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Facile synthesis of PbS nanorods induced by concentration difference

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ABSTRACT

This report describes a simple method to synthesize PbS nanorods by aqueous chemical method under ambient conditions without the surface-capping molecules or structure-directing templates. X-ray diffraction studies revealed that the prepared sample is a polycrystalline powder crystallized in face centered cubic (fcc) PbS structure with the crystallites orientated preferentially along the (200) direction. The SEM analysis shows the formation of PbS nanorods of width 80 nm and length 410 nm. The compositional analysis confirms the presence of Pb and S. The optical absorption study of PbS nanostructures shows the blue-shift with respect to those of the bulk counterpart due to quantum confinement effect. Electrical measurement reveals that the prepared PbS nanorods exhibits the semiconducting nature.
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1. Introduction

Lead sulfide (PbS) is an important π–π semiconductor material with a small bulk bandgap (0.41 eV at 300 K) and a large exciton Bohr radius of 20 nm. The band gap of PbS can be easily adjusted up to a few electron volts when the size of the particles is reduced. Such a significant widening of the band gap is associated with small effective masses of electrons and holes ($m_e = m_h = 0.09m_0$) as well as with a large exciton Bohr radius (20 nm) of PbS [1]. Nanomaterials of PbS have been discovered to have exceptional third-order nonlinear optical property with potential applications in optical devices such as optical switches [2]. A lot of effort has been focused on the synthesis of PbS nanostructures and recently complex PbS structures such as dendritic or flower-like structures have attracted much attention because of their interesting morphologies and potential applications [3–6]. Aqueous phase routes have been employed to obtain PbS microcrystals with a flower-shaped or clover-like structure [4,5]. Different dentritic PbS nanostructures can be synthesized through a surfactant-assisted hydrothermal process [3]. Although these methods could be used to prepare complex nanostructures, so far the synthesis of complex nanostructures is still in its infancy stage. Most of the complex structures were obtained through multi-step routes in which special precursors need to be prepared first or by using toxic surfactants or ligand as additives, which are harmful to the environment and people. Therefore, the development of conceptually simple, environmentally friendly, and general construction techniques for the massive fabrication of complex nanoscale structures is still a key issue in nanoscience and nanotechnology. To develop a general and simple method for controlled synthesis of different complex structures might not only benefit the application of such materials but also provide great opportunities to explore new structures. The present study investigates the properties of mechanically compacted pellets of nanosized PbS nanocrystals prepared by adding a highly concentrated solution of one reactant to a solution of another reactant with low concentration under ambient conditions without the surface-capping molecules or structure-directing templates. It was found that the large concentration difference of the reactants play key roles in controlling the diffusion process and the morphology of the resulting nanostructures. This method is facile and can be used to prepare a variety of inorganic materials.

2. Experimental

Three different routes were used to synthesize dendritic PbS nanocrystals. In the first route (Pb/S), lead acetate trihydrate (4 mmol) was added to 0.1 mmol/L thioacetamide solution in a beaker. After stirring for 50 min, the reaction system was left undisturbed for 17 h at room temperature. The black precipitate obtained was washed with distilled water several times to remove the excess reactants and byproducts, and then dried in air. For the second route (S/Pb), the synthesis procedure was identical to that for the first route except that the concentration of the two reactants was changed i.e., lead acetate trihydrate (0.4 mmol) powder was added to 2 mmol/L thioacetamide solution. In the third route

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(PbS), lead acetate solution with concentration of 1 mmol was added to equimolar thioacetamide solution. The volume of the solution for all three routes is 80 ml.

The prepared powder was characterized by X-ray diffraction (Bruker AXS D8 Advance diffractometer), using the Cu Kα radiation. Morphology and composition of the PbS powder were analyzed by a scanning electron microscope (JEOL Model JSM-6390LV) attached with the EDS analyzer. The UV–Vis absorption spectra were recorded using JASCO-UV/VIS/NIR double beam spectrophotometer. For electrical measurement, the synthesized powder was made in the form of pellet. The dimensions of the pellet are 1.01 cm diameter and 0.55 cm thickness. *I–V* characteristics were measured using Keithley instrument (Model 2612) in the temperature range 298–423 K. Electrical resistivity measurements in the temperature range 298–448 K were carried out using Four Probe method. The arrangement consists of PID controlled oven (model PID-200, Scientific Equipment and Services, Roorkee, India) in combination with constant current source (model LCS – 01) and digital micro voltmeter (Model DMV – 001).

3. Results and discussion

3.1. Structural analysis

The XRD pattern of PbS dendritic nanocrystals is shown in Fig. 1. It displays the overall phase composition and purity of the product. It shows strong and sharp diffraction peaks corresponding to face-centered cubic rock-salt structured PbS with the crystallites orientated preferentially along the (200) direction (JCPDS card no: 78-1901). By comparison with the data from JCPDS card no: 78-1901, its main diffraction peaks at 25.994°, 30.103°, 43.083°, 51.009°, 53.447°, 62.566°, 68.898°, 70.975°, 78.941° are corresponds to (111), (200), (220), (311), (222), (400), (331), (420), and (422) plane of cubic crystal lead sulfide. The strong, narrow and sharp diffraction peaks of Pb/S, S/Pb and PbS routes indicate that the particles are highly crystalline. The observed 2θ, *d*-spacing and standard (JCPDS:78-1901) values of PbS nanocrystals prepared by Pb/S route are given in Table 1. In the present investigation, the sample exhibits a preferential orientation along the (200) diffraction plane. To describe this orientation, we calculated the texture coefficient (TC) for all the planes using the expression

$$\mathrm{TC}(h\,k\,l) = \frac{I(h\,k\,l)/I_0(h\,k\,l)}{1/N[\sum I(h\,k\,l)/I_0(h\,k\,l)]}$$

where *N* is the number of diffraction peaks, where $I(hkl)$ is the measured relative intensity of a plane (hkl) and $I_0(hkl)$ is the standard intensity of the plane (hkl) taken from the JCPDS data. The value $TC(hkl) = 1$ represents powders with randomly oriented crystallites, while higher values indicate the abundance of crystallites oriented in a given (hkl) direction. The variation of *TC* for the peaks of the prepared PbS nanocrystals is presented in Table 1. It can be seen that the highest *TC* was in the (200) plane for PbS nanocrystals.

The average crystallite size was determined by measuring the full-width at half-maximum of the peaks using the Scherrer formula and the values are presented in Table 1. In order to address the uncertainty in Debye–Scherrer relation the mean crystallite sizes was estimated using Williamson–Hall (W–H) plot. Generally the diffraction peak broadening is expressed as $\beta_{h\,k\,l} = \beta_{ins} + \beta_{size} + \beta_{strain}$, where the individual full width at half maximum (FWHM) contributions are due to the instrumental broadening (β_{ins}), crystallite size (β_{size}) and the lattice strain present (β_{strain}) in the material respectively. Crystallite size can also be determined from the Williamson–Hall equation [7]:

$$\beta_{h\,k\,l}\cos\theta = \frac{K\lambda}{D} + 4\varepsilon\sin\theta$$

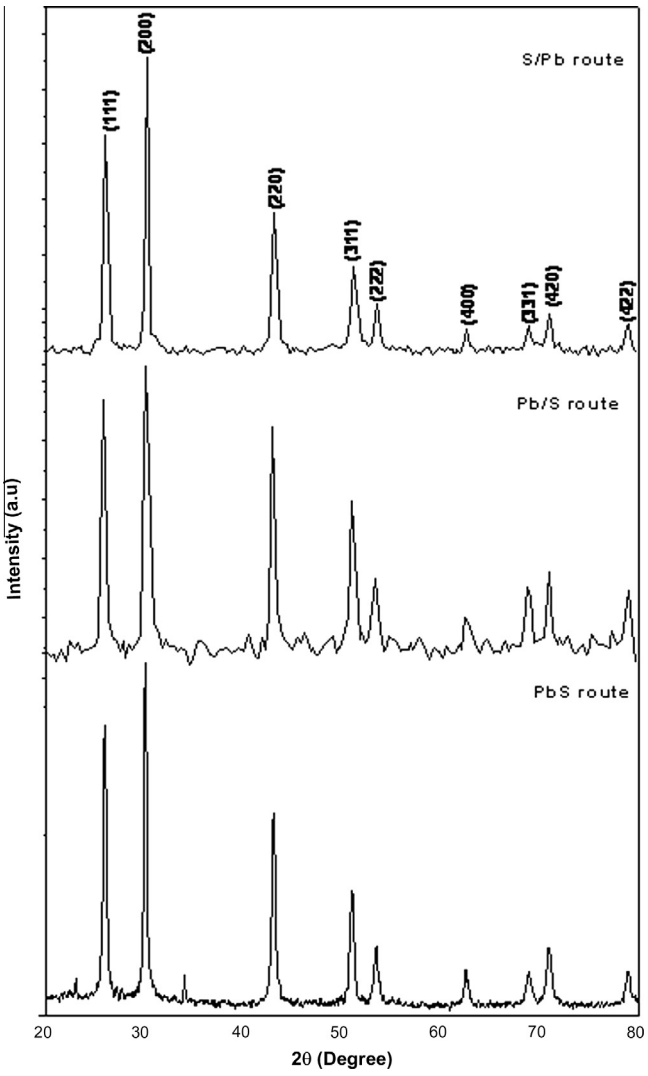

Fig. 1. XRD spectrum of PbS nanocrystals.

Table 1
Structural parameters of PbS nanocrystals prepared by PbS route.

2θ (°)		*d*-spacing (Å)		*h k l*	Lattice constant (Å)	Texture coefficient
Standard	Observed	Standard	Observed			
25.998	25.994	3.424	3.425	111	5.932	1.188
30.108	30.103	2.965	2.966	200	5.932	1.313
43.100	43.083	2.097	2.097	220	5.931	1.090
51.026	51.009	1.788	1.788	311	5.930	1.007
53.476	53.447	1.712	1.712	222	5.930	0.885
62.593	62.566	1.482	1.483	400	5.932	1.067
68.954	68.898	1.360	1.361	331	5.932	0.777
71.011	70.975	1.326	1.326	420	5.930	0.929
79.020	78.941	1.210	1.211	422	5.932	0.739

where $\beta_{h\,k\,l} = [(\beta_{sample})^2 - (\beta_{ins})^2]^{1/2}$. Here β_{sample} is the measured broadening of the peak which after correction with the instrumental broadening (β_{ins}) yields the corrected FWHM $\beta_{h\,k\,l}$. β_{ins} can be measured using a silicon single crystal. In this equation ε is the micro strain, *K* a shape factor having a value close to unity, λ the X-ray wavelength and *D* the crystallite size. From the intercept of the linear $\beta_{h\,k\,l}\cos\theta$ versus $4\sin\theta$ plot (Fig. 2), the crystallite size is estimated and the value is given in Table 2.

The lattice constant '*a*' for the cubic phase structure is calculated from the relation

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