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SIZE DEPENDENT LINEAR AND NONLINEAR OPTICAL PROPERTIES OF PbS NANOCRYSTALS SYNTHESIZED BY CHEMICAL METHODS

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ABSTRACT

Nanocrystals of semiconductors such as PbS provide a large scope for band-gap engineering as strong quantum confinement effects can alter the bulk band-gap value, rendering the material transparent in most of the visible range of the electromagnetic spectrum. This paper discusses the preparation and characterization of PbS nanocrystals in the matrix of a polymer, Nafion, showing large characteristic blue shift in optical absorption. XRD and TEM analysis were made for size and structural analysis. Nonlinear optical properties were measured by Z scan technique.

Keywords: Nanocrystals, optical properties, excitons

1. INTRODUCTION

Semiconductor nanocrystallites 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 sulphide (PbS) is a wide gap semiconductor with bulk band gap energy of 0.41 eV, corresponding to an optical cut-off of 3020 nm, with exciton Bohr radius (r_B) of 18 nm. PbS has been used in IR detectors and sensors[3]. Lead sulfide being a narrow band gap material offers large tunability. Band gap of *PbS* can be varied in a wide range, upto 2.3 eV, from the bulk value of 0.41 eV, by changing the mean cluster size of the nanoclusters [4].

Semiconductor nanocrystals as in suspension form in free standing solutions[5] or in a transparent matrix have attracted recent interest due to their potential in applications in nonlinear optics such as photonic switching [6]. Organic materials such as polymers [7-9] and inorganic materials such as glasses [10-13] have been used as host matrices for semiconductor nanocrystals. There are several aspects of recent interest on polymer-based nanocrystals 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 [14,15], acoustic and optical phonon confinement effects [16] and enhanced optical nonlinearity [17] in polymer-based *CdS* nanocrystals. This paper presents some recent results on preparation and characterization of *PbS* quantum dots in Nafion polymer in the size range 3 to 13 nm, within the regime of strong quantum confinement.

2. EXPERIMENTAL TECHNIQUES

The host matrix for the *PbS* quantum dots in the present work is Nafion, 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. Nafion contains nanopores in its structure, which facilitate easy formation of nanoclusters. It consists of a fluorocarbon backbone and an interconnected ionic cluster as shown in the Fig. 1.

Nafion 117 films (18 μm thicknesses) were cut into 3x3 cm^2 area and cleaned with boiling nitric acid followed by hot water until pH of the bath becomes neutral. Film was immersed in aqueous water lead acetate solution of 0.1 M for various time durations followed by immersion into ammonia solution. Samples with different immersion times were prepared and designated as A, B and C having immersion time of 1, 15, 60 minutes. Finally hydrogen sulphide gas was passed overnight to form PbS nanocrystals.

X-ray diffraction (XRD) was 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° and 10 second counting time so as to improve the signal to noise ratio. The samples were analyzed using Hitachi 8100 T transmission electron microscope, with acceleration voltage at 200 keV. Nafion samples for were prepared for TEM by slicing with ultramicrotome. Optical absorption spectra of the sample are recorded on a Hitachi U-3400 Spectrophotometer. *Z* scan experiments are done using the conventional geometry 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 microns. 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

XRD results (Fig. 2.) indicate the formation of PbS nanocrystals and with respect to immersion time the size of the nanocrystal increases. Sample A showed broad amorphous pattern while B and C can be indexed to that of cubic rocksaltstructure (JCPDS file no: 5-0592). Sample C showed sharp peaks, characteristic of larger nanocrystal size compared to A and B. Using Scherrer's formula nanocrystal size was calculated. Since sample A showed broad peak it was difficult to calculate the size. For B and C the size was calculated to be 8 and 12 nm respectively.

TEM photographs of sample A is shown in Fig. 3. a & b. Uniform sized nanocrystals of 5 nm distributed throughout the matrix of Nafion (dark particles corresponds to PbS nanocrystals). Fig. 3. b. shows the selected area diffraction (SAD) pattern of sample A. The SAD pattern in Fig. 3. b. can be indexed to cubic PbS nanocrystals.

Optical absorption spectra of samples A, B and C are shown in Fig. 4. Band gap energy for bulk PbS is at 3020 nm (0.41 eV). All the samples blue shifted from the bulk value due to surface quantization effects. Absorption onset for sample A, B and C are 630 nm, 858 nm and 1046 nm respectively. By applying Brus formula, the sizes of the nanocrystals were found to be 4.5 nm, 8.4 and 14 nm. The sizes calculated from the Brus formula matches with that of found from XRD. The observed PbS nanocrystals were much larger than the proposed ion cluster model. Interestingly nanocrystals were narrowly distributed in size, suggesting that the hydrophilic cavities were distributed homogeneously in the membrane structure. However, the hydrophilic cavities and channels must be structurally flexible enough to accommodate the formation of large PbS nanpcrystals.

In order to understand the mechanism of formation, the pH of the lead acetate solution in which Nafion was immersed is shown in Fig. 5. for sample B. There is an decrease in pH due to the release of H^+ ions as shown by the following mechanism:

$$\text{----}\ SO_3^-\ H^+ + Pb^{2+} \rightarrow \text{----}\ SO_3^-\ Pb^+ + H^+$$

Since perfluoro sulfonic acid is a strong acid it can deprotonate easily in solution. Since there is an increase in H^+ ion in solution, there was increase in pH decrease in solution indicating the formation of ion exchanged product. It also indicates that with the increase in immersion time there is also increase in the number H^+ of getting replaced with Pb^{2+}. This consolidates the view that with the increase in lead ion content, the size of the PbS nanocrystal also increase.

Thermal lens effect was observed on passing a low power cw helium–neon laser beam through sample A and is studied using the z scan geometry. Fig. 6. 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 was measured as a function of the incident input intensity. The result is depicted in Fig. 7. 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. 3) show that samples B and C 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 A, 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 [17] 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.

4. CONCLUSION

PbS nanocrystals of different sizes were prepared in the matrix of Nafion by tuning the process parameters. Nafion membrane seems to be flexible in its structure so that in can accommodate sizes more than 4 nm although the pore size is 4 nm. XRD and TEM analysis indicates the presence of PbS nanocrystals in the size range 5 to 15 nm.. Optical absorption exhibits the signature blueshift in the onset, indicating strong quantum confinement effect. 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.

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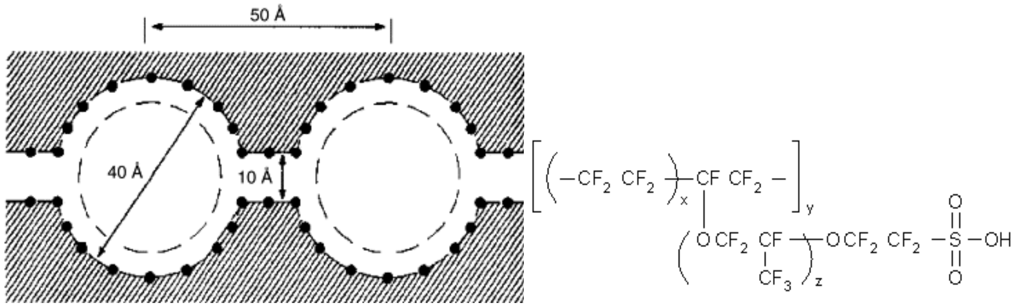
FIGURES



a b

Fig.1. a. The ion cluster model for Nafion and b. Chemical structure of Nafion.

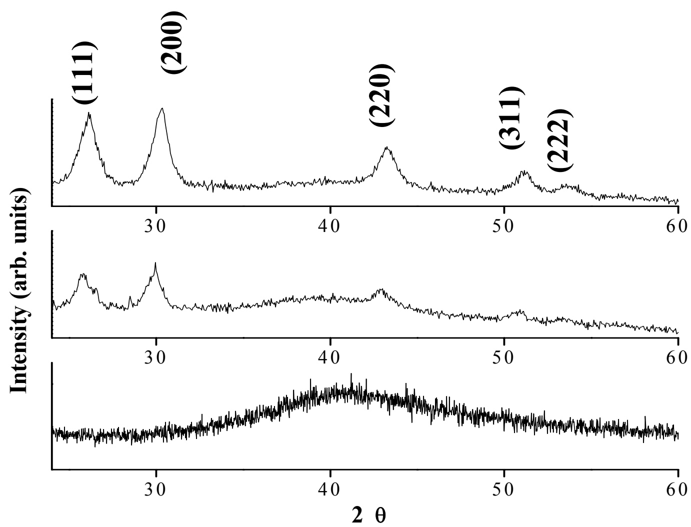
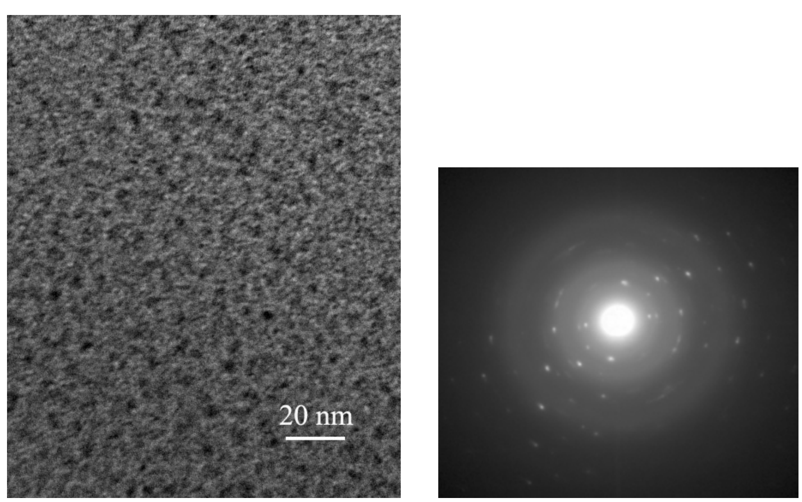


Fig.2. XRD pattern for sample A, B and C



a b

Fig. 3. TEM micrograph of sample A (a) and SAD pattern (b).

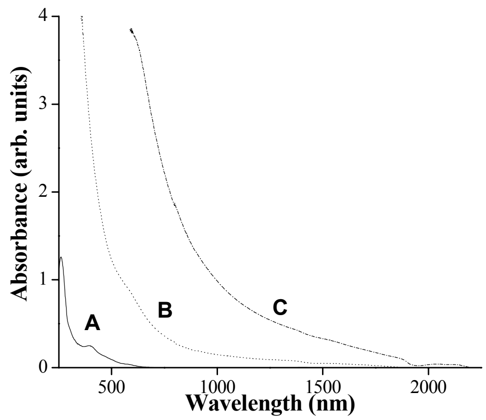


Fig. 4. Optical absorption spectra for sample A, B and C

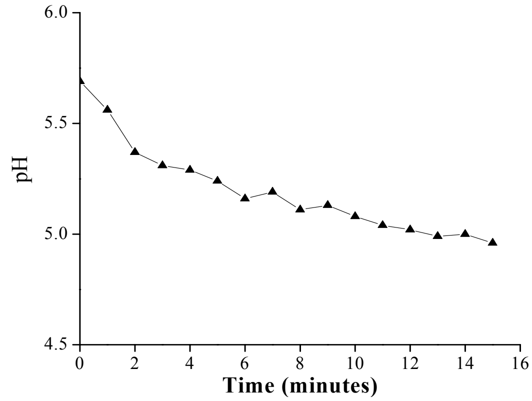


Fig. 5. pH variation with time for sample B

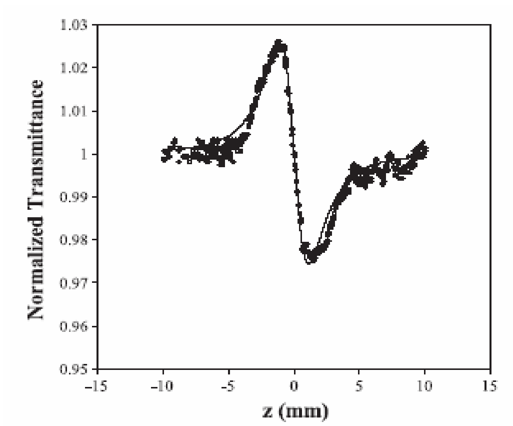


Fig. 6. Closed z scan trace of sample A

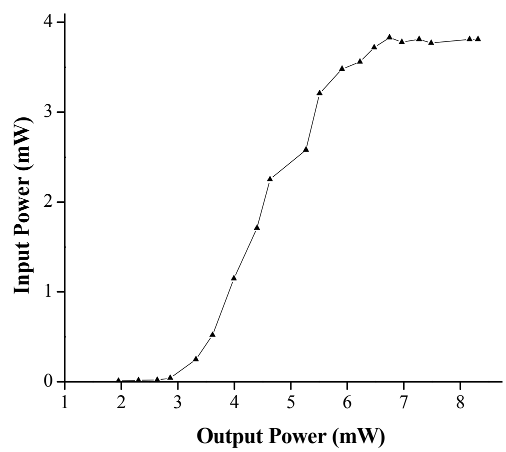


Fig. 7. Optical limiting in PbS Nafion for Sample A