Excitation wavelength dependent photoluminescence emission behavior, UV induced photoluminescence enhancement and optical gap tuning of Zn$_{0.45}$Cd$_{0.55}$S nanoparticles for optoelectronic applications

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Abstract

In the present study, we investigate the excitation wavelength ($\lambda_{\text{ex}}$) dependent photoluminescence (PL) behavior in Zn$_{0.45}$Cd$_{0.55}$S nanoparticles. The deconvoluted PL emission bands for nanopowders and nanocolloids reveal noticeable spectral blue shift with decreasing $\lambda_{\text{ex}}$ accompanied by intensity enhancement. This unusual behavior is explained in terms of selective particle size distribution in nanostructures, advancing of fast ionization process at short $\lambda_{\text{ex}}$; and solvation process in polar solvent. In addition, we attributed the UV-induced PL intensity enhancement and blue shift of the optical gap to the reduction in particle size by photo-corrosion process associated with the improvement in the quantum size effect; surface modification due to cross-linkage improvement of capping molecules at NPs surface; the creation of new radiative centers and the formation of photo-passivation layers from ZnSO$_4$ and CdSO$_4$ and photo-enhanced oxygen adsorption on Zn$_{0.45}$Cd$_{0.55}$S nanoparticles surface.

1. Introduction

Zn$_x$Cd$_{1-x}$S nanoparticles (NPs) alloys have exhibited novel size-dependent properties (i.e. physical, chemical and biological). It is found that properties of these ternary alloys NPs could be controlled either by variation of its particle size or changing composition (i.e. Zn to Cd molar ratios) [1–13]. These semiconductor compounds 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 and optical sensors [18], and nonlinear optical devices [19].

It is well known that the optical absorption properties and photoluminescence (PL) behavior of QDs are strongly dependent on surrounding medium and surface conditions [20,21]. Becker et al. [22] have investigated UV irradiation effect on PL of II-VI semiconductor nanostructures and attributed the observed enhancement of PL quantum yield in ZnS NPs to the blocking of nonradiative surface states via oxygen adsorption process on the surface of nanoparticles (NPs). Photoinduced enhanced PL emission in Zn$_x$Cd$_{1-x}$S NPs colloids can be attributed to surface state passivation by photo-adsorbed oxygen and H$_2$O molecules [10–12]; rearrangement of NPs surface by photopolymerization accompanied by cross-linkage improvement of polymeric chain of EDTA capping agent on NPs surface [11,15]; reduction in nanocrystallites size due to photo-oxidation and photo-corrosion; as well as the formation of ZnSO$_4$ and CdSO$_4$ passivation layers leading to improvement in surface properties. Henglein [23] and Bol et al. [24] suggested that photolysis is the most prominent reason for the enhancement of luminescence quantum efficiency, while Dunstan et al. [25] proposed that the creation of new radiative recombination centers by photoinduced effects leads to enhancement in the PL quantum yield of ZnS NPs. Bhargava et al. [26,27] assumed that PL quantum efficiency enhancement is ascribed to improvement in the quantum size effect due to size reduction by UV irradiation of ZnS NPs and/or the decrease of nonradiative recombination centers by photopolymerization of the passivation molecules at the NPs surface. Later et al. [28], proposed a model in which the efficiency of energy transfer from the host lattice of ZnS to the doped impurities increases with increasing UV exposure time, moreover, Isobe et al. [29], assumed that the energy transfer from the polymer to the NPs is responsible for the increase of PL quantum efficiency. On the