



Microwave-assisted synthesis of lead sulfide (PbS) nanostructures from a newly single molecular precursor

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Abstract

Lead sulfide nanostructures were synthesized by microwave irradiation of S-methyl dithiocarbazate lead (II) complex precursor in DMSO. Lead sulfide nanostructures were characterized using X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR), transmission electron microscopy (TEM), scanning electron microscopy (SEM). The optical properties of these samples were examined by UV-visible and photoluminescence spectroscopy. The band gap energy was obtained as 1.12 and 1.15 eV for the nano-rods and nano-cubes respectively, a blue shift from the bulk value (0.4 eV) which could be ascribed to quantum confinement effect. The result established the significant effect of the precursor type on the morphologies of the PbS.

Introduction

Lead sulfide (PbS) is an important IV-VI group semiconductor and bulk lead sulfide has cubic crystal structure and narrow direct band gap 0.42 eV at room temperature (300K) has a large excitonic Bohr radius about 18 nm [1,2]. It has dielectric constant and very high carrier mobility [3]. The XRD analysis shows that PbS nanoparticles have face centre cubic structure. The crystalline size obtained using XRD is about 15 nm by using Debye Scherrer formula where as determined from hall-williamson relation was found to be 21 nm. The TEM image shows particle size distribution is not uniform. To observe blue shift due to quantum confinement. We obtained UV-Vis spectrum. The single-source precursor routes use a metal source precursor routes use a metal organic/organometallic complex as the precursor for the growth of the target compound at the preferred stoichiometry [4]. There are many advantages with the use of single source precursor over other sources [5-7]. Also, SSPs are mostly stable to air with low toxicity and are easy to handle on microwave irradiation pathways are often at low temperature and cleaner, leading to the production of crystalline nanomaterial with very low impurities [8]. Bulk and nanocrystalline PbS can be synthesized using solvothermal techniques employing single-source precursors (SSPs) [9-10] and much work has been devoted to the investigation of microwave assisted methods to favour stable size-tunable nanocrystalline PbS [11-16]. The morphology and purity of the crystalline PbS can be manipulated by altering the nature of the SSPs. In some syntheses, the by-products generated during thermolysis of these SSPs act as capping agents that stabilize the PbS formed [17]. Alternatively, capping agents (e.g., DMSO) can be added to provide stability or morphological control.

Microwave-assisted method has the advantage of short time of reaction compared to other methods. The PbS nanoparticles by microwave irradiation method usually involves a lead salt and sulphur sources such as sulphur powder, thioacetamide, thiourea and dithiocarbazate have reported [18-22]. Sun et al. [23] have reported the microwave-assisted synthesis of PbS nanocrystals using lead diethylthiocarbamate. Microwave irradiation has a penetration characterises which makes it possible to homogeneously heat up the reaction solution. The result is uniform nucleation and rapid crystal growth [24].

In this work, we have first time reported synthesis of PbS a new Pb (II) dithiocarbazate complex with oxygen-rich ligands, second is examined as an SSP for PbS submicron single-crystal formation. The polyhydroxylated complex was compared to the alkyl DTC complex, 1, to examine the influence of intramolecular oxygen on the thermal decomposition and formation of PbS. The thermolysis mechanisms were investigated using in situ synchrotron powder X-ray diffraction experiments. Experimental conditions were adjusted to evaluate the influence of reaction temperature and heating rate on the morphology of the PbS product. The crystalline PbS products were characterized, and selected crystals were used to create a novel lead sulfide-based thermistor.

Experimental

1.1 materials used-

Analytical grade chemicals and reagents potassium hydroxide (KOH) Hydrazine hydrate, carbon disulfide, ethanol, methyl iodide, 4-Hydroxy benzaldehyde, lead acetate metal salt obtained from sigma- Aldrich are used as received without further purification.

Instrument used: Electrical stirrer, water bath, ultra sonication microwave oven.

1.2 Synthesis of PbS nanoparticles

The process was derived into four steps-

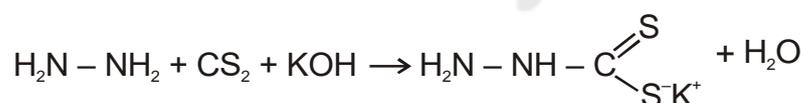
Synthesis of S-methyl dithiocarbazate

The synthesis of SMDTC was carried out as previously [25]. 11.4g (0.2 moles) of KOH dissolved in (9:1) 70 ml absolute ethanol and then 10g (0.2 mole) of 100% hydrazine hydrate (NH₂.NH₂) was added in the cooled to 0°C solution slowly with constant stirring and the mixture cooled to 0°C in ice, salt both. Another solution of CS₂ 15.2g (0.2 mole) is prepared by adding in 12.5 ml ethanol was added dropwise via a dropping funnel to the mixture, while the mixture was still being kept in the ice, salt both and vigorous mixing was performed via a mechanical stirrer. After constant stirring for one hours. The two layer formed which lower yellow oily layer were separated using a separating funnel, and was later dissolved in 12ml of cold 40% absolute ethanol maintain at 5-7°C. The mixture was kept in an ice bath, again and 28 g (0.2mole) of methyl iodide with vigorous stirring. After continued for 30 minutes more. The milky mixture formed was then filtered by filtration and was with water and finally left to dry over silica gel.

Yield : 50%

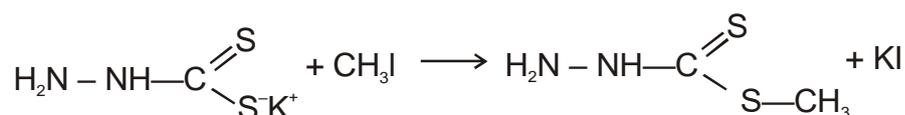
M.P : 82°C

Potassium salt of dithiocarbazic acid



Structure of Potassium salt of dithiocarbazic acid

Methylation of potassium salt of dithiocarbazic acid by methyl iodide to give S methyl dithiocarbazate

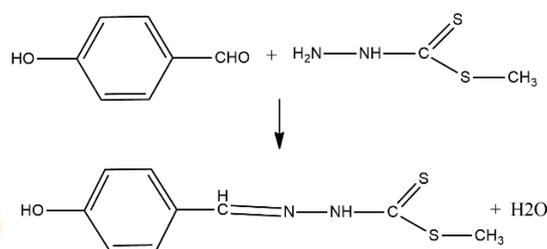


S-methyl dithiocarbazate (SMDTC)

Synthesis of Schiff base of SMDTC ligand

The novel Schiff base were prepared by the simple condensation reaction between 4-Hydroxy benzaldehyde and S-methyl dithiocarbazate. 1.23g (0.01 moles) of SMDTC was dissolved in 30 ml of absolute ethanol and then heated on a heating plate with constant stirring in order to ensure the complete dissolving of the SMDTC. Similarly, 1.221 g (0.01moles) of 4-Hydroxybenzaldehyde was mixed with 30 ml of absolute ethanol and heated on a heating plate, which was later followed by mixed both of the reactant followed by addition of 2-3 drops of conc. H₂SO₄. The mixture was kept

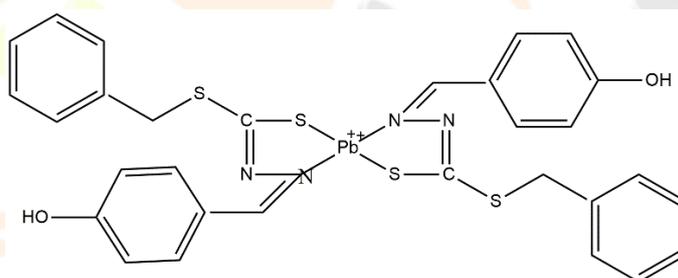
on the heating plate and then cool in ice bath until the Schiff base precipitated. The Schiff base precipitated was filtered via suction filtration and washed with cold ethanol and dried over silica gel.



S-methyl- β -N-(4-Hydroxybenzylidene) dithiocarbazate

Synthesis of lead (II) metal complexes:-

The Schiff bases 0.507g (0.002 mole) were dissolved in hot glycerol (20ml). This was added to a solution of metal salt 0.379g (0.001 mole) in glycerol (10ml) in 2:1 molar ratio. The resultant solution becomes coloured. The mixture was heated on water bath and refluxed for 30-60 minutes, when crystals of metal complexes started appearing. Then refluxing was stopped and the reaction mixture was allowed to stand overnight where upon coloured crystals were formed. Precipitate was filtered off and the complex was purified in vacuum oven anhydrous CaCl_2 in a desiccator.



Bis-[S-methyl- β -N-(4-Hydroxybenzylidene) dithiocarbazate] lead (II).

Synthesis of lead sulfide nanoparticles

1 gm of lead complex was dissolved in 20 ml DMSO in a round bottom flask. A ultrasonic treatment was given to a mixed it thorough for 30 minutes. For ultrasonic environment the mixture is immersed into an ultrasonic bath heated at 80°C for 6 hours. Ultrasonic vibrations were generated by piezoelectric sandwich transducer at 40 KHz resonant frequency. The solution was kept for aging for another 30 minutes and then heated in microwave oven and was irradiation the beaker was placed at the centre of the microwave oven and was irradiated with 90% power (800w) for scheduled time. Heating it for 10 minute with 800w power microwave resulted spontaneous formation of PbS nanoparticles. The solution was cooled and washed with absolute methanol and chloroform. Precipitate was centrifuged and dried in air. Nanoparticles were collected and thoroughly washed with water and ethanol

Characterization of Schiff bases and their metal complexes

FTIR spectra ($4000\text{-}400\text{ cm}^{-1}$) were obtained as KBr pellet using a FTIR-105627 Perkin-Elmer spectrophotometer, JEOL-JMS-D 300 mass spectrometer, ^1H NMR(400MHz), ^{13}C NMR Agilent technologies Bruker 400MHz spectrometer 6250. LABTRONICS modal LT-110 Digital Automatic Melting point Apparatus in an open capillary.

Characterization of the synthesized Schiff base ligands [S-methyl- β – N-(4-hydroxy benzylidene) dithiocarbazate

FTIR and Raman spectral analyses of ligand

S.No	FTIR Bands cm^{-1}	Assignments
1	3262	O-H Stretching vibration
2	3023	N-H Stretching vibration
3	2973	C-H Stretching vibration
4	1775	C=N Stretching vibration
5	1422	N-N Stretching vibration
6	1380	C-N Stretching vibration
7	893	C-S-C Stretching vibration

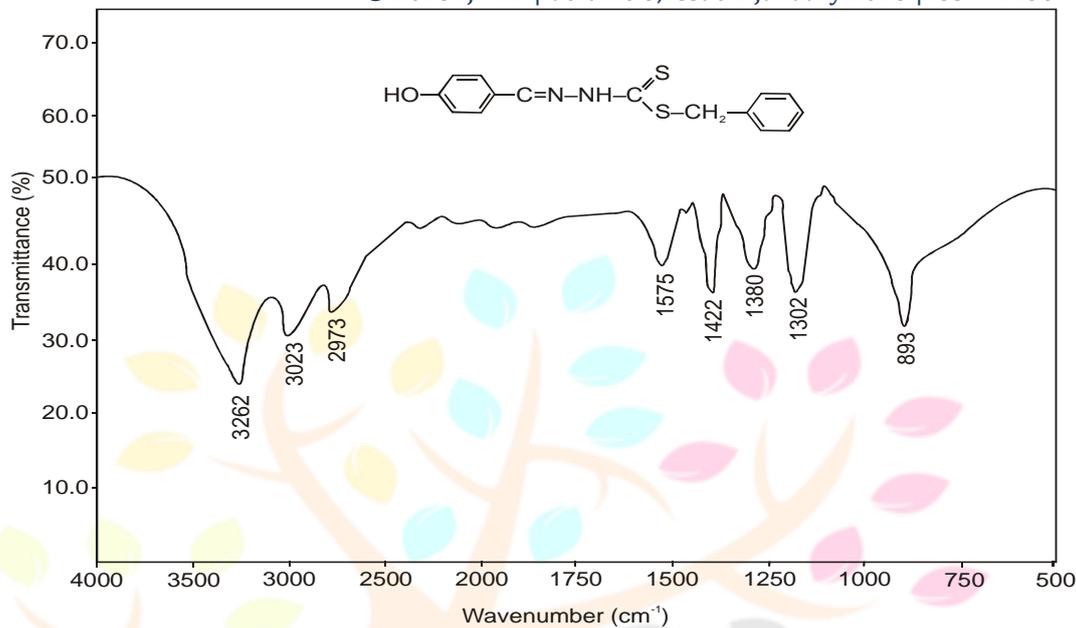


Fig. FTIR Spectra

¹HNMR spectral analyses of ligand

¹HNMR (500 MHz, CDCl₃, ppm) δ : 2.66 (s, CH₃), 3.93 (3H) 6.97-8.04 (m, 4H-PH) 10.47 (SNH)

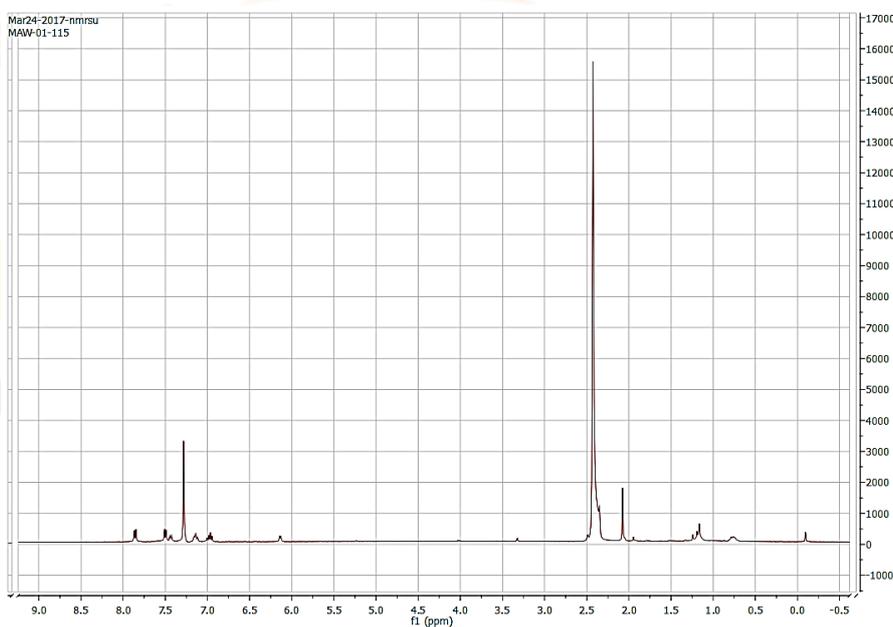


Fig. ¹HNMR spectra of S-methyl- β – N-(4-hydroxybenzylidene) dithiocarbazate

Thermal Gravimetric Analysis (TGA)

TGA measurement of the ligand was performed by TGA-50 SHIMADZU-00652 instrument at heating rate of 10°C/min under nitrogen atmosphere. The TGA curve of ligand exhibit three random weight loses.

*First estimated weight loss of 41.69 is attributed to CH₃S molecule as a gas .

*Second and third stage of the compound exhibit weight loss of 32% and 11% decomposition as gases at 100°C and 583°C finally residue (ash)

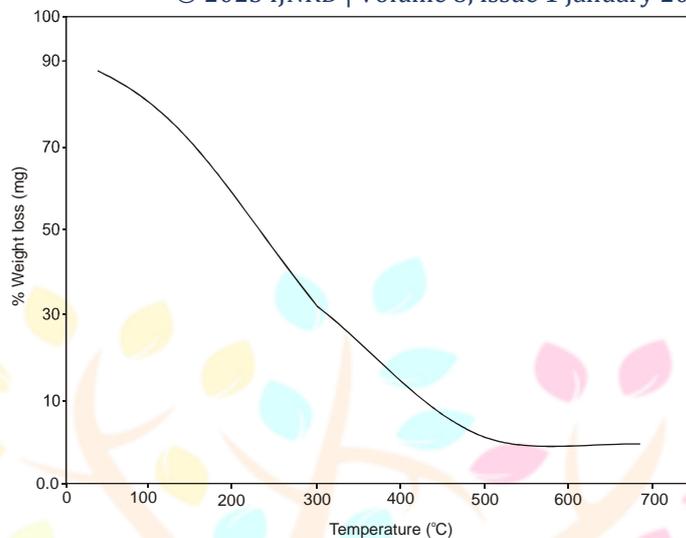


Fig. TGA curve of S-methyl- β – N-(4-hydroxybenzylidene) dithiocarbazate

Particles were collected and characterized by structural, morphological and optical characterization. Powder X-ray diffraction patterns were obtained from using X Pert Pro PAN analytical X-ray diffractometer in the 2θ ranging from 20° to 80° with $\text{CuK}\alpha$ radiation of wavelength 1.54 \AA . TEM and HRTEM micrographs were obtained by TECHAI G2F20 operated at 300 KV using a drop of suspension of the sample in ethanol on carbon coated copper grid. Optical spectra of the PbS structures quartz in the range 200-900 nm were obtained using Perkin Elmer Lambda 25 spectrophotometer. Photoluminescence spectra were obtained using Perkin Elmer PL-55 with exciton at 300 nm.

Results and discussion

XRD studies for PbS nanoparticle obtained for lead complex of 4- Hydroxybenzaldehyde Schiff base of SMDTC gave face-centre cubic structures JCPDC 067776 card. Reflections of the peaks are small and broad, indicates small size of the particles. The broad peak in the XRD patterns formation of fcc exploit due to microwave heating causing rapid formation of PbS nanostructure..

The size of the synthesized ter and ethanol.XRD Studies lead II sulphide nanoparticles are calculated using Scherrer equation

$$D=0.9\lambda/\beta\cos\theta$$

°Where λ represents wavelength of X rays, β represents half width at full maximum and θ is the diffraction angle]. The average grain size were 4.5, 5.2, 6.6, and 7.0 nm for 20° , 40° , 60° , 80° respectively.

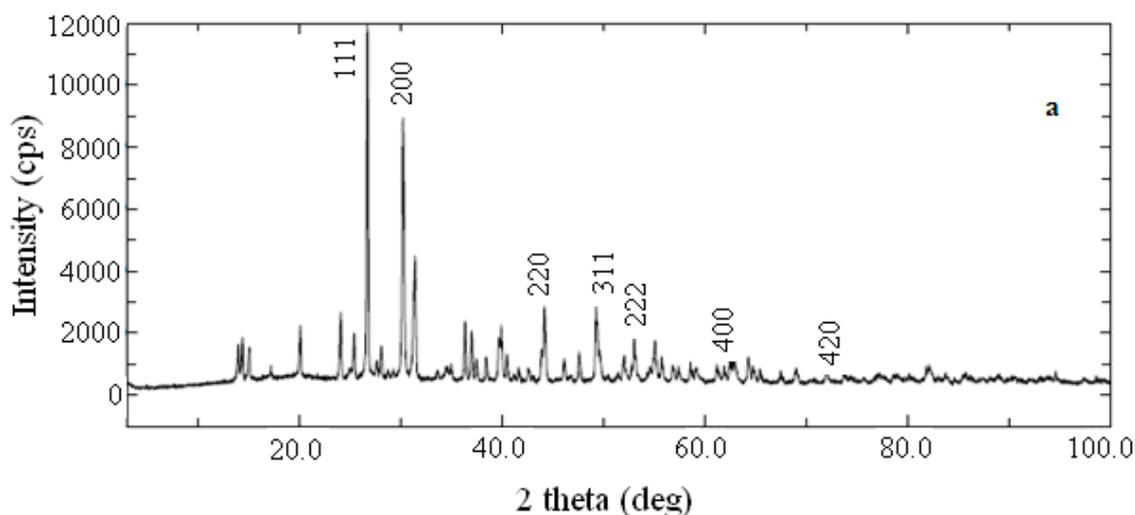


Fig. 1 XRD pattern of PbS nanoparticles

FTIR Studies

The FTIR spectrum of the lead II sulphide sample is shown in the figure 2. The FTIR spectrum for lead II sulphide nanoparticles show peak at 3448.65 cm^{-1} corresponds to the free O-H group, and the peaks at 1764.40 cm^{-1} and 1624.57

cm⁻¹ are due to the presence of hydroxyl group of water. The peaks at 879.30 cm⁻¹ and 829.49 cm⁻¹ indicates the Pb-S band. The peak at 624.79 cm⁻¹ is due to S-S bond and the peak at 477.29 cm⁻¹ is due to the presence of lead sulfide.

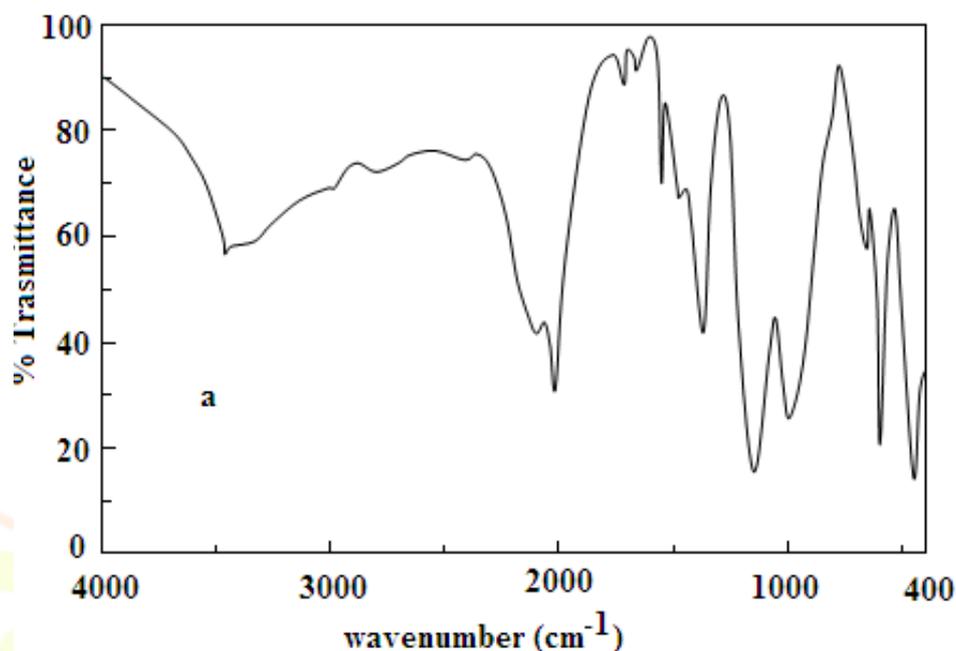


Fig. 2 FTIR spectra of PbS nanoparticle

UV Studies

The band gap of the prepared sample lead (II)sulfide was determined by using UV visible studies. Figure.3 shows the UV-Visible absorption spectra for lead (II) sulfide nanoparticles and the maximum absorption is at 275 nm wavelength. Figure.4 shows the graph is to find and band gap of lead (II)sulfide nanoparticles, the optical band gap of lead (II)sulphide is 3.5 eV.

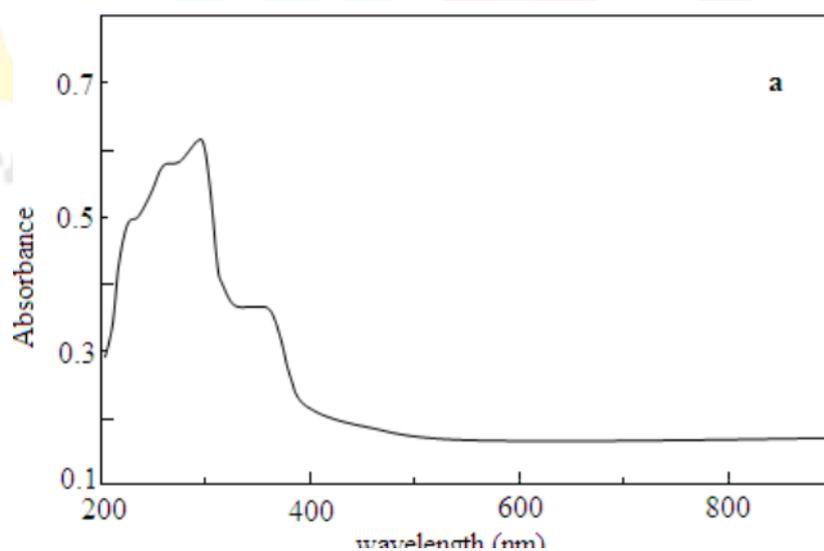


Fig.3 U.V. spectra of PbS nanoparticles

SEM Studies

Scanning electron microscopy was used to analyze the morphology and size of the synthesized lead (II)sulphide nanoparticles. Figure 4 shows the SEM images of the lead II sulphide nanoparticles at various magnifications. The SEM images of lead II sulphide nanoparticles show nanoparticles with spherical shape. In this case the particles sizes are slightly increased and is also observed that the particles are distributed with

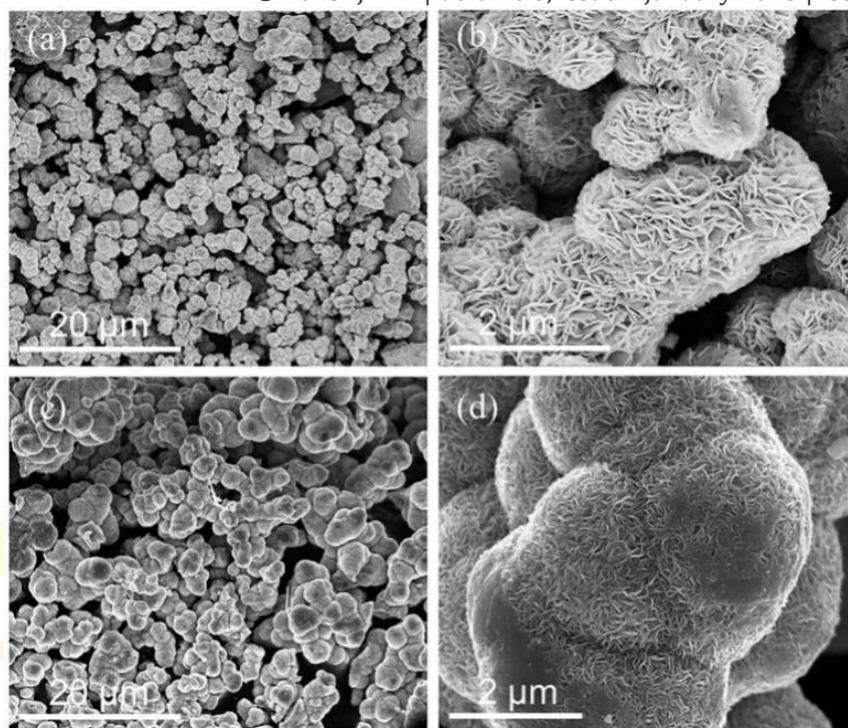


Fig. 4 SEM image of PbS nanoparticles

TEM Studies

The effect of reaction time on the morphologies of PbS nanocrystals was investigated by TEM (Fig. 5). They were found that the PbS nanoparticles were formed by ultrasonic irradiation for 1 h. They were increased in size for the prolonging reaction time. For 5 hour sonochemical reaction time, the product still retained their shape as spherical nanoparticles. By using TEM analysis, PbS samples were spherical nanoparticles with different size range, depending on the length of reaction time. Their average particle sizes were 20.77 ± 7.77 , 29.39 ± 5.76 and 82.86 ± 20.96 nm for 1, 3 and 5 h, respectively. The longer the sonochemical processing time was used, the larger the crystallite size was achieved. For 5 h sonochemical processing time, the facets and angles of the nanoparticles became more obvious. Particle size of the products was synthesized in all size with very narrow distribution, implying that their sizes were rather uniform – in favor with the luminescent property

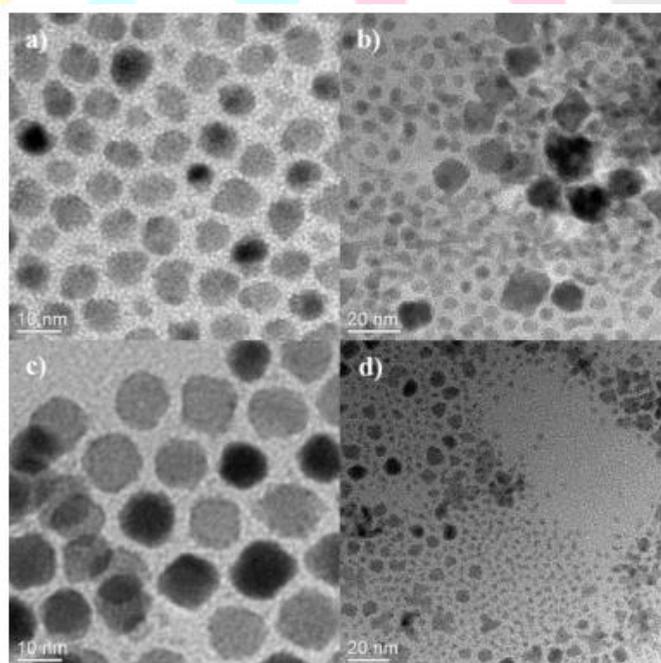


Fig. 5 TEM image of PbS nanoparticles

PL Studies

Fig. 6 shows photoluminescence (PL) spectrum of PbS nanoparticles excited by 254 nm wavelength at room temperature. It shows a strong and broad emission band centred at 390 nm, due to the transition of electrons from the conduction band

edge to combine with holes trapped in the Pb²⁺ interstitial sites. The synthesized PbS nanoparticles exhibit a blue-shift in the PL spectrum comparing to its bulk material, caused by the quantum size effect.

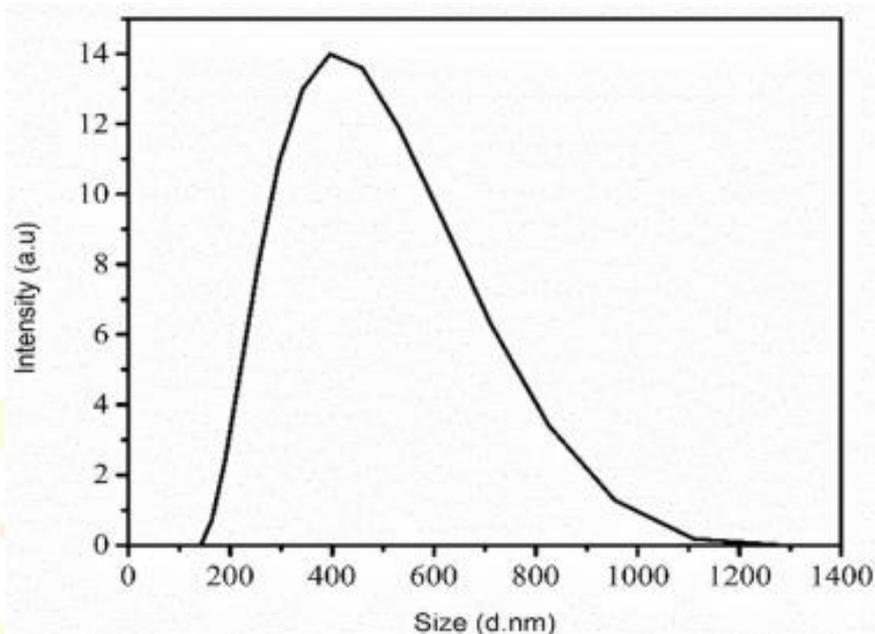


Fig. 6 Photoluminescence spectra of PbS nanoparticles

Conclusion

In the present paper, acceptable and simple route to the synthesis of PbS nanostructures by microwave irradiation in DMSO. It is suggested that this is facile microwave irradiation route to PbS nanorods and nanocubes could be used for the synthesis of nanostructures of other technologically important chalcogenide semiconductors. The XRD analyse as a pure PbS phase with a face-centered cubic lattice. Several minima were observed in the FTIR spectra at 829 cm⁻¹ of PbS bond, which is due to plasma-resonance absorption. The morphology and the shape and size 20 nm and a density of 400 μ m of nanoparticles were determined by scanning electron microscopy (SEM). The three dimensional showed the surface fine structure and size of The short reduction time result in increasing product purities by reducing unwanted side-reactions compared to conventional heating methods.

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