Synthesis and characterization of PbS nanoparticles in ethanolic solution stabilized by hydroxypropyl cellulose

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Systems containing semiconducting nanoparticles have attracted considerable attention in recent years [1–22] and are particularly interesting for opto-electronic applications [4, 9–11]. Due to their narrow gap energy of 0.41 eV at 300 K, light electron and hole masses and large Bohr radii of 9 nm, PbS nanoparticles exhibit stronger quantum size effect and larger third-order non-linear susceptibility than other semiconductors [9, 13, 16, 19–31]. Recently, PbS nanoparticles have been synthesized in liquid media, coatings, glasses and xerogels [16, 17, 20–28, 32]. Until now, stabilized PbS colloids with fine structured absorption spectra have been obtained in aqueous and methanolic solutions and films in the presence of poly(vinyl alcohol) (PVA) and in xerogels with [N(2-aminoethyl)3-aminopropyl)]-triethoxysilane [21–27, 32–34]. Other polymers such as ethylene-15% methacrylic-acid copolymer (E-MAA) [17], sodium polyphosphate [23] and poly(ethylene glycol) (PEG) [23] could stabilize PbS nanoparticles only for a short time or with less structured absorption due to the broad size distribution. It has been believed that the synthesis conditions for PbS nanoparticles exhibiting fine-structured absorption are critical and that they can only be obtained in aqueous or methanolic media of $Pb(ClO_4)_2$ or $Pb(CH_3COO)_2$ in the presence of PVA [27]. Any variation from the above critical conditions such as replacing the solvent with ethanol or using another stabilizer will lead to colloids without fine structures [27]. Until now, there has been no report about the stabilization of PbS colloids having fine-structured absorption in ethanol using other stabilizers such as hydroxypropyl cellulose (HPC). In the literature, HPC has been used as a viscosity-increasing agent for sol–gel processing [35] and as a steric stabilizer for TiO_2 and ZrO_2 gel powders [36] and ZnS nanoparticles [37]. In this letter, the stabilization of PbS nanoparticles in ethanolic solution using HPC is reported. The absorption spectra of the colloidal solutions and the time dependence of emission are investigated.
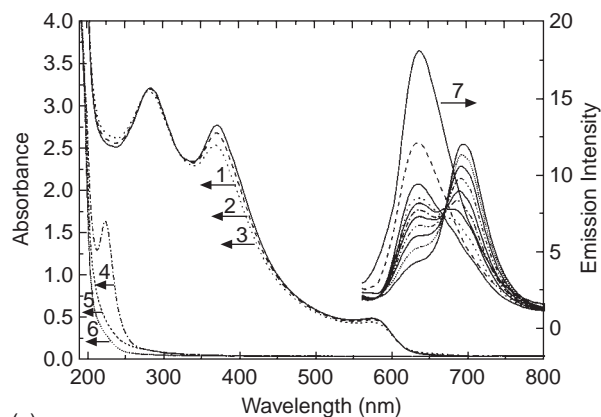
A 0.01 M Pb^{2+} ethanolic solution was prepared by diluting 0.3 ml $Pb(ClO_4)_2$ aqueous solution (50% in water, 1.7 M, Fluka) into 50 ml of ethanol. Fifty ml of 2.0 wt % HPC (molecular weight 100 000, Al-drich) ethanolic solution, 1.0 ml of 0.01 M Pb^{2+} solution and 49 ml of pure ethanol were mixed by vigorously stirring at room temperature in an ambient atmosphere. After stirring for 10 min, 1 ml of H_2S gas was injected into the above mixtures with a syringe leading to a wine-red PbS colloidal solution. Thin films were dip-coated on fused silica glass from the above solution. They were dried at room temperature in an ambient atmosphere before characterization.

Absorption spectra were taken at room temperature using a Hitachi U3000 spectrophotometer with a 10 mm fused silica cuvette. Emission spectra were recorded by means of a Hitachi F-3010 fluorescence spectrophotometer excited at 460 nm by a 150 W Xe lamp. X-ray diffraction (XRD) measurements were carried out in a Siemens D500 diffractometer by CuK_α radiation using θ-2θ powder scanning method from $2\theta = 20°$ to $60°$ with a step of $0.01°$. XRD samples were prepared by evaporating ethanol from the PbS solution under a pressure below 1×10^4 Pa at 50 °C. High-resolution transmission electron microscope (HRTEM) investigations were performed by means of a Philips CM 200 field emission gun (FEG) transmission electron microscope with a Schottky-type FEG generating the beam of energy up to 200 keV. Samples were prepared by dipping a copper grid coated with carbon film in the as-prepared PbS ethanolic colloids.

Optical spectra of the PbS colloids exhibit three absorption peaks at 573 nm (2.16 eV), 372 nm (3.34 eV) and 282 nm (4.40 eV) with an absorption on-set at 625 nm (1.98 eV) due to the strong quantum confinement effect (Fig. 1a). The tremendous increase of absorption from spectrum 4 to structured spectra 1–3 is caused by PbS nanoparticle formation. These fine-structured peaks are similar to those of PbS colloids stabilized by PVA in an aqueous and methanolic solution, suggesting the characteristic optical property of narrow-sized PbS nanoparticles [23]. However, the peak heights and positions are different from other systems, indicating a different size and size distribution, according to Gallardo [23]. The peaks are attributed to the electronic transitions between the split energy levels of PbS nanoparticles: $1s_h \rightarrow 1s_e$, $1p_h \rightarrow 1p_e$ [19] and $1d_h \rightarrow 1d_e$ [18], respectively (Fig. 1b). Here, electron transitions allowed by the selection rules, i.e., $\Delta l = 0$, $\Delta m = 0$ and $\Delta n \neq 0$, are presented (in the absence of Coulomb interaction). If the Coulomb

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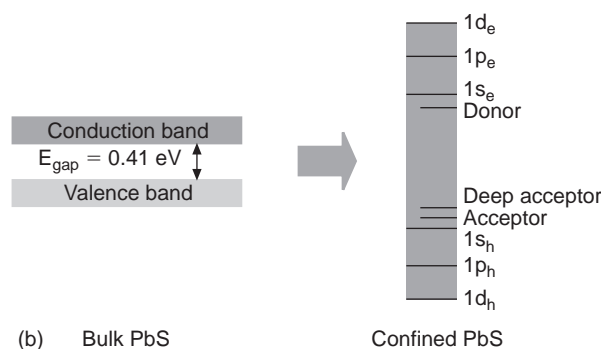
Figure 1 (a) Absorption (1 3) and emission (7) spectra of 1×10^{-4} M PbS colloids stabilized by 1.0 wt% HPC at different times after preparation. Absorption spectra: (1): 10 min; (2): 60 min; (3): 120 min. Reference: (4): 1×10^{-4} M Pb^{2+} ethanolic solution with 1.0 wt% HPC (without S^{2-}), the peak at 223 nm is the Pb^{2+} peak; (5): 1.0 wt% HPC ethanolic solution; (6): pure ethanol. Emission spectra (7) (from top to bottom at left side): 1 min; 10 min; 30 min; 50 min; 60 min; 70 min; 80 min; 90 min; 100 min; 110 min; 120 min. (b) Schematic representation of the energy diagram for the strong quantum-confined PbS colloids.

interaction is considered, the selection rules are no longer strictly obeyed when the first electron-hole pair has already been excited and $\Delta l \neq 0$ is weakly allowed [38]. The three peaks remain at the same positions, and the peak intensities slightly decrease during aging for 2 h at room temperature. It is assumed that this is due to a slight particle growth or agglomeration and a slight size distribution broadening during aging. The PbS colloids are stable for 16 h with a fine-structured absorption spectrum at room temperature. They can be stabilized with a fine-structured absorption for up to 60 days by keeping at −15 °C. The PbS concentration could be increased up to 5×10^{4} M without any precipitation keeping 1.0 wt% of HPC. This high-concentration PbS solution has a deep wine-red color and still exhibits the fine-structured absorption spectrum.

Moreover, the emission spectra demonstrate a time-dependent fluorescence behavior (Fig. 1a). Just after preparation, a strong emission peak is detected at 636 nm. Thereafter, this peak gradually becomes weak over 2 h. Meanwhile, another peak emerges at 691 nm 50 min after preparation, and then the peak intensity increases gradually over another hour. The peak at 636 nm (1.95 eV) may be attributed to the excitonic fluorescence or a shallow-trap involved transition. The long wavelength peak at 691 nm

(1.79 eV) is caused by a deep-trap-related transition. The co-existence of two emission peaks was also found in PbS aqueous and methanolic solution stabilized by PVA [23, 25], PbS acetonitrile solution stabilized by PEG [26], CdS(Se) nanoparticle−doped $K_2O−B_2O_3−SiO_2$ glasses [39] and CdS nitro-methane-containing solution [40]. However, no time-dependent emission behavior has been reported. It is assumed that during the aging process, different trap states are formed in the band gap possibly because of chemical reactions on the particle surface with the surrounding medium or with the dissolved oxygen.

The absorption spectrum of the as-dip-coated coatings also presents three peaks similar to the PbS colloidal solution (Fig. 2). However, these peaks become broader and weaker. That is to say, stabilized PbS nanoparticles still exist in coatings after dip-coating and drying. Due to their lability, PbS particles grow or agglomerate further, and the size distribution broadens slightly during film preparation, resulting in peak broadening.

The XRD patterns show broad crystalline peaks that match well with PbS (galena) JCPDS Card No. 5-592; the mean particle size (D) was calculated to be between 3.2 nm [calculated from (2 0 0) peak] and 3.6 nm [calculated from (2 2 0) peak] from the X-ray line broadening using Scherrer's equation [17].

An HRTEM structure image of PbS microcrystallites reveals the crystalline lattice of cubic PbS with $d = 0.21$ nm $[(h\,k\,l) = (2\,0\,0)]$ and 0.18 nm $[(h\,k\,l) = (3\,1\,1)]$, respectively (Fig. 3a). The average particle size was statistically estimated as 4.7 ± 0.6 nm from 80 individual particles (Fig. 3b). This value is larger than the calculated mean size from XRD possibly due to particle agglomeration and measurement or calculation errors from both methods.

In conclusion, PbS nanoparticles with an average particle size of 4.7 nm have been synthesized in ethanol using HPC as a new stabilizer, effectively extending their critical synthesis conditions. The PbS ethanolic solutions exhibit a fine-structured absorption spectrum due to the quantum confinement effect.
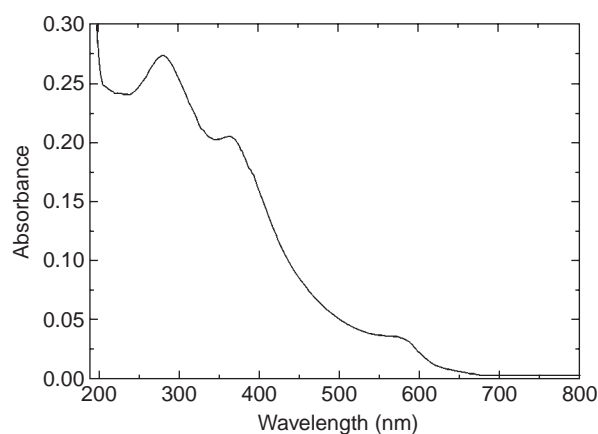

Figure 2 Absorption spectrum of a 200 nm thick as dip-coated coating containing PbS colloids in an HPC matrix on fused silica glasses.
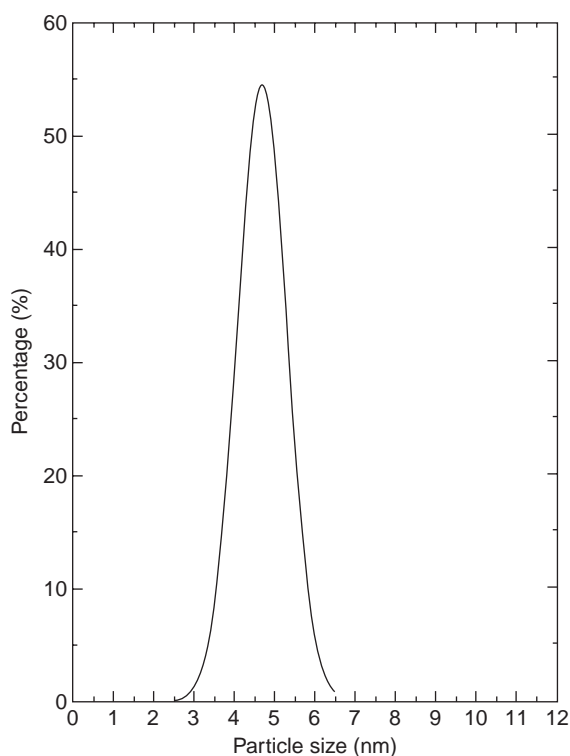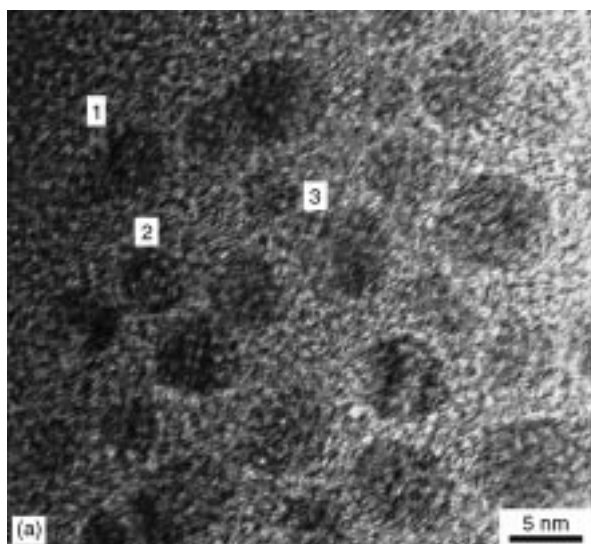
Figure 3 (a) Typical HRTEM image of HPC-stabilized PbS nanoparticles in ethanol. Particles 1, 2 and 3 clearly reveal the crystalline lattice of cubic PbS with d 0.21 nm (2 0 0) and 0.18 nm (3 1 1), respectively. (b) The Gaussian distribution of PbS particle size from 1×10^{-4} M PbS ethanolic solution stabilized by 1.0 wt % HPC, as statistically estimated from HRTEM images.

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