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Nanoscale multilayer PbS thin films fabricated by liquid–liquid interface reaction technique for solar photovoltaic applications

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Abstract

In the present communication, the self-assembly of nanocrystalline PbS at the liquid–liquid interface is reported. The PbS nanocrystals were, subsequently, transformed in the form of thin films by dip coating. The resultant films were characterized by SEM-EDAX, TEM-SAED, XPS and UV–visible spectroscopy. Pyramidal features at the nanometer scale and a sharp excitonic peak at 656 nm are the salient aspects of this work. The band gap of the order of 1.8 eV (associated with the excitonic feature) is ideally suited for solar photovoltaic applications.

Keywords: PbS; Nanostructures; Liquid–liquid interface; Nanopyramid

1. Introduction

Interest in nano-materials has fuelled up from the idea that they may boast superior electrical, chemical, mechanical or optical properties—at least in theory. Especially, nanocrystalline semiconducting materials possessing crystallite sizes comparable with Bohr radius exhibit quantum size effect (QSE), which leads to atom like discrete energy states within the nanocrystal that are, in turn, a function of the nanocrystal diameter. As many optical and electronic properties are dependent upon the energy and density of the electron states, engineering the size of the tiny structures can alter them. Many properties including onset of absorption (band gap), peak fluorescence wavelength, non-linear effects, electro- and magneto-optic effects can be tailored or enhanced. The absorption properties are of particular importance in photovoltaic applications. Semiconductor nanocrystals are potentially ideal for greatly enhancing the efficiency of solar cells, concomitantly, decreasing the cost of their fabrication. It is intriguing to think of photovoltaic (PV) devices based on nanocrystalline semiconducting films. Since nanocrystals can be engineered such that the band gap falls between 1.4 and 2 eV, they can be used to optimise single junction solar cells and therefore can offer a best chance of approaching the Shockley–Quessier efficiency limit of 31%. An encouraging breakthrough in realizing the maximum attainable thermodynamic conversion efficiency of solar photon conversion past the Shockley–Quessier limit, upto 66% can be achieved for nanocrystal based solar cells by utilizing hot photo-generated carriers to produce higher photo-voltages or higher photocurrents or by creating multiple junction cells [1].

In this context, we foresee Q-PbS as a big chill pertaining to its large Bohr radius (20 nm), high dielectric constant (17.3) and a narrow band gap of 0.41 eV, ensuring strong quantum confinement. Most importantly, the band gap in Q-PbS can be tuned to any desired value between 0.41 and 5 eV [2]. In particular, this excellent band gap engineering amenability can make Q-PbS a forerunner in solar photovoltaic conversion which demands absorption between 1.4 and 2 eV [3]. With this application in mind, we have noted that till date, numerous reports related to the synthesis of Q-PbS involving stabilization in strong organic/inorganic matrix supports [4–8], polymers [9,10] forming nanocomposite, etc., are available. Other approaches using inverse micelle [11,12] as protecting media or microemulsion [13] systems as nanoreactors, microbial synthesis [14], syntheses at air/water interface using amphiphilic monolayers [15,16] as stabilizers or epitaxial formation on fatty acid monolayers [17] (using Langmuir–Blodgett method) have received considerable attention. It is well established that the stability of the nanocrystallites, particle size and consequent properties of nanoparticles strongly depend on the specific method and the experimental conditions of preparation. This can be related to the inherent property of the nanoparticles, namely the spontaneous aggrega-

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tion by minimizing the surface energy. Because of the possibility of using liquid phase and relatively low processing temperatures, it is possible to create junctions on inexpensive substrates such as coated glass, metal sheets, etc., and dispense with the costly microfabrication techniques used to make contemporary solar cells. In the present study, we used the liquid–liquid interface reaction technique (LLIRT) [18] that allowed us to produce thin nanocrystalline particulate films of Q-PbS. The important feature of the method is that it is free from capping/stabilizing agents.

2. Experimental

2.1. Materials

The chemicals used in the present work were of analytical grade. Lead nitrate (99%, Aldrich), oleic acid (99%, Sigma), carbon tetrachloride (S.D. fine) were purchased. All the chemicals were used as received except carbon tetrachloride that was distilled and stored on molecular sieve type 4A. Deionised water was used for all experiments.

2.2. Method of preparation of film

In this method, 0.2 ml solution of carbon tetrachloride (CCl_4) saturated with H_2S was spread initially with the help of a syringe on a water surface containing 10^{-4} M $Pb(NO_3)_2$ in polypropylene tray (15 cm × 15 cm × 2 cm). The reaction occurs at the interface resulting in a nanocrystalline PbS thin film. After all the CCl_4 had evaporated, an oleic acid piston (pressure 30 dyn/cm) was used to compress the film slowly. The film was transferred onto a glass substrate (1 cm × 1 cm × 0.25 cm) by immersing vertically in the solution at a constant rate of 0.5 cm/min and lifting it vertically at the same rate so that the film covers the dipped area. This operation was repeated many times to get the desired film thickness.

2.3. Measurements

The Q-PbS samples prepared by the LLIRT were characterized by transmission electron microscopy (TEM) along with selected area electron diffraction (SAED) followed by energy dispersive analysis by X-rays (EDAX), X-ray photoelectron spectroscopy (XPS) and optical spectroscopy.

The optical absorbance measurements of the sample were conducted in the range 600–800 nm, with a resolution of 2 nm. All the measurements were done on single beam UV–vis diode array spectrophotometer (Hewlett-Packard 8452). Transmission electron micrographs and electron diffraction patterns of the virgin samples were obtained using JEOL, JEM-1200 EX electron microscope. For TEM examination, the film was deposited on a copper grid coated with collodion. The EDAX studies of the samples were carried out on JEOL (6360 LA) SEM instrument. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a VG Scientific (UK) ESCA-3-MK-II electron spectrometer with Mg Kα (1253.6 eV) radiation.

3. Results and discussions

The samples can be depicted as an assemblage of many freestanding nanopyramids by the transmission electron micrographs presented in Fig. 1 (black/grey contrasts in white background). Pyramids with a square base and a triangular top were clearly observed even in the low-magnification TEM image

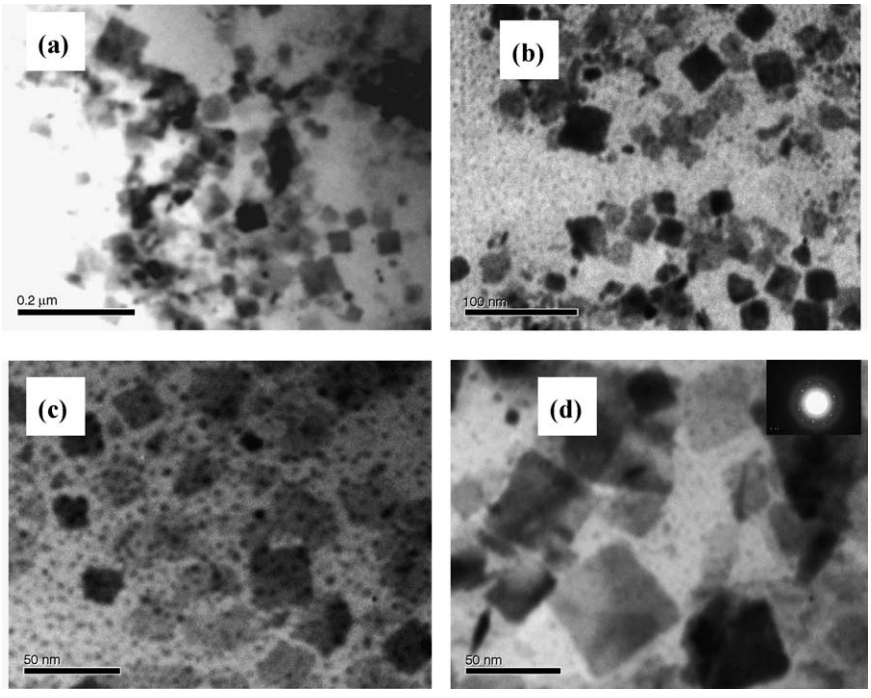

Fig. 1. Transmission electron micrographs (a–d) of PbS Thin film featuring nanopyramids.