synthesis process.

Figure 1 shows Zn K-edge XANES spectra measuring at energy range of 9.5 to 10.5 keV for CdSe/ZnS nanoparticles, where the absorption peak of Zn ions located at 9.65 keV indicates the existence of zinc ions in core-shell structured CsSe/ZnS particles. Even though CdSe/ZnS nanoparticles were synthesized with various Zn/S molar ratios from 0.5 to 4.5, the location of X-ray absorption edge appearing in these XANES spectra are somewhat the same without no substantial peak shift. Along with an increase of sulfur amount added in the precursor, the valance and chemical bonding for zinc ions are rather stable. During the course of synthesizing CdSe and ZnS nanoparticles, which are with hexagonal closely packed (HCP) wurtzite structure; the morphology of resultant crystallites will be altered accordingly as being derived from a Se or S ion source of excess amount. Since the Cd ion along the $[00\bar{1}]$ direction is chemically bonded to three nearest neighbor ions and remains a dangling bond, thereby three dangling bonds on the plane of (001) would exhibit higher chemical potential to render inhomogeneous crystal growth rates in different crystalline directions and this would result in prolonged crystallite shape.

Figure 2 represents the radial distribution function of CdSe/ZnS quantum dots with various Zn/S molar ratios from the Fourier transform of its XANES spectrum at Zn

K-edge, where we found a strong peak of Zn-Se bonding with bond length of 0.24 nm. Furthermore this result would support the synthetic performance for ZnS shells to cover the surface of CdSe quantum dots with a stable covalent bonding between Zn and Se atoms. Previously we used the organic reagent to modify the surfaces of CdSe nanoparticles, its less stable surface modification at CdSe quantum dots by organic surfactants did not enhance a substantial quantum confinement effect due to loss of charge carrier easily trapped and consumed at the surface energy levels. The current result by using ZnS for the surface modification of CdSe quantum dots would effectively improve both quantum efficiency and photoluminescence gain of core-shell CdSe@ZnS quantum dots through the reduction of number of dangling bonds.

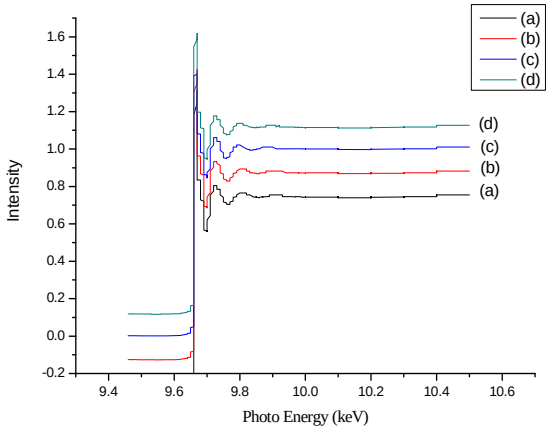

Fig. 1: Zn K-edge XANES spectra of CdSe/ZnS nanoparticles with various Zn/S molar ratios(a) 0.5, (b) 1.0, (c) 3.0, (d) 4.5.

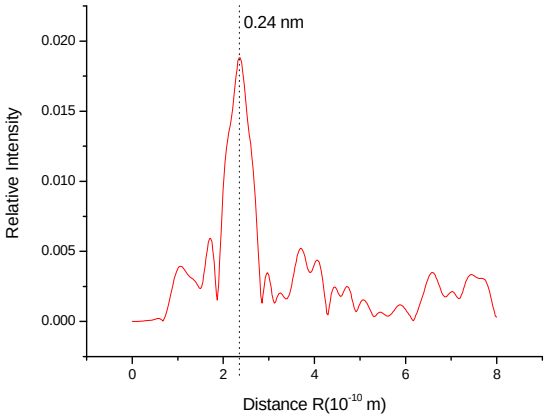

Fig. 2: The radial distribution function of CdSe/ZnS quantum dots with various Zn/S molar ratios from the Fourier transform of its XANES spectrum at Zn K-edge.