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Influence of surfactant structures in luminescence enhancement dynamics during nucleation and growth of aqueous ZnS nanoparticles and their photoactivation due to illumination with UV/visible light

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ABSTRACT

Nanostructured semiconductor architectures have attractive optical properties mainly including bright photoluminescence (PL) resulting from the radiative recombination of charge carriers on surface states. Various approaches have been employed for the modification of surface states of these nanostructures to design new nanomaterials with enhanced PL primarily in aqueous medium to enable their applications in biological samples. Here, we report the varying efficiencies of three commercial surfactants viz. cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC) and cetylpyridinium chloride (CPyC) on the dynamics of PL emission enhancement during initial growth and Ostwald ripening of ZnS nanoparticles (NPs). The counterion has been estimated to behave differently to govern the PL enhancement. The exceptionally high tendency of CPyC in PL enhancement has been assigned to participation of π-electrons of pyridinium ring. The impact of UV-light in photoactivation of surfactant stabilized ZnS NPs has been utilized in exploring significance of surfactants in improving the surface emitting states in water soluble semiconductor NPs.

1. Introduction

Fluorescent semiconductor nanocrystals are materials possessing characteristic spectral emission, which is tunable to a desired energy by the selection of particle size, size distribution and surface passivating agents. Zinc sulfide (ZnS) is a versatile technologically important semiconductor material and fundamental milestone for many photonic and optoelectronic applications of quantum-confined species, e.g. photodetectors, light emitting diodes, lasers and biological levels [1–3]. With recent advances in colloidal chemistry, efforts have been made to synthesize high quality semiconductor nanoparticles (NPs) in the liquid phase either by aqueous or non-aqueous route. Unfortunately, because of nonradiative recombination of charge carriers at the surface sites that compete with band edge emission, a low photoluminescence (PL) is often observed in as prepared NPs. One of the critical aspects about the formation of these materials is to control the electronic states, i.e. the exciton or the surface states, to increase the PL properties. Strategies should therefore be aimed to reduce nonradiative recombination either by confining the exciton pairs to the interior of the crystal or by removing the surface traps. This can be achieved by various methods like passivation with long chain organic surfactants, doping with metal ions and growing an inorganic shell of material with a larger band gap [4]. Surface modification is also necessary to obtain water soluble materials, which are most often used in biological applications. However, due to complexity of photochemistry in inorganic semiconductor nanocrystals, the exact mechanism about origin and variation in PL emission properties is still unclear. For NPs possessing large surface to volume ratios, PL properties are generally related to surface structure. Of all the properties that characterize PL, intensity of the PL signal has received the maximum attention in the analysis of interfaces because it depends on the rate of radiative and nonradiative events, which in turn depends on the density of nonradiative interface states [5]. Dynamic growth processes play an important role in defining the surface structure of NPs and hence the PL properties. Interpretation of PL evolution behavior during nucleation and growth of NPs is therefore essential in order to elucidate the role of surface state and surface passivation in PL improvement and photostability. Though numerous reports [6–9] exist in pertinent literature regarding PL enhancement of ZnS colloids either by doping or generating ZnS shell on core of some other material; limited studies explain PL in relation to surface passivation in aqueous as well as non-aqueous media. Many of these studies used different types of passivating agents under very different surrounding environments, leading to poorly understood surface chemistry. Han et al. [10] demonstrated that amount and nature of surfactant not only control the size but also the luminescent properties of

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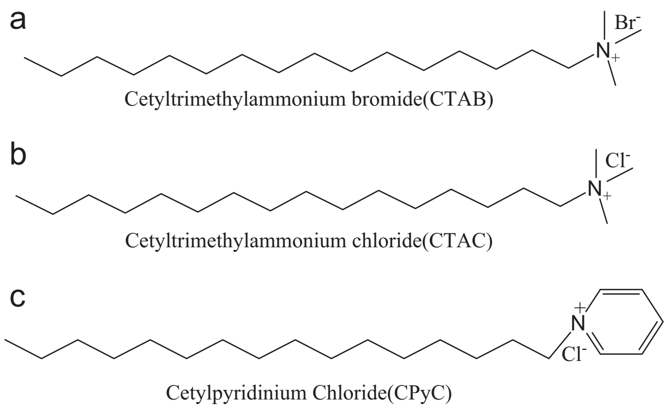

Fig. 1. Molecular structure of (a) CTAB, (b) CTAC and (c) CPyC.

Mn^{2+} doped ZnS NPs. Tang et al. [11] investigated the energetic positions of the surface states and shallow and deep traps in ZnS NPs prepared in reverse micelle of AOT. Chatterjee et al. [12] have compared the varying PL and optical properties of growing ZnS NPs in the presence of cysteine and mercaptoethanol. The results reveal that PL due to sulfur vacancy defects has not been witnessed in mercaptoethanol-capped ZnS NPs because of effective passivation. Another important route for PL enhancement has been through light irradiation of semiconductor NPs, called photoactivation or photobrightening. Cordero et al. [13] were the first to show the effect of light irradiation in TOP/TOPO-CdSe NPs. After that Cruz et al. [14] have investigated the effects of UV-irradiation on surface-passivated and unpassivated ZnS:Mn and assigned the increase in PL intensity to a corresponding increase in radiative transition probability. Cao and Huang [8] reported that the irradiation-induced luminescence enhancement effect was not persistent for Mn^{2+}-doped ZnS NPs prepared in AOT micelles and the irradiation resulted in decrease in size of the NPs. However, the relationship between originating PL emitting states and synthesis environments, specifically including aqueous surfactant solution, during nucleation and growth has not been clarified to date. Moreover, since PL properties of semiconductor NPs are very sensitive to surface structure, which is mainly determined by the synthesis methods, the mechanisms of PL enhancements may not be necessarily identical for different methods.

With this aspect in view, some interesting behavior pertaining to PL enhancement mechanisms during nucleation and growth of ZnS NPs in aqueous environment due to interaction of surfactants having different structures, which are utilized as passivating and stabilizing agents, has been presented in the present work. In addition, PL enhancement due to photoactivation with UV-light and the comparative aspects of surfactant induced tendencies of NPs to retain the enhanced PL for longer time have been presented in relation to the surfactant structure. The molecular structures of three surfactants used for the stabilization of ZnS NPs having the same hydrophobic chain length (C_{16}) but with different head groups and counterions are shown in Fig. 1.

2. Experimental details

2.1. Chemicals used

Zinc acetate ($Zn(OAc)_2$, 99%) and sodium sulfide ($Na_2S \cdot xH_2O$, 58% assay) were purchased from CDH, India. CPyC (99%) was supplied by Himedia Laboratories, India. CTAB (99%) and CTAC (25% in water) were from Sigma Aldrich and Fluka, respectively. All the chemicals were used as received without further purification. Water used in the preparation of solutions was double distilled.

2.2. Synthesis of surfactant stabilized ZnS NPs

ZnS NPs were synthesized keeping $Zn(OAc)_2$:Na_2S molar ratio as 1:2 at room temperature in aqueous solution of three cationic surfactants using our earlier reported chemical precipitation method [15]. Typically, certain volume of aqueous Na_2S solution was added to 10 ml of aqueous surfactant solution (3 mM), so as to make the final concentration of 1.4 mM. The solution was kept at room temperature for half an hour for equilibration and then aqueous zinc acetate solution was added with gentle shaking to obtain the final Zn^{2+} concentration of 0.7 mM. The appearance of very light turbidity indicates formation of ZnS NPs.

3. Characterizations

The ZnS NPs were characterized using Hitachi (H-7500) transmission electron microscope (TEM) operating at 90 kV. Samples for TEM studies were prepared by placing a drop of ZnS NPs dispersed in aqueous surfactant solution on a carbon coated Cu grid and the solvent was evaporated at room temperature.

UV–vis absorption and PL emission spectra were recorded with a Jasco-530V spectrophotometer and Perkin Elmer LS55 luminescence spectrometer, respectively, using quartz cuvette of 1 cm path length. The PL excitation wavelength was 320 nm. During measurements, first PL spectra were recorded for the aqueous surfactant solutions and then these spectra were used for background correction during the PL emission measurements of respective surfactant stabilized ZnS NPs, so as to obtain the PL emission of NPs without any interference from surfactant itself. For time evolution absorption and PL emission studies, the ZnS NPs were produced by adding required volume of aqueous zinc acetate solution into aqueous surfactant solution containing sodium sulfide with gentle shaking. The resultant solution was then immediately transferred into quartz cuvette and placed in the spectrophotometer. Ten spectra were recorded in automatic mode at a time interval of 2 min without disturbing the sample to avoid any experimental error. The mixing time was about 40–45 s before starting the spectral measurements. UV-irradiation of colloidal solutions was carried out in sealed 10.0 mm glass flasks using a UV-cabinet from Popular India Limited fitted with a mercury lamp as UV-light source (254 nm).

4. Results and discussion

In our earlier work [15,16] on synthesis and stabilization of ZnS NPs in aqueous medium, we have established the reliability of cationic surfactants to control the size of the NPs. The surfactants have been shown to stabilize the NPs by adsorption through head group (or micellar adsorption) leading to formation of nearly surfactant bilayer over NPs surface. In order to explore the additional role of these surfactants in modification of surface electronic states, in the present report, the evolution of PL emission during nucleation and growth of ZnS NPs in relation to surfactant structure has been investigated.

Before monitoring the detailed PL emission behavior, the shape and size of ZnS NPs in three surfactants have been characterized. Fig. 2 displays TEM images of aqueous ZnS NPs (0.7 mM) stabilized in CTAB, CTAC and CPyC (3 mM each). Well dispersed NPs having nearly spherical morphology with a diameter of approximately 6–7 nm are evident in all three surfactants.