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Chemical synthesis and functional properties of multi-ligands passivated lead sulfide nanoparticles

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ABSTRACT

Lead sulfide (PbS) nanoparticles were synthesized using multi-capping ligands such as thioglycerol and polyvinyl alcohol. X-ray diffraction patterns showed the formation of cubic crystal structure of PbS. Optical studies revealed the formation of trap level free nanoparticles and very low full width half maximum of photoluminescence peak. Addition of polyvinyl alcohol led to strong quantum confinement with high photoluminescent intensity. Surface morphology of the PbS nanoparticles revealed the formation of spherical particles with the size of 15–20 nm. High resolution transmission microscopy analysis confirmed the high crystalline nature of the nanoparticles and core–shell like morphology of polyvinyl alcohol surrounded on thioglycerol-capped PbS nanoparticles. Fourier transform infrared spectra confirmed the presence of organic ligands on the PbS nanoparticles.

1. Introduction

In the recent years, the synthesis of size confined semiconductor nanostructures has received much attention due to their unique electrical and optical properties. Narrow size particles exhibited the size dependent optical properties [1–5]. Binary IV–VI semiconducting nanoparticles have been widely used in opto electronic applications. Among the IV–VI class of materials, Lead Sulfide (PbS) has attracted great attention owing to its potential applications in the fields, such as Infra-red detectors, mid infra-red lasers, solid state lasers and solar absorbers [6–10]. PbS is an important direct band gap material having large excitonic Bohr radius (18 nm) [11,12]. PbS exhibits the third-order nonlinear optical properties with 30 time larger than that of GaAs and 1000 times larger than that of CdSe nanoparticles. These novel properties make use of them in the photonic and optical switching device application. PbS nanoparticles can be synthesized in different methods, such as solvothermal method, microwave assisted heating, wet chemical route and micro emulsion technique, etc., [13–16]. Among these methods, wet chemical route is considered as a viable method for large scale production and inexpensive when compared to other methods. However, the factors such as agglomeration and Ostwald ripening led to the formation of larger size particles with irregular morphologies. Surface passivation by organic ligands on the nanoparticles is required to control the agglomeration and Ostwald ripening process. In our previous reports, we have synthesized the PbS nanoparticles using triethylamine (TEA) and N-methylaniline (NMA) as capping ligands [17,18]. TEA-capped PbS nanoparticles possessed the spherical particles with sizes of 10–15 nm and NMA-capped PbS nanoparticles had the spherical morphology with an average size of 5 nm. The obtained results indicated that the capping ligands had significant effect on the functional properties of PbS nanoparticles. Therefore, it is very important to investigate the other capping ligands on the functional properties of PbS nanoparticles. On the other hand it is proved that polymer is used as a matrix in assembling the nanoparticles. The optical properties of the semiconducting nanoparticles can be altered by surface chemical modification other than quantum size effects. [19–22]. In the present work, a facile approach is employed to synthesize the PbS nanoparticles capped with thioglycerol (TGL) and poly vinyl alcohol (PVA). The optical, structural, surface morphological properties of PbS nanoparticles are described. The possible growth mechanism of the multi-capping ligands on PbS nanoparticles is discussed.

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2. Experimental procedure

Lead acetate, thioacetamide, thioglycerol and PVA were analytical grade and used without further purification. 0.2 M of lead acetate and 0.2 M of thioacetamide were dissolved in 50 mL of deionized water under continuous magnetic stirring. After a few minutes, 0.1 M of thioglycerol was added drop wise to the solution. The color of the solution turned to black, indicating the formation of PbS nanoparticles. Similar reaction procedure was adopted for the TGL-capped PbS in PVA matrix. After addition of the thioglycerol, 0.001 M of PVA was added drop wise to the thioglycerol-capped PbS nanoparticles**.** The above processes were performed at room temperature. Both solutions were stirred continuously for 12 h. Finally, the products were dried at 90 °C in a hot air oven.

XRD patterns were recorded using X'per PRO (PANalytical) Diffractometer with a monochromatised CuKα (λ =1.5406 Å) radiation in 2θ ranging between 20°and 80° at the scanning rate of 0.017° per 20.67 sec's. Optical absorption measurement was performed using Varian Cary 5E UV–vis–NIR spectrophotometer in range of 200–800 nm. PL spectrum was obtained by using Fluorolog-3-11 spectrophotometer (Jobin Yvon) using a 254 nm excitation wavelength material. FTIR spectrum was recorded using Perkin Elmer spectrophotometer in the wavelength region 4000 cm^{-1}–450 cm^{-1}. TEM photographs were recorded using JEM 3010 (JEOL) working at 200 kV accelerating voltage.

3. Results and discussions

Fig. 1(a), (b) and (c) shows the XRD patterns of uncapped PbS, TGL-capped PbS and TGL-capped PbS in PVA matrix, respectively. All the peaks of the synthesized PbS nanoparticles could be indexed as PbS face centered cubic structure using standard JCDPS card: 79-1897. It was clearly seen that the broadening effect has taken place due to the addition of capping agent and polymer matrix. There was no significant change in the position of the peaks. It shows that the capping agent controlled the growth of nanoparticle and did not influence on phase change. The particle size of both the TGL-capped PbS nanoparticles and TGL-capped PbS nanoparticles in PVA matrix were calculated using Debye Scherer formula and the size of the particles was found to be 15 nm (TGL-capped PbS) and 5 nm (TGL-capped PbS in PVA matrix). No impurity level peaks were observed. Formation mechanism of TGL-capped PbS nanoparticles and TGL-capped PbS nanoparticles in polyvinyl alcohol was shown in Fig. 1(d). The formation mechanism was as follows: Reaction between the lead acetate and thioacetamide takes place and it leads to the

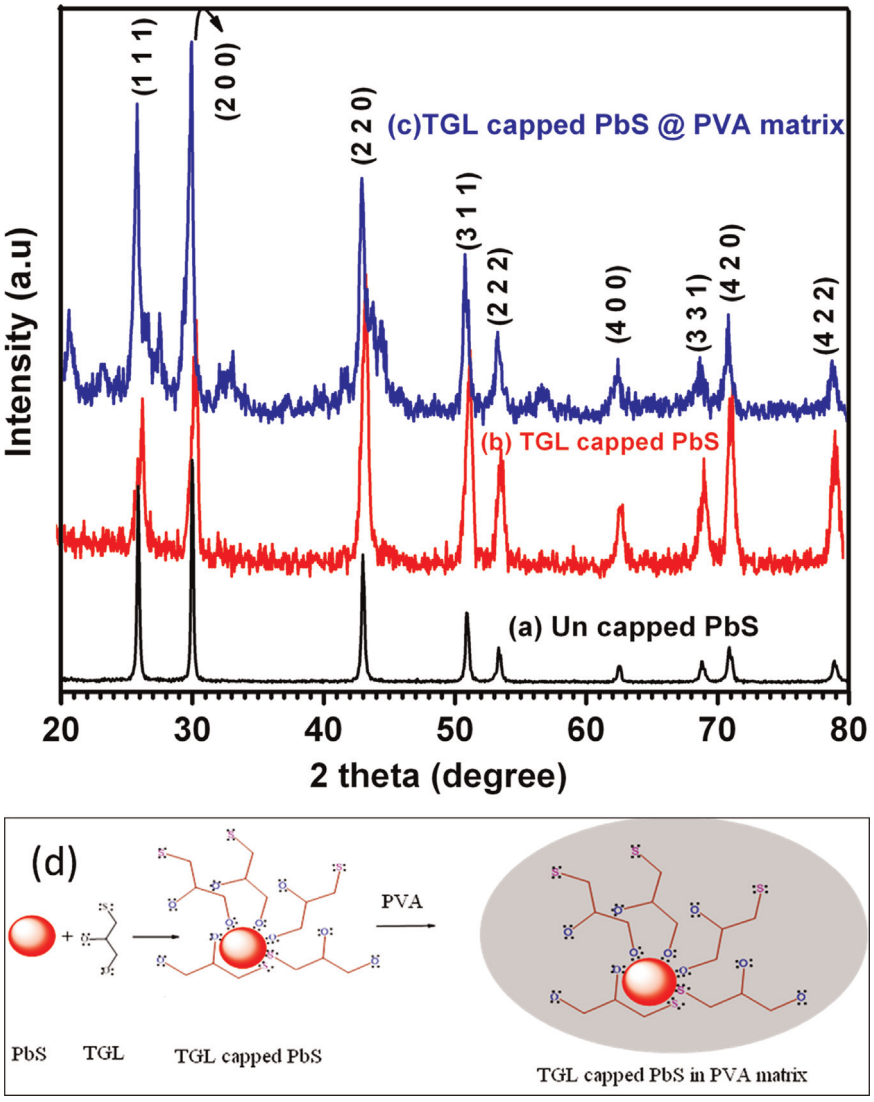

Fig. 1. XRD patterns of (a) uncapped, (b) TGL-capped PbS, (c) TGL-capped PbS nanoparticles in PVA matrix and (d) formation mechanism of PbS nanoparticles.