

PbS - Nanoparticles Embedded in Polymer Matrix: Preparation and Characterization

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Abstract Formation of nano-sized PbS in PEO – polymer matrix at room temperature is being reported. SEM showed the particle size distribution while TEM affirmed the formation of nano particulates of PbS. The size distribution was further supported by UV/VIS absorption of the colloid. At room temperature a wide variation in the size of the particles was observed depend on sulfuration and salt concentration. The detailed characterization of these nano - PbS doped in polymer electrolyte are also discussed.

Keywords Pbs Nanoparticles, Polymer Electrolytes, SEM, TEM

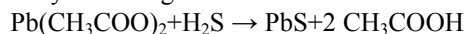
1. Introduction

Small inorganic semiconductor crystallites in the form of colloids have attracted researchers due to their very interesting properties[1]. The experimental verification of the transformation between molecular and bulk properties in small aggregates is being highly persuaded. Large number of studies has been reported so far on the formation of nano crystallites of semiconductors in zeolite and polymer matrix as well[2-5]. The various properties of nano-crystals has become the topic of both theoretical[6,7] and experimental interest[8-12]. In most of the studies, nano-crystalline semiconductors belonging to the II-VI group have been taken up while the studies related to IV-VI are rather scanty. PbS is an important member of this family. It is one of the earliest materials studied for its interesting photoconductive properties which has been exploited by many researchers[13]. The basic problem associated with colloidal semiconductors like CdS, PbS is that the lifetime of the photo-generated electron/hole pair is very short. Therefore, for fast electron transfer reactions, a very high concentration of reagents is required. However, such high concentrations destabilize the colloid. In order to prevent such a stability problem, dispersion of colloids into polymer matrix is a novel alternative. Keeping this thing in mind we have doped the nano-PbS particles into an ion conducting polymeric matrix. The polymer electrolyte chosen for the present study is PEO:NH₄I (80:20) which is predominantly a proton conducting polymer electrolyte[14,15] and maintain good

ionic conductivity and mechanical stability.

2. Experimental

To prepare polymeric membranes dispersed with semiconductor, Pure PEO (Mol. wt. 6×10^5 , Aldrich) was dissolved in dehydrated methanol to which stoichiometric ratio of anhydrous NH₄I (purity, Aldrich) was added to give PEO:NH₄I weight ratio as 80:20. This solution was thoroughly stirred at 400C for 5 hours for complete complexation. After that we added a dilute solution of lead acetate to it drop by drop. As soon as the drop falls, H₂S was bubbled through the viscous solution (at 30 ml./min.) for 2-3 minutes which resulted in the formation of PbS. A fresh Pb-acetate drop was added and sulfuration was done as above. This continued till the desired weight ratio of Pb-acetate gets added. The bubbling rate (sulfuration) was controlled by flowmeter. Colloidal particles of PbS was formed in PEO-matrix by following reaction



The desired weight percent of Pb-acetate salt (1, 5, 10 wt%) and bubbling rate of H₂S (30, 60, 120 ml/min.) were varied to obtain the different films. This PbS-dispersed polymer electrolyte viscous solution was poured into petri dishes for solution casting into film form. After drying it in room ambient for several days, the film were finally dried under vacuum to eliminate all traces of solvent. These nano-PbS embedded in polymer matrix were characterized with JEOL JSM-5800 LV scanning electron microscope, PHILLIPS TEM instrument (Model EM-CM 12). The band gap of the dispersed PbS was evaluated by UV/visible absorption spectra using Hitachi (model U-3400) spectrophotometer. For calculation of the energy band gap the equation, as given below, was employed

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$$\alpha h\nu = A(h\nu - E_g)^n$$

where $h\nu$ denotes the energy of the incoming photon in electron volt, α is the absorption coefficient of the material, E_g is the energy band gap, A is a constant and the exponent n is 1/2 for direct band gap materials [16].

3. Results and Discussions

To confirm the presence/formation of lead sulfide we have recorded the XRD diffraction patterns of PbS doped polymer films. The known prominent peaks of bulk PbS are at $2\theta = 26.1$ and 30.3 . Unfortunately, near these angles some PEO-peaks are also present and it is difficult to distinguish. Hence, we carried out XRD measurement at a slow scan rate. A typical XRD pattern in the range $2\theta = 24-32^\circ$ is shown in figure 1 for films containing 5 and 10 wt% of PbS. The results of an approximate deconvolution of these peaks into peaks assigned either to PEO or PbS are also shown in figure 1. The dominant particle sizes determined from this data using Scherrer formula [17] are lies between 10-15 nm. The SEM photographs of different (PEO:NH₄I)+PbS films with different composition and sulfuration are given in figure 2. It was obvious from the comparison of figures 2 a and 2 b that more was the amount of Pb-acetate in the starting solution, bigger aggregated PbS gets dispersed.

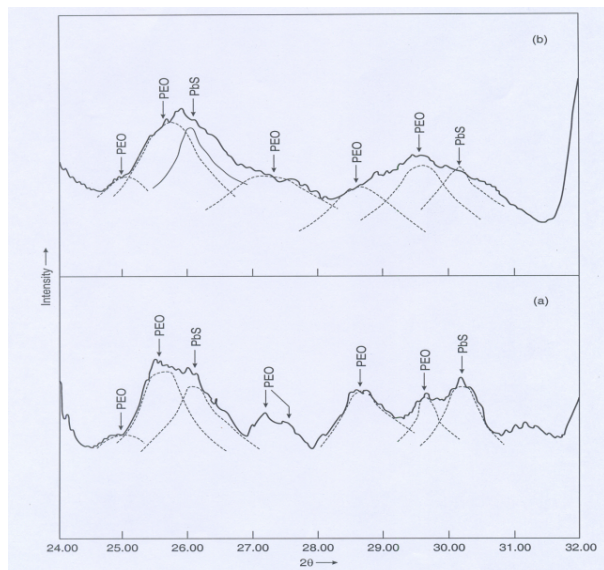


Figure 1. The deconvoluted XRD peaks of (PEO:NH₄I)+PbS composite membrane containing (a) 5 wt% and (b) 10 wt% of PbS

Further the bubbling rate of H₂S which controls the rate of sulfuration resulting in the formation of PbS. When bubbling rate was 30 ml/min., particles of small size are observed (figure 2a). When we increase the bubbling rate (120 ml/min.) larger particulates of PbS are observed (figure 2c). From these micrographs we can conclude that for obtaining small particles we must keep low salt concentration and low sulfuration rate. It was also clear that the dispersed PbS particles changes with the amount of salt Pb(CH₃COO)₂ in the polymeric solution and bubbling rate of H₂S. Our SEM could see

only larger particles (less than 10 micron) and hence TEM study was used to evaluate the exact particle size of PbS crystallites/clusters, particularly of those which had nm-size. The TEM micrograph of a typical (PEO:NH₄I)+5 wt% PbS film at 60 ml/min. are shown in figure 3. There was an obvious size distribution in micrograph showing small (3-5 nm) as well as large particle/clusters (30-50 nm) of PbS. Interestingly these PbS nanoparticles are well interconnected forming a channel which probably assisted in the transportation of ionic conduction. The small particles (nano-size) play an important role in the “size quantization effect” and hence change in the absorption spectra of the polymer film as discussed in the later section.

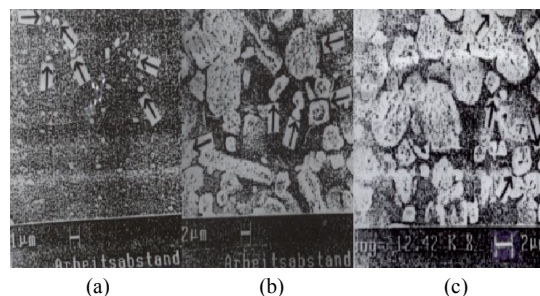


Figure 2. SEM micrographs of (a) (PEO:NH₄I)+1 wt% PbS (b) (PEO:NH₄I)+5 wt% PbS at 30 ml/min. and (c) (PEO:NH₄I)+1 wt% PbS at 120 ml/min. polymer electrolyte films

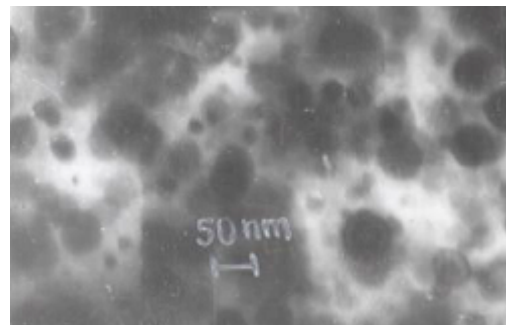


Figure 3. TEM micrograph showing size distribution of PbS nanoparticles in polymeric matrix

It is reported that the band gap of a specific material does not only depend on its structure but the size also has a controlling factor. Once the particle reaches nano-meter size, quantum effects come into play and the effective band gap increases [18-20]. The experimental determination of band gap of PbS from the optical absorption presented some problems. The band gap for bulk PbS is ~ 0.37 to 0.42 eV which puts the absorption edge in the wavelength region ~ 3300-2800 nm, but in this region the interference from strong H₂O bonds introduced ambiguity. If the particle size of PbS decreases (≤ 5 nm) the band gap may change to 1.2 eV to 3.5 eV (visible/UV region). For reconfirmation of nano size distribution, we have recorded the absorption spectra of PbS-doped polymer in the visible region (800-450 nm.). The UV/visible absorption spectra of a typical PEO:NH₄I+1 wt% PbS film prepared at 120 ml/min. is shown in figure 4. It was obvious that the absorption was continuously increasing in the 800-450 nm. region. Based on this absorption spectra we

have evaluated the band gap (E_g) from the intercept on $h\nu$ axis of $(\alpha h\nu)^2$ Vs $h\nu$ plot shown in figure 5.

It may, however, be noted that there is no sudden change in absorbance because of simultaneous presence of particles of all sizes (and hence different values of E_g). More than one intercept on $h\nu$ axis (and hence different values of E_g) are clearly seen in figure 5. The band gap evaluated varies from 1.9 eV to 2.2 eV reconfirms the formation of nano particulates which was supported by TEM study.

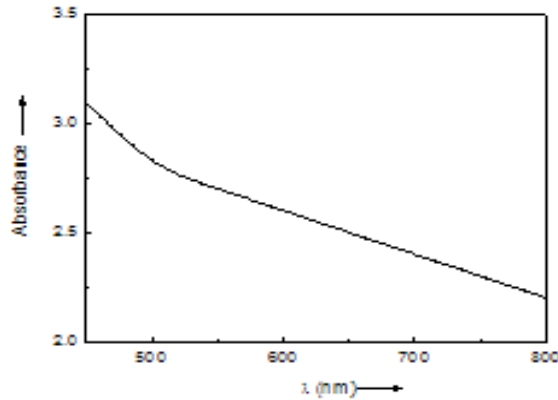


Figure 4. The absorption spectra of PEO:NH₄I+1 wt% PbS polymer electrolyte film prepared at 120 ml/min

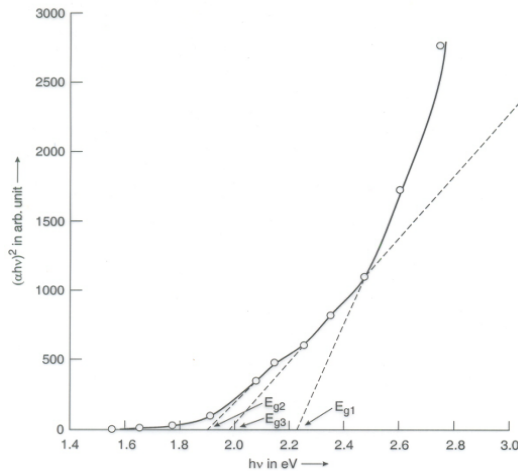


Figure 5. The $(\alpha h\nu)^2$ Vs $h\nu$ plot of PEO:NH₄I+1 wt% PbS polymer electrolyte film prepared at 120 ml/min

Wagner's polarization method was used to measure the ionic & electronic transference number of (PEO:NH₄I)+PbS polymeric membranes using formula.

$$t_{ion} = (1 - t_e) = i_T - i_f / i_T$$

where t_{ion} is the ionic transference number, i_T is the initial total current (due to ion + electron) and i_f is the final saturation current due to the electrons only. The current Vs time plots are shown in figure 6 for different samples of (PEO:NH₄I)+ x PbS ($x = 1, 5, 10$ wt%) prepared at H₂S bubbling rate of 120 ml/min. along with the data for pure PEO:NH₄I ($x = 0$) film. Similar curves were obtained for samples prepared at 30 and 60 ml/min. bubbling rate. The calculated values of ionic transference number (t_{ion}) are listed in table 1. It is well known that if the material is purely ionic in nature the ionic transference number $t_{ion} \sim 1$. From this table it

is clear that our PbS-doped polymer films was mixed (ionic + electronic) conductor in nature and nearly 20 % electronic conductivity could be introduced. The a.c. measurement of electrical conductivity is done (figure not shown here) to avoid polarization in the solid electrolytes. Here we have used the well known impedance spectroscopic technique to evaluate the true bulk conductivity. The values of total conductivity (σ_T); ionic conductivity ($\sigma_i = t_{ion} \cdot \sigma_T$); electronic conductivity ($\sigma_e = t_e \cdot \sigma_T$) and t_{ion} are calculated using above said formulas.

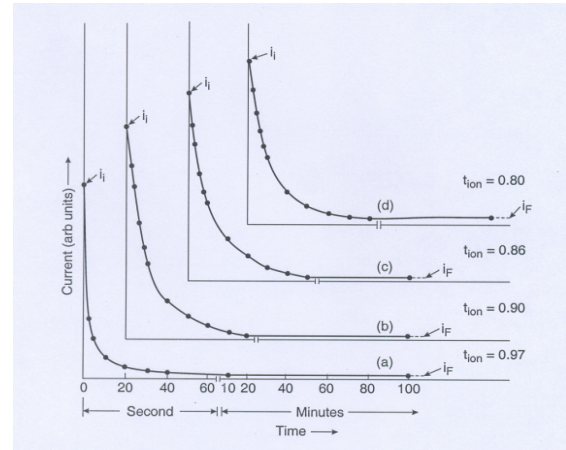


Figure 6. Polarization curves showing the current variation with time for different PEO:NH₄I polymer electrolytes with (a) no PbS (b) 1 wt % PbS (c) 5 wt% PbS (d) 10 wt% PbS. at 120 ml/min. bubbling rate.

Table 1. Calculated values of t_{ion} for (PEO:NH₄I)+PbS polymer films using Wagner's polarization method

Composition (wt% of Pb salt)	t_{ion} at 120 ml/min.	t_{ion} at 60 ml/min.	t_{ion} at 30 ml/min.
1	0.90	0.93	0.95
5	0.86	0.88	0.90
10	0.80	0.85	0.88

Some important observations based on electrical characterization are summarized below

(i) The increase in σ_T is not only due to the increased σ_e but there is, as well, a substantial increase in σ_i due to interface effect present in the ionic composite systems.

(ii) The maximum σ_e is for the film prepared at "high" bubbling rates as expected since such a condition gives a low band gap PbS (bigger particulates).

(iii) The σ_i is higher for films at "low" bubbling rates. This can be explained on the basis of well known size effect in ion conducting composites where the interface area is responsible for providing the ion conduction path and which increases as the particle size decreases.

4. Conclusions

Hence, we have successfully prepared the PbS nano particles in the PEO - polymer electrolyte matrix using chemical sulfuration method. A size distribution of particles was observed in XRD/SEM which were supported by UV/VIS

optical absorption spectra and TEM micrographs. Low salt concentration and bubbling rate was found to be suitable for the formation of smaller (nano) particulates of PbS. Further we have shown that the doping of semiconductor could be a novel approach to modify the electrical properties of polymer electrolytes.

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