Size-dependent structural phase transitions and their correlation with photoluminescence and optical absorption behavior of annealed Zn$_{0.45}$Cd$_{0.55}$S quantum dots

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ABSTRACT

In this paper, we investigate the effect of thermally induced structural phase transitions on the photoluminescence (PL) and optical absorption behaviour of Zn$_{0.45}$Cd$_{0.55}$S nanoparticles (NPs). Analysis of X-ray diffraction (XRD) patterns and high-resolution electron microscope (HRTEM) images reveal that the as-synthesized sample possesses zinc-blende-type cubic structure. In addition, at annealing temperature ($T_a$) 400 °C, the cubic structure transforms completely into the wurtzite-type hexagonal structure. Furthermore, the second phase transition of the as-synthesized sample has observed at 700 °C, where the cubic structure has transformed into mixed polycrystalline phases of hexagonal ZnO, cubic CdO, monoclinic CdSO$_3$, and orthorhombic ZnSO$_4$ structures. These new phases have also confirmed from the analysis of Raman and FTIR spectra. Analysis of UV–visible optical absorption spectra demonstrates that Increasing $T_a$ results in the decrease of optical band gap due the improvement in crystallinity accompanied by the increase in the particle size. The PL emission bands at an excitation energy of 3.818 eV exhibit redshift and a decrease in the intensity with increasing $T_a$ up to 500 °C. Meanwhile, further increase in $T_a$ up to 700 °C results in the enhancement of green emission intensity. On the other hand, PL emission spectra at 3.354 eV and $T_a$ 700 °C, reveal a dramatic increase in the emission intensity nearly by one-order of magnitude with respect to its value of the as-synthesized sample. This behaviour is ascribed to the incorporation of oxygen-related defects via thermal annealing in air, which act as additive radiative centers. Also, we have interpreted the observed spectral blue shift of PL emission spectrum with increasing excitation energy.

1. Introduction

Semiconductor quantum dots (QDs) have attracted great attention due to their novel and unique size-dependent physical, chemical and biomedical properties. It is found that a ternary alloy of Zn$_x$Cd$_{1-x}$S nanocrystals have a specific advantage since their properties can be tuned either by the variation of size or composition by changing Zn to Cd molar ratios [1–13]. They have been regarded as promising candidates for many applications such as photocatalytic hydrogen production [14], biological markers [15, 16], photovoltaic devices [17], field emitting devices [9], chemical sensors [18] and nonlinear optical devices [19].

Phase transformation of II-VI semiconductor bulk compounds from the cubic to the hexagonal structure takes place at transition temperature higher than that of the corresponding nanostructures, for example, the transition temperature of bulk ZnS at about 1023 °C [20]; meanwhile, phase transition in ZnS NPs takes place at lower temperatures 225 °C [21] and 400 °C [22]. In addition, the phase transformation from the cubic to the hexagonal structure in nanomaterials depends mainly on the crystallite size ($D$) and is different from that of the bulk crystals [23], where activation energy of phase transformation in bulk material is higher than that of the nanoparticles [22, 24]. In addition, structural defects in nanocrystals can be annealed out more easily at annealing temperature ($T_a$) lower than that in bulk [24, 25]. Huang et al. [21] suggested a model for the phase transformation, assuming that nucleation occurs at the surface and growth involves the collective movement of atoms at the cubic-hexagonal interface. It is well known that the optical absorption properties and PL emission behaviour of QDs