Strong quantum confinement effects in polymer-based PbS nanostructures prepared by ion-exchange method

K. Suresh Babu, C. Vijayan, R. Devanathan

Abstract

Nanostructures of narrow band-gap semiconductors such as PbS provide a large scope for band-gap engineering as strong quantum confinement effects can alter the bulk band-gap value all the way from 0.41 to 2.3 eV, rendering the material transparent in most of the visible range of the electromagnetic spectrum. This paper discusses the preparation and characterization of polymer-based PbS nanostructures showing large characteristic blue shift in optical absorption. Enhancement in electrical resistivity is observed as a result of quantum confinement. This material is found to exhibit strong thermal lens effects, which is utilized to achieve optical limiting at low laser power levels.

1. Introduction

Semiconductor nanocrystals are known to exhibit unique size-dependent optical properties, which render them attractive from the viewpoint of integrated photonic devices. Quantum confinement effects are particularly important if the crystallite dimension is less than a critical size known as the exciton Bohr radius of the material [1,2]. Controlled variation of nanocrystallites size results in remarkable changes in properties from molecular to bulk. Also, by doping polymers or glasses with these small semiconductor clusters and utilizing their large resonant third-order optical nonlinearity, new composite photonic materials can be prepared. Efforts are on to develop novel types of nanomaterials with large scope for band-gap engineering in a form easily adaptable for device applications. Lead sulfide being a narrow band-gap material offers large tunability. Band gap of PbS can be varied in a wide range, up to 2.3 eV, from the bulk value of 0.41 eV, by changing the mean cluster size of the nanoclusters [3].

Semiconductor nanocrystals in a transparent matrix have attracted recent interest due to their potential in applications in nonlinear optics such as photonic switching [4]. Organic materials such as polymers [5,6] and inorganic materials such as glasses [7–10] have been used as host matrices for semiconductor nanostructures. There are several aspects of recent interest on polymer-based nanostructures such as their stability, dopant–host interactions, surface effects and nature of quantum confinement which continue to be open issues. It is essential to systematically address these issues not only for understanding the electronic processes, but also for their realizing their full potential applications.

Earlier work from our laboratory on polymer-based CdS nanoclusters in the regime of strong confinement had resulted in new findings on exciton confinement effects on optical absorption and fluorescence, photoacoustic response [11,12], acoustic and optical phonon confinement effects [13] and enhanced optical nonlinearity [14] in polymer-based CdS nanostructures. This paper presents some recent results on preparation and characterization of PbS quantum dots in Nafion polymer within the regime of strong quantum confinement. We also report on the observation of optical nonlinear properties and enhanced electrical resistivity in these quantum dots. To the best of our information, these are the first results on band-gap engineering of polymer-based PbS nanostructures prepared by an ion-exchange method.
2. Experimental details

The host matrix for the PbS quantum dots in the present work is Nafton, a cation-exchange polymer available commercially in the form of transparent sheets. These sheets have good mechanical strength, chemical inertness and temperature stability and are widely used in humidity sensors and proton exchange membrane in fuel cells. Nafton contains nanopores in its structure, which facilitate easy formation of nanoclusters. It consists of a fluorocarbon backbone and an interconnected ionic cluster [15,16].

Nafton 117 films of thickness 18 µm are cleaned in boiling nitric acid and then repeatedly washed with boiling water until the pH of the water bath becomes neutral. The dried films are immersed in a 0.1 M lead acetate trihydrate solution for varying amounts of time and ultrasonically agitated to clean the surface. Samples designated A, B and C are obtained after immersion times of 24, 12 and 1 h, respectively. After ammonia passivation, films are finally exposed to hydrogen sulfide gas and dried under vacuum. X-ray diffraction (XRD) is carried out using Shimadzu Horizontal Diffractometer using Cu-Kα radiation (λ = 1.5418 Å), in the step-scan mode with a step width of 0.02° (2θ) and 10-s counting time so as to improve the signal-to-noise ratio. Optical absorption spectra of the sample are recorded on a Hitachi U-3400 Spectrophotometer and conductance measured at room temperature using HP 4192A LF impedance analyzer. Z scan experiments are done using the conventional geometry [17] with a helium neon laser at 20 mW as the source. The optical limiting set up consisted of a converging lens to focus the beam to a spot size of about 20 µm. The sample is placed at the focal point so that the nonlinear absorption is maximum and defocusing occurs at a lower threshold. The light coming out is collected through an aperture and made to fall on a photodetector. As the intensity of light increases, defocusing occurs expanding the beam so that the amount of light passing through the aperture decreases, protecting the sensor.

3. Results and discussion

The XRD pattern for bulk PbS and representative samples A and B containing PbS quantum dots are shown in Fig. 1 along with that of Nafton. The diffraction peaks correspond to cubic rock salt structure of PbS (ICPDS file No. 5-592) with the lattice parameter of 5.92 Å. The mean nanocluster diameter of the sample A is found to be 15 nm (using Scherrer formula) [18]. For other samples (with presumably smaller cluster sizes), signal-to-noise ratios are rather poor in the XRD pattern in spite of slow scanning and no detailed size analysis could be attempted with these data.

Fig. 2 shows the optical absorption spectra of samples A, B and C. The maximum wavelength limit of the instrument used is 2600 nm and a bulk PbS sample would be opaque in this range. However, all the quantum dot samples show optical absorption cut-off much shifted from the bulk value of 3020 nm (corresponding to band gap of 0.41 eV) signifying quantum confinement. From the tight binding approximation model [1], the mean cluster diameter can be calculated and is found to be 13 nm for sample A, 8 nm for sample B and 3 nm for sample C. Accordingly, the samples show different colors ranging from light yellow to brownish red. The calculated sizes are also in the range of the rough estimates made from line broadening in XRD. A quantitative comparison, however, is not attempted in view of the poor signal-to-noise ratio in XRD.

Fig. 3 shows the variation of ac resistivity of the pure Nafton as well as Nafton incorporated with nanostructures. Samples A and B, with mean nanoparticle sizes 13 and 8 nm, respectively, show almost similar values of resistivity at high frequencies. However, sample C, with mean cluster size 3 nm shows an increase in resistivity compared to the other samples. An enhancement in the resistivity in the case of very small cluster sizes has been reported earlier in the case of CdS nanoclusters embedded in Nafton [19].

Electrical conduction in Nafton membrane is known to be by way of the Grothus mechanism of proton transport [20], brought about by the motion of hydrogen ions in the sulphonic groups assisted by water molecules in the pores of the polymer. The ion-exchange process during the formation of PbS nanoclusters in Nafton membrane initially causes the hydrogen ions of Nafton to be replaced by less mobile lead ions. Later during the reaction with hydrogen sulfide, several of these lead ions form PbS molecules and in the process get released from the sulphonic groups. These lead ions are probably replaced by hydrogen ions. This effect is larger in the case of clusters of larger diameter, as a larger number of lead ions would have replaced hydrogen ions.
initially during formation. Consequently, a larger numbers of lead ions would get replaced by hydrogen ions in the sulphonic groups during the formation of larger PbS clusters, leading to an enhanced conductivity and hence lower resistivity in comparison with samples having smaller nanoclusters. The effective increase in the ratio of surface area to volume in the case of smaller clusters also could be a contributing factor. The possibility of other contributions to the mechanism of proton transport depending on the actual size of the embedded nanostructures cannot be ruled out and the embedded PbS nanoclusters could also play a role. Proton transport in these materials can be fully understood only though more detailed and systematic measurements on the size dependence of conductivity in a wide size range of nanoclusters and further work is in progress in this direction.

Thermal lens effect was observed on passing a low power cw helium–neon laser beam through sample C and is studied using the z scan geometry. Fig. 4 shows the z scan trace obtained. The prefocal peak and post focal valley are indicative of the formation of a negative lens, which leads to self-defocusing. This is utilized in the optical limiting set up using which the transmitted optical intensity from the sample is measured as a function of the incident input intensity. The result is depicted in Fig. 5.

In both z scan and optical limiting experiments, a laser beam is passed through the sample, and hence, the sample is required to be sufficiently transparent to allow a beam of detectable intensity to pass through the sample. This is possible in semiconductor nanostructures only if the optical cut-off is sufficiently blue-shifted from the wavelength of the laser wavelength used, 632 nm in the present work. The optical absorption spectra (Fig. 1) show that samples A and B are opaque at the laser wavelength. It was not possible to
pass the laser beam through these samples and hence z scan and the optical limiting experiments could not be performed with these samples. The laser wavelength falls in the tail end of optical absorption cut off in the case of sample C, making it possible for the beam to pass through.

The defocusing nature of the sample is dependent on the aperture size and the focal length of the condensing lens used in the optical module. The threshold for limiting is found to be 6 mW. The output remains constant at about 4 mW even when the input is close to 8 mW. Earlier work on CdS [14] had indicated that nonlinearity observed is large in the regime of strong quantum confinement where the particle size is much smaller than the exciton Bohr diameter. The nonlinearity being probed here is of thermal origin as the source used is a low power cw laser. Further experiments are underway using high power laser pulses in the nanosecond and picosecond regime to probe nonthermal contributions to nonlinearity in these samples and also to investigate systematically the effect of nanoparticle size on the nonlinearity.

In summary, PbS quantum dots in the regime of strong quantum confinement are synthesized and stabilized in Nafion polymer with a wide range of cluster sizes, by a simple room temperature ion-exchange technique. The signature blue shift observed in optical absorption spectra of the samples is quite large compared to the bulk value, in agreement with the predictions of the tight binding approximation. An increase in electrical resistivity is obtained in the case of films with extremely small PbS nanoparticles. Temperature dependence of the refractive index in these materials leads to self-defocusing effect as measured from the z scan experiment. This is utilized to demonstrate the use of the material for optical limiting applications at low powers.

Acknowledgements

The authors acknowledge the help provided by Ms. Kaladevi Sendhil in the z scan and optical limiting experiments, financial assistance from Government of India and the valuable suggestions provided by the reviewer of the paper.

References