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Nonlinear optical properties of the PbS nanorods synthesized via surfactant-assisted hydrolysis

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Abstract

PbS nanorods were synthesized by surfactant-assisted homogenous hydrolysis. The products were characterized by UV–vis spectrophotometer, X-ray powder diffraction (XRD) and transmission electron microscope (TEM). PbS nanorods were measured by the *Z*-scan technique to investigate the third-order nonlinear optical (NLO) properties. The result of the NLO measurements shows that the PbS nanorods have the third-order nonlinear optical properties of both NLO absorption and NLO refraction with self-focusing effects. The nonlinear absorption coefficient and refractive index of the PbS nanorods are 2.16×10^{-9} m/W and 3.52×10^{-16} m^2/W respectively.

Keywords: Lead sulfide; Nanorods; Third-order nonlinear optical (NLO) properties

1. Introduction

Nanomaterials are very interesting because of their unique properties and their potential applications in many fields. The nonlinear optical properties of semiconductor nanocrystals have attracted much attention because of their large optical nonlinearity and short response time [1–4].

PbS is a direct band gap IV–VI semiconductor with a band gap of 0.41 eV and an exciton Bohr radius of 18 nm at room temperature. Much attention has been focused on PbS nanomaterials because they have exceptional third-order nonlinear optical properties and application for optical devices [5–8].

The properties of nanomaterials depend not only on their chemical composition, but also on their structure, shape, size and size distribution. The size, shape and surface characteristics have a strong influence on the optical properties of nanocrystals. Therefore, much attention has been paid in controlling these parameters to manipulate the optical properties of PbS nanocrystals. Many synthetic methods have been developed to synthesize nanocrystalline PbS particles with various sizes and shapes in a controllable manner [9–17]. It has been reported that the use of a surfactant or polymer is an effective method to obtain 1D PbS nanostructure [13,18–21].

Recently, nonlinear optical properties of 1D nanomaterials aroused more attention because of their unique geometrical and electronic structure [22–24]. In this letter, we reported a surfactant-assisted homogenous hydrolysis reaction route for preparing PbS nanorods in the presence of sodium dodecyl sulfate (SDS) as surfactant. The third nonlinear optical properties of PbS nanorods were investigated by the *Z*-scan technique with 8 ns pulses at 532 nm.

2. Experimental

All of the reactants were analytical-grade and were used directly without any further purification. The PbS nanorods were synthesized using the surfactant-assisted homogenous hydrolysis method. In a typical experiment, 0.38 g $PbAc_2\cdot3H_2O$ and 0.58 g sodium dodecyl sulfate (SDS) were put into a 60 ml jar with 40 ml distilled water. The solution was stirred at 40 °C for 30 min. Then, 0.19 g thioacetamide (TAA) was dissolved in 10 ml distilled water and put into the previously prepared solution under stirring. The resulting solution was kept stirring

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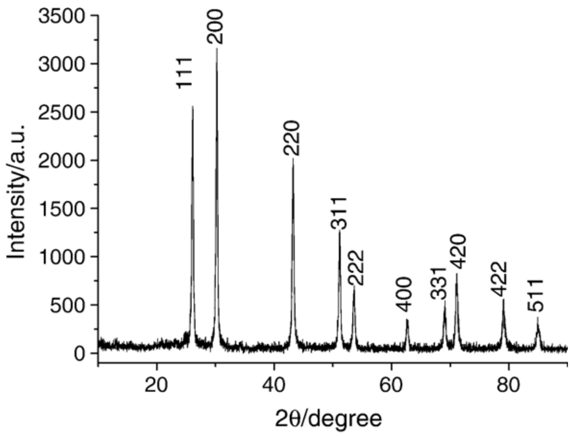

Fig. 1. XRD pattern of the as-prepared PbS nanorods.

at 40 °C for 3 h. The crystalline PbS nanorods were obtained by centrifugation. After that, the resulting black solid products were washed with distilled water and absolute ethanol for several times, respectively, to remove the by-products, and finally dried in a vacuum at 60 °C for 4 h.

These products were characterized by X-ray power diffraction (XRD) using a Rigaku D/Max-γ X-ray diffractometer with graphite monochromatized Cu Kα radiation (λ=1.54178 Å). TEM images were taken with a JEOL JEM-100SX transmission electron microscope, using an accelerating voltage of 100 kV.

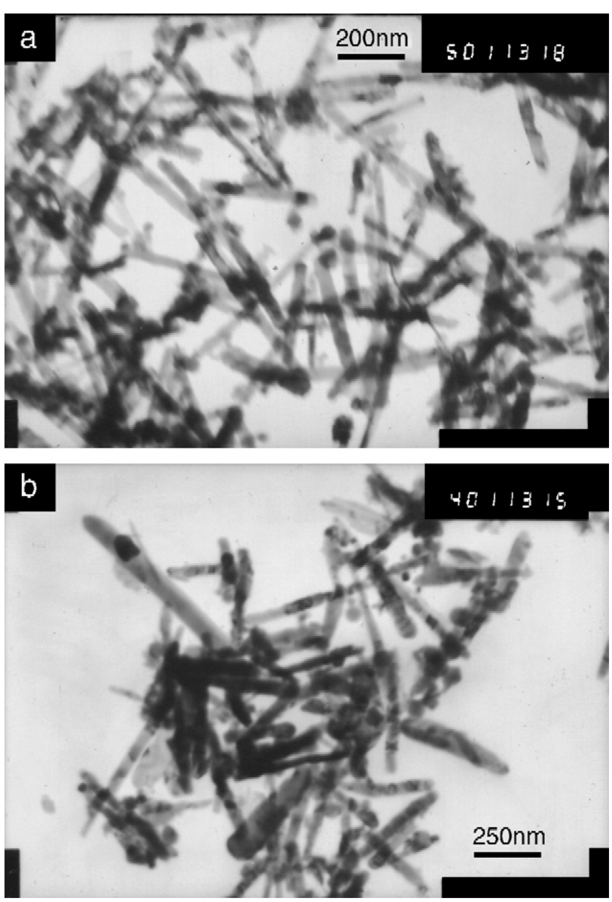

Fig. 2. TEM images of the as-prepared PbS products in different molar ratios of Pb^{2+}/SDS: (a) 1:1; (b) 1:2.

The nonlinear optical properties of the sample were measured by the Z-scan technique [25]. Nonlinear optical measurements with nonlinear absorption and nonlinear refraction of nanorods dispersed in DMF solutions are investigated with 532 nm laser pulses of linearly polarized 8 ns duration (I_0=2.73×10^{11} W m^{-2}) generated from a frequency-doubled, Q-switched Nd:YAG laser. The laser pulse was focused by a focusing lens with f=30 cm focal-length. The incident and transmitted pulse energies are simultaneously measured by using two energy detectors linked to an energy meter. DMF solutions of the samples of the PbS nanorods are placed in a 2 mm quartz cuvette for NLO measurements.

3. Results and discussion

The XRD pattern of the as-synthesized PbS products was shown in Fig. 1. All the diffraction peaks could be indexed to cubic PbS with the cell constant a=5.920 Å, which was very close to the value in the JCPDS card (card No. 5-592). No obvious characteristic reflection peaks from other impurities could be detected in the XRD pattern. The strong and sharp reflection peaks in the XRD pattern indicated that PbS products were well crystallized.

The morphologies of the products were characterized by transmission electron microscopy. Fig. 2a showed the typical TEM micrographs of PbS nanorods obtained under the typical experimental condition. As could be seen in Fig. 2a, the obtained nanocrystalline PbS products are rod-like with a diameter of 20–60 nm and a length of 200–600 nm.

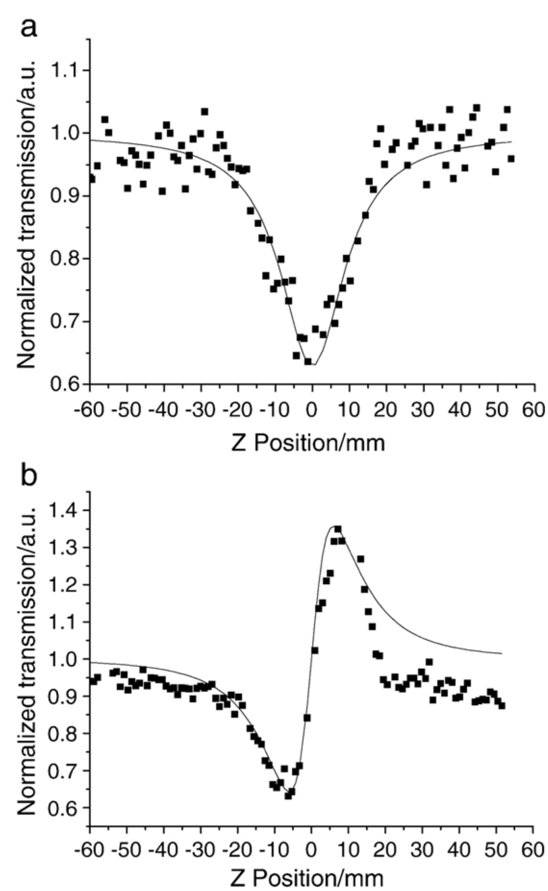

Fig. 3. (a) Z-scan data of open aperture and (b) Z-scan data of close aperture: (square dot) experimental data; (solid line) theoretical curve.

The formation of 1D PbS nanostructure is difficult because of its highly symmetric rock-salt structure. In order to control the morphology of the prepared PbS products, SDS was added into the solution as a surfactant. In order to investigate the influence of SDS on the formation of PbS nanorods in this reaction system, the following experiments were performed. The first experiment was carried out under the same synthetic conditions, but no surfactant SDS was added. The product was examined by TEM and only irregular particles were observed. Then we carried out the above-mentioned reactions in different amounts of SDS. TEM images of the as-synthesized products are given in Fig. 2. The results clearly reveal that the morphologies of the as-synthesized PbS products with different amounts of SDS are different. It is of irregular PbS nanoparticles obtained in the reaction system without SDS. When the molar ratio of Pb^{2+}/SDS is adjusted to 1:2, PbS nanorods were also the major parts in the obtained products (shown in Fig. 2b). However, the obtained PbS nanorods are less uniform in length and diameter. These results indicate that the presence of surfactant SDS plays an important role in the formation of nanorods. Moreover, the amount of surfactant SDS could affect the uniformity of PbS nanorods.

The formation process of PbS nanorods in the presence of SDS could be described as follows. When thioacetamide was added to the Pb^{2+} solution, it gradually released sulfide ions by hydrolysis. Then the released sulfide ions combined with lead ions to form PbS nanocrystals. The presence of surfactant could kinetically control the relative growth rates of different crystal planes by chemically or physically adsorbing on the surfaces of the growing nanoparticles [26]. When an appropriate amount of surfactant SDS was added into the reaction system, the SDS molecules may be selectively absorbed and bond to some PbS surfaces which lead to anisotropic growth. Therefore, the PbS nanorods will be formed in the presence of SDS.

The NLO properties of the PbS nanorods were investigated with 532 nm laser using the Z-scan technique. Typical results from the Z-scan experiments on the PbS nanorods are demonstrated in Fig. 3. The normalized transmission for the open aperture (Fig. 3(a)) is given by Eq. (1) [25], which is used to describe a third-order NLO absorptive process:

$$T(z, s=1) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}}, \text{ for } |q_0|<1 \tag{1}$$

where $q_0(z)=\alpha_2 I_0 L_{\mathrm{eff}}/(1+z^2/z_0^2)$, α_2 is the nonlinear absorption coefficient, I_0 is the intensity of the incident laser beam, $L_{\mathrm{eff}}=[1-\exp(-\alpha_0 L)]/\alpha_0$ is the effect thickness of the sample, α_0 is the linear absorption coefficient of the sample and L is the sample thickness, $z_0=\pi\omega_0^2/\lambda$ is the diffraction length of the beam, where ω_0 is the spot radius of the pulse at focus and λ is the wavelength of the laser pulse. Fig. 3(a) shows the typical NLO absorptive effect of the PbS nanorods, in which the square dots are the experimental data from the Z-scan measurements. It can be seen that the theoretical curve fits well with the experimental data. The value of α_2 is 2.16×10^{-9} m/W for the PbS nanorods.

The nonlinear refractive properties of nanorods, which are shown in Fig. 3(b), are assessed by dividing the normalized Z-scan data obtained under closed-aperture configuration by the normalized Z-scan data obtained under open-aperture configuration. In Fig. 3(b) the valley–peak pattern of the corrected transmittance curves shows the characteristic self-focusing behaviour of the propagating light in the samples. The difference between the normalized transmittance values at the valley and peak position, $\Delta T_{\mathrm{p-v}}$, is related to the effective third-order nonlinear refractive index n_2 (m^2/W) by Eq. (2) [25,27].

$$n_2 = \frac{\lambda\alpha_0}{0.406(1-S)^{0.25}\pi I_0(1-e^{-\alpha_0 L})} \cdot \Delta T_{\mathrm{p-v}} \tag{2}$$

The n_2 value calculated from Fig. 3(b) is 3.52×10^{-16} m^2/W for the PbS nanorods.

4. Conclusions

In brief, PbS nanorods have been synthesized by surfactant-assisted homogenous hydrolysis. SDS involved in the reaction procedure plays an important role in the formation of nanorods. NLO measurements show that the obtained PbS nanorods exhibit the third-order nonlinear optical properties of both NLO absorption and NLO refraction with self-focusing effects. These results show that the PbS nanorods with large nonlinear absorption coefficient and refractive index are promising materials for applications in optical devices.

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