



# Carbon – Science and Technology

ISSN 0974 – 0546

<http://www.applied-science-innovations.com>

ARTICLE

Received : 07/06/2013, Accepted : 13/08/2013

---

## Special Section on Advanced (Non-Carbon) Materials

### Effect of precursors on the solid-state synthesis of semiconducting PbS nanostructures

Sujata Kasabe<sup>(A)</sup>, Manish Shinde<sup>(B)</sup>, Parag Adhyapak<sup>(B)</sup>, Uttam Mulik<sup>(B)</sup>, Dinesh Amalnerkar<sup>(B,\*)</sup>

(A) Abasaheb Garware College, Karve Road, Pune - 411004, Maharashtra, India.

(B) Center for Materials for Electronics Technology, Panchawati, Off Pashan Road Pune - 411008, Maharashtra, India.

\* Corresponding Author : Phone :+91-20-25898390.

In this communication, we report facile and economical *in-situ* preparation of lead sulphide (PbS) nanorods and nanocubes within the Polyphenylene sulphide (PPS) matrix. PPS plays a dual role in the synthesis of the resultant nanostructures as - (i) a chalcogen source and (ii) a stabilizing matrix. We studied the effect of change of lead precursor from lead nitrate to acetate on the morphological properties of the resultant nanostructures. The effect of molar ratios of the reactants (1:1, 1:5, 1:10, 1:15 and 1:20) on the morphology of the products was also studied. The resultant nanocomposites were characterized by various physico-chemical techniques like X-ray Diffractometry (XRD), SEM equipped with EDAX, TEM and UV-Visible spectroscopy. The *prima-facie* observations suggest effective formation and subsequent entrapment of lead sulphide nanorods and nanocubes, respectively, when lead acetate and lead nitrate precursors were used. Additionally, simultaneous occurrence of nanocrystalline cubic lead as an impurity phase is noticed in case of heated admixtures for both the precursors.

**Keywords :** PbS, solid-solid reaction, nanostructures, TEM, PPS.

---

**1 Introduction :** Recently, IV-VI group semiconductors have attracted considerable attention at the nanoscale and number of studies related to the synthesis and characterization of these materials have been reported [1 - 5]. In particular, lead sulphide (PbS) with its infrared, small direct band gap of 0.41 eV (at 300 K), larger excitation Bohr radius of 18 nm and large optical dielectric constant (17.2) allows for the strong quantum confinement (the band gap may shift to even in the visible range) with relatively large nanocrystals [6, 7] as compared to many other semiconductors. Due to its functional nature, it has been widely used in many fields such as Pb<sup>2+</sup> ion exchange sensor [8], photography [9], IR detector [10] and solar absorber [11]. Due to its better non-linear optical properties than GaAs or CdS at a given particles size, it may be useful in optical devices such as optical switch [12]. It may be noted that synthesis of one dimension (1-D) nanostructures is an arduous task but may render interesting optical, electronic and magnetic properties at the nanoscale. Therefore, material chemists have been exploring an ideal single step method to prepare these nanostructures. Nevertheless, the challenge has been and remains to be the control of the size, size distribution, morphology, and organization of nanostructures. Hitherto, various 1-D and quasi 1-D forms of PbS nanostructures, including nanowires [13], nanorods [14], nanobelts [14] and hierarchical shapes like dendritic [14], flowers [15], star-shaped [16] and clover

[17] like nano/micro structures have been produced using combination of various polymers and surfactants. Lead sulfide nanocubes have been synthesized using hydrothermal [18] and organic ligand assisted [19] routes. However, to the best of our knowledge, synthesis of nanocomposite of polymer/1-D PbS nanostructures using the polymer as inherent chalcogen source has not been seriously attempted [19, 20]. In this context, *vide* this communication, we ventured into the synthesis of 1-D PbS nanostructures within polyphenylene sulphide matrix using facile and novel solid state reaction method with the intention to study the effect of change of lead precursor from lead nitrate to acetate on the morphological properties of the resultant nanostructures. PPS acts as stabilizer as well as a chalcogen precursor [21]. Besides, PPS with its excellent mechanical and chemical resistance properties (in addition to the polymer being inherently self-extinguishing) can be extruded/processed in any desired shape/form, which could be an important aspect from the perspective of nanocomposites based device fabrication.

## 2 MATERIALS AND METHODS :

**2.1 Materials :** Polyphenylene Sulphide (PPS) with number average molecular weight of 10,000, lead nitrate, lead acetate and acetone were obtained from Aldrich (99 % purity) and were used as received.

**2.2 Synthesis of nanocomposites:** Lead nitrate and lead acetate salts were used as Pb source, respectively, in two sets of experiments. The melting temperature ( $T_m$ ) of PPS is  $285\text{ }^{\circ}\text{C}$  and its thermal decomposition starts at  $\sim 450\text{ }^{\circ}\text{C}$ . Therefore, the reaction temperature of  $285\text{ }^{\circ}\text{C}$  was chosen for the synthesis of PbS in PPS matrix as at the melting temperature, sulphur will be loosely bound and some of the loosely bound sulphur may react with the lead to form PbS.

*In-situ* synthesis of lead sulfide in polymer matrix via proposed solid state route was carried out by varying the molar concentration of the reactants (lead nitrate / lead acetate : PPS) with ratios such as 1:1, 1:5, 1:10, 1:15 and 1:20. For such reactions, the two reactants were admixed in stated molar ratio in an agate pestle-mortar using acetone. The resultant admixture, after drying at room temperature, was subjected to heating at  $285\text{ }^{\circ}\text{C}$  (melting temperature of PPS) in an alumina crucible for six hours under an ambient atmosphere. Subsequently, it was naturally cooled down to room temperature. The obtained products with 1:1 molar ratio for both the salts were fluffy blocks, which could be easily pulverized to fine powder. The obtained products with other molar ratios mainly 1:5, 1:10, 1:15, 1:20 were in the form of solid mass, which could be crushed (with increasing difficulty as the molar ratio changes from 1:5 to 1:20) in order to get the product in powder form.

**2.3 Physicochemical characterization :** For structure determination, powdered X-ray diffractograms were recorded with Rigaku Miniflex X-Ray Diffractometer using Ni filtered  $\text{CuK}_{\alpha}$  radiation. The surface morphology and particle size were determined using a Scanning Electron Microscopy (SEM; Philips – XL 30). For SEM analysis, the samples were prepared by (dispersing the resultant powders in ethanol followed by ultrasonication treatment for 10 min) mounting a drop of nanocomposite solution on an aluminum stub and allowing it to dry in air. In order to prevent the charging effect associated with SEM, the samples were sputter-coated with Au-Pd. Fine-scale microstructure examination was accomplished by Transmission Electron Microscopy (TEM) using Philips CM-200 TEM instrument. A drop of the typical powdered sample dispersed in acetone was spread on a copper grid coated with colloidal for TEM analysis.

## 3 RESULTS AND DISCUSSION :

**3.1 X-ray Diffraction Analysis :** The powder XRD studies were performed to ascertain the formation of PbS in polymer matrix. Figures (1 and 2) show typical X-ray diffractograms of samples corresponding to five different molar ratios (1:1, 1:5, 1:10, 1:15, 1:20) of  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Pb}(\text{CH}_3\text{COO})_2$  with PPS, respectively, heated at  $285\text{ }^{\circ}\text{C}$  with constant reaction time of six hours. For the sake of

comparison, XRD of pure PPS pre-heated at same temperature and time is also reproduced. As shown in Figure (1) and (2 b-f), the peaks at  $2\theta = 26.32, 30.40, 43.44, 51.32, 53.82, 62.88, 71.26,$  and  $79.30$  degrees can be readily indexed as face – centered – cubic PbS structure with a lattice constant,  $a = 5.942 \text{ \AA}$  in agreement with the reported value (JCPDS Card No. 5-592 having  $a = 5.936 \text{ \AA}$ ). The diffraction peak at  $2\theta=20.9^\circ$  corresponds to pure PPS (plot ‘a’ in Figure 1 and 2) whereas the peak at  $2\theta=31.0^\circ$ , can be ascribed to the (100) reflection of lead, indicating the presence of lead as minor phase (Figure 1).

The strong but broadened peak at  $2\theta = 30.40^\circ$  (Figure 1 and 2) indicates that the material has good crystallinity and small size. Secondly, it is clearly recognized that the (200) diffraction peak of the nanocrystals is much stronger than that of the other diffraction peaks. In other words, the intensity distribution of all the observed X-ray diffraction peaks of the nanocrystals deviates drastically from the characteristics pattern of bulk PbS (galena) powder. It appears that the PbS nanorods are preferentially oriented in such a way that their (100) planes are parallel to the substrate surface. This might perhaps facilitate one dimensional growth of PbS nanorods.

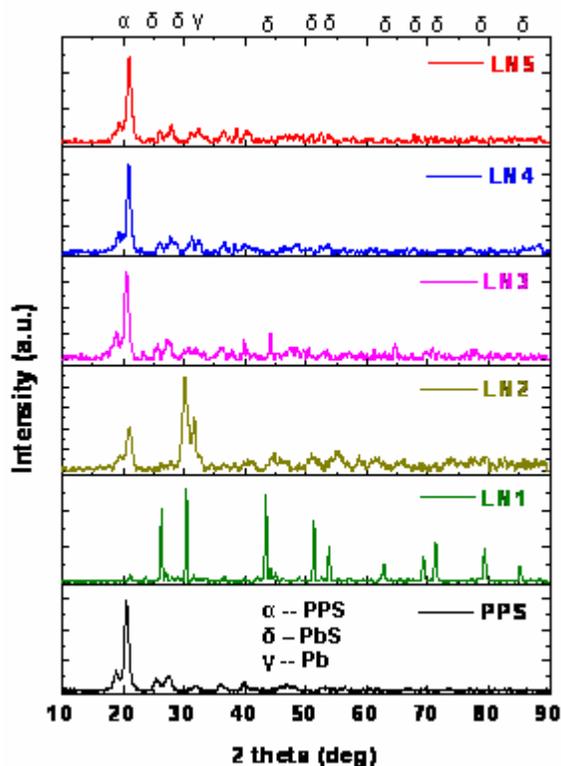


Figure (1) : X-Ray diffractograms corresponding to (a) PPS and heated admixtures of lead nitrate with PPS in molar ratios of (b) 1:1, (c) 1:5, (d) 1:10, (e) 1:15, and (f) 1:20.

Another observation from Figure (1 and 2) is that the intensity distribution of the diffraction peaks depends on the molar concentration ratio Pb precursor / PPS used to prepare the nanorods. For example, the intensity ratio ( $I_{200} / I_{111}$ ) of the first two highest intensity peaks in the XRD pattern increases with increase in Pb precursor / PPS ratio. A large intensity ratio ( $I_{200} / I_{111}$ ) is correlated to a higher degree of orientation of the (100) lattice plane and vice versa<sup>14</sup>. The primary particle size has been calculated from FWHM values of the strongest diffraction peaks associated with PbS for 1:1 molar ratio. Such an exercise furnished the crystallite size values in the range of 19 nm for samples corresponding to lead nitrate as precursor and 15 nm for corresponding sample prepared using lead nitrate as precursor.

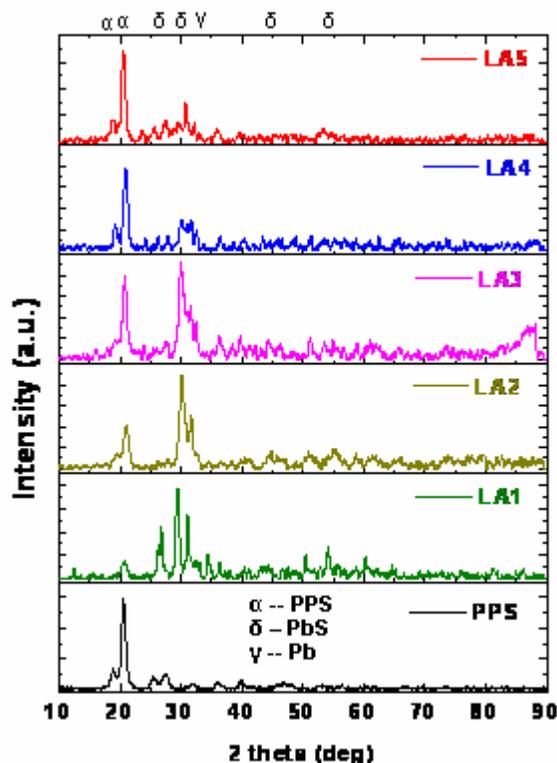


Figure (2) : X-Ray diffractograms corresponding to (a) PPS and heated admixtures of lead acetate with PPS in molar ratios of (b) 1:1, (c) 1:5, (d) 1:10, (e) 1:15, and (f) 1:20.

**3.2 Scanning Electron Microscopy :** The morphological study of heat treated samples was first carried out using SEM analysis. The scanning electron photomicrographs (SE mode) for the samples corresponding to lead nitrate : PPS scheme in 1:1 and 1:5 molar ratio are shown in Figure (3). It is interesting to observe that the heat treated product of equimolar concentration exhibits formation of rod like structures along with few nanoparticles dispersed in the polymer matrix (Figure 3 a). The number of nanorods is found to be less as compared with that of particles.

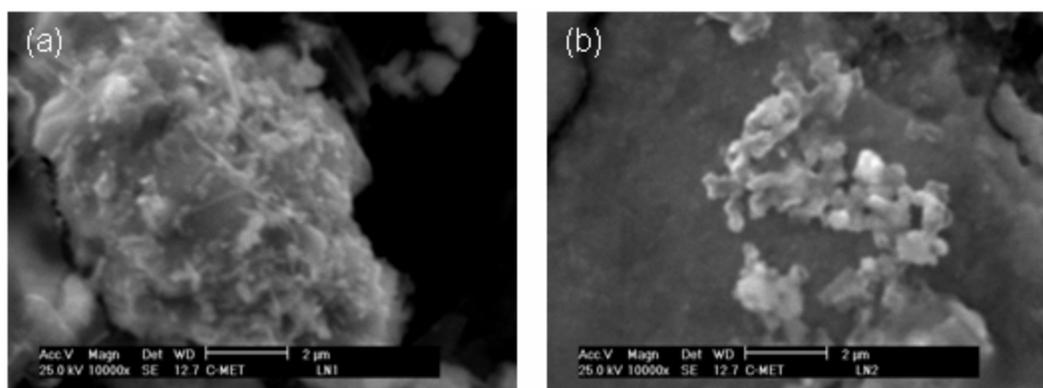


Figure (3) : SEM photomicrographs (SE Mode) corresponding to heated admixtures of lead nitrate with PPS in molar ratio of 1:1 (a) and 1:5 (b).

With increasing PPS concentration (for 1:5 molar ratio sample) instead of nanorod formation, aggregation of nanoparticles is noticed in the sample (Figure 3b). In case of samples prepared using lead acetate : PPS scheme, the sample prepared using 1:1 molar ratio displays the bundles of nanorods entangled with each other (Figure 4a). The nanorods are closely packed in bundles of approximately 5 to

6  $\mu\text{m}$  in width. The volume of nanorods is larger as compared with the volume of nanoparticles which is also supported by TEM (Section 3.3). Increase in the polymer content also affected the morphological structure. The SEM image of 1:5 molar ratio sample (Figure 4b) clearly shows the nanorods dispersed in the polymer matrix. High polymer content also makes the imaging of nanorods difficult. Moreover, the observed thickness and length of the nanorods is less as compared with 1:1 molar ratio samples which is also evidenced by TEM.

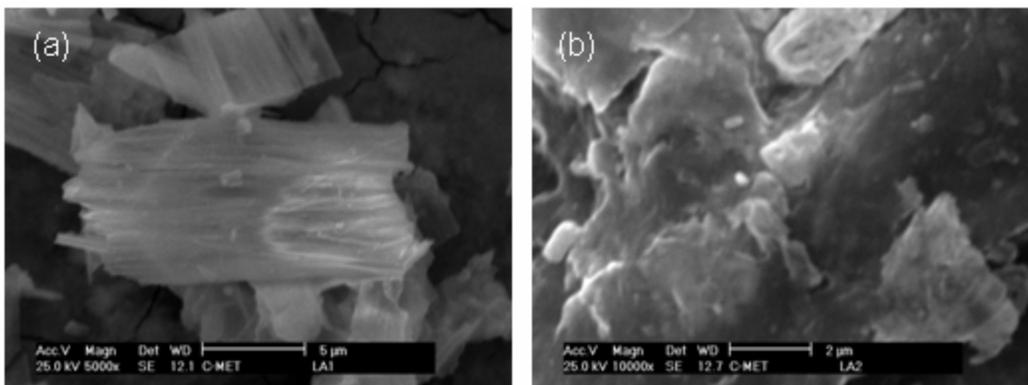


Figure (4) : SEM photomicrographs corresponding to heated admixtures of lead acetate with PPS in molar ratios of (a) 1:1, (b) 1:5

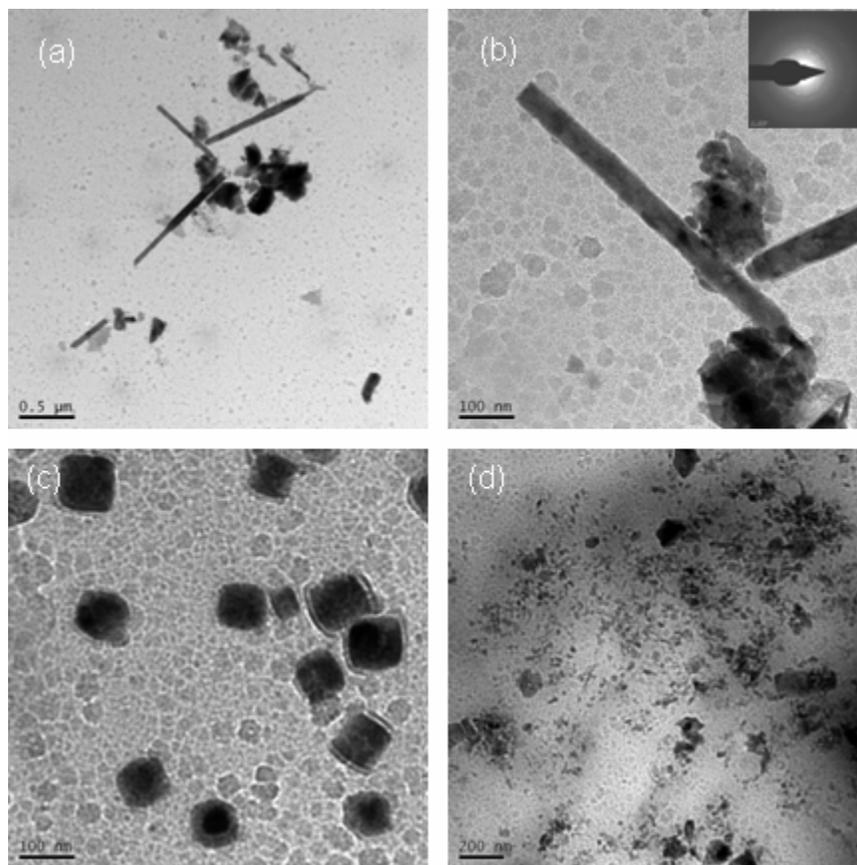


Figure (5) : TEM images corresponding to heated admixture of lead nitrate with PPS for 1:1 molar ratio at (a), (b) and (c) (with low and high scale magnification) and for 1:5 molar ratio at (d)

**3.3 Transmission Electron Microscopy:** The morphology and particle sizes within polymer matrix were further investigated by transmission electron microscopy (TEM). Figure (5) displays lower and higher magnification images of samples prepared using lead nitrate : PPS heated admixtures with different molar ratios. As noticed from earlier SEM findings, the equimolar admixture sample displays rod-like morphology. From the TEM micrographs of lower magnification, rod-like morphology along with some nanoparticles (Figure 5a) can be easily seen. Observation of the TEM micrograph with higher magnification clearly indicates the presence of PbS nanorods with diameter 50 nm and length 650 nm (Figure 5b). The presence of spots with rings in SAED pattern (Figure 5b inset) signifies random positioning of single crystalline nanoparticles in polycrystalline pattern for this sample. In addition to nanorods, the PbS nanocrystallites having cubic (rock-salt type) structure with 25 nm size were also observed in this sample (Figure 5c). Furthermore, increasing concentration of PPS affected the morphology of the sample. In case of 1:5 molar ratio samples, only aggregates of nanoparticles (with size 25 to 50 nm) were seen. Thus nanorod formation has been observed typically in equimolar sample for lead nitrate : PPS scheme.

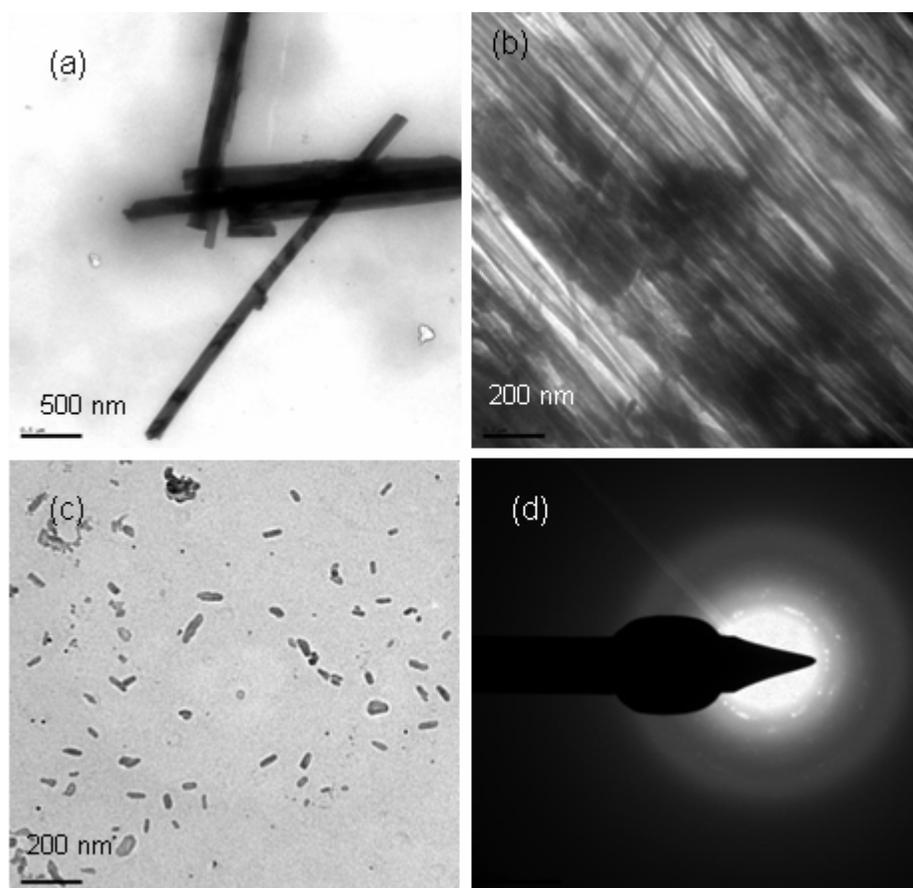


Figure (6) : TEM images corresponding to heated admixture of lead acetate with PPS in molar ratios of (a) and (b) 1:1 (with low and intermediate scale magnification), (c) 1:5, and the associated electron diffraction patterns in (d).

Figure (6) presents TEM images of powder products obtained from the reaction of lead acetate and PPS with different Pb precursor : PPS molar ratios of 1:1 and 1:5, respectively. These images reveal that the product is mainly composed of PbS nanorods and the dimensions of nanorods are 20 - 100 nm in diameter and 200 – few microns in length, depending upon the molar ratios used for the reaction. It was

found that not only the average particle size, but also the average aspect ratio (the ratio of length to width) of the PbS nanorods is affected by the change in the Pb precursor/ PPS molar ratio.

When the PbS nanorods were formed with the molar ratio of Pb-salt /PPS being 1:1, they have a relatively large aspect ratio and a narrow size distribution. The PbS rods are 3.4  $\mu\text{m}$  in length and 80 - 100 nm in width. The average aspect ratio is  $\sim 42$ . Although few much smaller PbS nanoparticles are also present in the TEM image (Figure 6b), their volume is small as compared with that of the rods. However, with increase in the molar ratio from 1:1 to 1:5, the PbS nanorods are formed with less aspect ratio (Figure 6c). The PbS nanorods are 60 nm in length and 16 nm in width. Thus, the average aspect ratio is  $\sim 4$ .

The concentration of the nanoparticles is also observed to be increased on increasing the polymer content in the reaction. Some of these ultrafine particles are supposed to be formed during the TEM sample preparation because with increase in the polymer content the material becomes rock solid mass which need to be crushed (with great difficulties) in order to get the powder. During this process, nanorods might have suffered from severe strain, which may perhaps lead to fracture and breakage to smaller particles. The selected area electron diffraction pattern of PbS nanorods (representative sample of 1:5 molar ratio) is shown in Figure (7d). The identified lattice spacings closely match with those pertaining to the cubic fcc structure of PbS as reported elsewhere [14]. The SAED rings evidently indicate the polycrystalline nature of the product, whereas, the spots imply the single crystalline nature of the product.

The above results confirm that PbS can be grown in the form one-dimensional rods and three-dimensional cubes with a preferred (100) orientation parallel to the substrate surface. The question as to why such a highly symmetric cubic crystal can grow in one dimension with a large aspect ratio point directly to the role of PPS as a precursor. The polymer network perhaps liquefies at melting temperature (285  $^{\circ}\text{C}$ ) and consequently, the solid-solid boundary transforms in to solid- liquid boundary thus changing the reaction interface. Thus the sulphur moiety of the polymer selectively forms a bond between  $\text{Pb}^{2+}$  of lead salt. Here PPS plays a dual role of sulphur precursor as well as surfactant. During simultaneous cyclization and sulphidation process, PPS can bond to solid surface and selectively adsorb on some facets of crystals to control crystal growth direction consequently. In mixed system of PbS - PPS, the adsorbed PPS on the surface of PbS subcrystals may also interact strongly leading to aggregation of PbS subcrystals. In the present case, when 1:5 molar ratio of lead acetate/PPS is used, it may be preferentially adsorbed on the facets parallel to (100) axis direction of PbS nanocrystals leading to preferential growth along the (100) direction. When the amount of PPS used exceeded a certain value, it probably not only limited the diameter of nanorods but also the length. In other words, under the condition of too much PPS in the reaction system, a small part of PPS may be adsorbed on (100) crystal face, resulting in the decreased of length. The observed results are similar to those reported by L. Dong *et. al.* while using CTAB as a surfactant [15]. In another report, Stoll and his co-workers have simulated the bridging flocculation process of inorganic/ polymer hybrids. They pointed out that at certain inorganic ion/ polymer concentration ratio, the inorganic / polymer hybrids could develop into 1-D morphology automatically [20]. Thus size of the PbS nanorods can be selectively tuned by varying the Pb precursor/PPS molar ratio. In addition, when lead nitrate precursor was used as the source of lead as compared to lead acetate, the aspect ratio of nanorods was less. This may be attributed to the inherent nature of the lead precursor. During the reaction, lead nitrate would release lead ions faster, while lead acetate would release them slowly as lead ions form a complex with acetate ions. This slow release of ions facilitates formation of longer rods with greater aspect ratio.

**4. Conclusions :** In summary, by means of a simple one-pot reaction, PbS nanorods and nanocubes in PPS matrix using different metal salts like  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{CH}_3\text{COO})_2$  as precursors have been

successfully prepared. The preferred orientation of (100) plane is characteristically observed in all diffractograms. The morphology of the product was found to be affected by change in (i) lead precursor and (ii) molar concentration of the Pb precursor/PPS ratio. Such suitably tuned PbS nanostructures may be useful for many opto-electronics devices such as IR detectors and optical switches.

### References :

- [1] M. T. Nenadovic, T. Rajh, O. I. Micic, Size quantization in small semiconductor particles, *J. Phys. Chem.* 89 (1985) 397 - 399.
- [2] T. K. Leolidou, Walter Caseri, U. W. Suter, Size Variation of PbS particles in high-refractive-index nanocomposites, *J. Phys. Chem.* 98 (1994) 8992 - 8997.
- [3] Y. Wang, A. Suna, W. Mahler, R. Kasowski, PbS in polymers- from molecules to bulk solids, *J. Chem. Phys.* 87 (1987) 7315 - 7322.
- [4] R. Tassoni, R. R. Schrock, Synthesis of PbS nanoclusters within microphase-separated diblock copolymer films, *Chem. Mater.* 6 (1994) 744 - 749.
- [5] M. Moffitt, A. Eisenberg, Size control of nanoparticles in semiconductor-polymer composites. 1. Control via multiplet aggregation numbers in styrene-based random ionomers, *Chem. Mater.* 7 (6) (1995) 1178 - 1184.
- [6] L. E. Brus, Electron–electron and electron-hole interactions in small semiconductor crystallites :  
  
The size dependence of the lowest excited electronic state, *J. Chem. Phys.* 80 (1984) 4403 - 4409.
- [7] P. T. Guerreiro, S. Ten, N. F. Borrelli, J. Butty, G. E. Jabbour, N. Peyghambarian, PbS quantum-dot doped glasses as saturable absorbers for mode locking of a Cr:forsterite laser, *Appl. Phys. Lett.* 71 (1997) 1595 - 1597.
- [8] H. Hirata, K. Higashiyama, Analytical study of the lead ion-selective ceramic membrane electrode, *Bull. Chem. Soc. Jpn.* 44 (1971) 2420 - 2423.
- [9] P. K. Nair, O. Gomezdaza, M. T. S. Nair, Metal sulphide thin film photography with lead sulphide thin films. *Adv. Mater. Optics Electron.* 1 (1992) 139 - 145.
- [10] P. Gadenne, Y. Yagil, G. Deutscher, Transmittance and reflectance in situ measurements of semicontinuous gold films during deposition, *J. Appl. Phys.* 66 (1989) 3019 - 3025.
- [11] T. J. McMahon, S. N. Jaspersen, PbS-Al selective solar absorbers, *Appl. Optics* 13 (1974) 2750 - 2751.
- [12] R. S. Kane, R. E. Cohen, R. Silbey, Theoretical study of the electronic structure of PbS nanoclusters, *J. Phy. Chem.* 100 (1996) 7928 - 7932.
- [13] D. Yu, D. Wang, Z. Meng, J. Lu Y. Qian, Synthesis of closed PbS nanowires with regular geometric morphologies, *J. Mater. Chem.* 12 (2002) 403 - 405.
- [14] Y. Wang, Q. Dai, X. Yang, B. Zou, D. Li, B. Liu, M. Z. Hu G. Zou, A facile approach to PbS nanoflowers and their shape-tunable single crystal hollow nanostructures: Morphology evolution, *Cryst. Eng. Comm.* 13 (2011) 199 - 203.
- [15] L. Dong, Y. Chu, Y. Liu, M. Li, F. Yang, L. Li, Surfactant-assisted fabrication PbS nanorods, nanobelts, nanovelvet-flowers and dendritic nanostructures at lower temperature in aqueous solution, *J. Colloid Interface Sci.* 301 (2006) 503 - 510.
- [16] M. S. Niasaria, A. Sobhani, F. Davar, Synthesis of star-shaped PbS nanocrystals using single-source precursor, *J. Alloys and Compounds*, 507 (2010) 77 - 83.
- [17] Y. Ni, H. Liu, F. Wang, Y. Liang, J. Hong, X. Ma, Z. Xu, PbS crystal with clover like structure: Preparation, characterization, optical properties and influencing factors, *Cryst. Res. Technol.* 39 (2004) 200 - 206.

- [19] M. Navaneethan, J. Archana, K. D. Nisha, S. Ponnusamy, M. Arivanandhan, Y. Hayakawa, C. Muthamizhchelvan, Organic ligand assisted low temperature synthesis of lead sulfide nanocubes and its optical properties, *Mater. Lett.* 71 (2012) 44 – 47.
- [20] S. Stoll, J. Buffle, Computer simulation of bridging flocculation processes: The role of colloid to polymer concentration ratio on aggregation kinetics, *J. Colloid Interface Sci.* 180 (1996) 548 - 563.
- [21] S. Waghmare, M. Shinde, U. Mulik, D. Amalnerkar, One-Pot synthesis of semiconducting PbS nanorods within polyphenylene sulphide matrix, *J. Nanosci. Nanotech.* 11 (2011) 5098 - 5101(4).