Solvothermal synthesis and characterization of zinc sulphide nanoparticles

Deepti Mishra, Priyanka Prabhakar, Swati Lahiri, S S Amritphale* & Navin Chandra
Materials From Wastes, Nanomaterials & Interdisciplinary Studies Division, CSIR-Advanced Materials and Processes Research Institute, Hoshangabad Road, Bhopal 462 064, India
Email: ssamritphalerrl@yahoo.co.in

Received 12 February 2013; revised and accepted 18 November 2013

Zinc sulphide nanoparticles have been synthesized by solvothermal approach involving refluxing of an aqueous solution of zinc acetate and sodium sulphide in presence of ethylene glycol and cetyl trimethyl ammonium bromide as surfactant. The nanoparticles have been characterized by X-ray diffraction, Fourier transform infrared spectroscopy, field emission scanning electron microscopy, energy-dispersive X-ray spectroscopy, differential scanning calorimetry, thermogravimetric analysis, ultraviolet-visible spectroscopy and transmission electron microscopy. The FESEM results indicate that the particles are almost spherical in shape with size varying in the range of 27.7–49.5 nm, whereas TEM micrograph indicates formation of particles of size in the range of 5–8 nm. EDX spectrum reveals the predominance of carbon, zinc, oxygen and sulphur.

Keywords: Zinc sulphide, Nanoparticles, Solvothermal method

Nanotechnology is an emerging area of research in the recent years. There has been increased interest in synthesis and study of nanoparticles due to their smaller size and larger surface area. This interest has been extended to the synthesis of nanoparticles of semiconducting materials due to their structure and optical properties. Among these are zinc sulphide nanoparticles which show special photovoltaic properties such as photoluminescence and electroluminescence and therefore have a broad application spectrum in the areas like optical coatings and light-emitting materials.

Zinc sulphide nanoparticles of different shapes and size have been successfully synthesized by different methods. However, development of novel energy efficient methods for their synthesis and tailoring of reaction conditions in order to obtain particles of desired shape and size is still a challenging task. Further, it has been reported in literature that spherical ZnS nanoparticles of size around 50 nm were used for determination of level of C-Reactive Protein (CRP) in serum which can be used to indicate myocardial infarction risk. Therefore, in the present work efforts have been taken to synthesize ZnS nanoparticles of size around 50 nm as it can be an attractive prospect for use in biomedical application also.

Herein, we report the synthesis of ZnS nanoparticles by solvothermal approach using zinc acetate and sodium sulphide as precursors for zinc and sulphide ions respectively. CTAB is used as capping agent to control the shape and size of nanoparticles. Ethylene glycol is a strongly polar solvent, having high boiling point, miscible with water and with the ability to dissolve salts of metal precursors. It can acts as a weak reducing agent and stabilizing agent. It also prevents aggregation of nanoparticles and retains uniform colloidal dispersion. The synthesized particles were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), ultraviolet-visible spectroscopy (UV-vis) and transmission electron microscopy (TEM).

Experimental
Extrapure zinc acetate, ethylene glycol and purified sodium sulphide flakes (Merck) and analytical grade CTAB (Rankem) were used as source materials for synthesis. Doubly distilled water was used for preparation of solutions and for washing purpose.

For synthesis of ZnS nanoparticles, stoichiometric amount of the reactants i.e., 100 mL aqueous solution of zinc acetate (27.43 g), sodium sulphide (9.755 g), ethylene glycol (200 mL) and CTAB (1.9 g dissolved in 20 mL water) were mixed thoroughly and refluxed using a heating mantle at 198–200 °C temperature for a period of around 10 hours. The resulting solution was allowed to cool down to ambient temperature. The product was obtained in the form of a white coloured gel at the bottom of the flask which was removed by filtration using Whatmann 42 filter paper, washed thoroughly three to four times using doubly distilled water and then finally with acetone. The...
resultant gel was dried in an air oven at 60 °C for 4 hours. CTAB is a cationic surfactant and ionizes to form CTA\(^+\) while Na\(_2\)S ionizes to form S\(^2-\) and HS\(^-\) ions which may interact with CTA\(^+\). ZnS nanoparticles are capped by CTA\(^+\) with excess HS\(^-\) ions adsorbed on the surface of surfactant aggregates.

\[
(\text{CH}_3\text{COO})_2\text{Zn} + \text{Na}_2\text{S} + \text{CTAB} \xrightarrow{\text{H}_2\text{O}} \text{ZnS-CTA}^+ + 2\text{CH}_3\text{COONa}
\]

The X-ray diffraction pattern of the synthesized zinc sulphide nanoparticles was obtained with the help of D8 advance X-ray diffractometer using Cu K\(_\alpha\) radiation. The X-ray diffraction intensity was recorded as a function of Bragg’s 2\(\theta\) in the angular range of 5–70°. The size and shape of the particles were determined by FESEM (model Nova NanoSEM-430, Comfei) and chemical composition was determined by EDX (model X-MAX, Oxford). For FESEM and EDX, a small quantity of sample was sonicated in acetone for a period of 15 minutes, mounted and dried in a vacuum desicator. TEM micrographs were recorded on a transmission electron microscope (FEI Tecnai F20 ST) with accelerating voltage of 200 KV at CSIR-NCL, Pune. IR spectra was recorded in the range of 500-4000 cm\(^{-1}\) on FTIR spectrometer (Bruker Alpha). TGA and DSC curves were obtained on TGA /DSC analyser (Toledo TGA/ DSC-1, Mettler Co.) by heating the sample at a heating rate of 10 °C/min from 30 °C to 1200 °C under nitrogen atmosphere. UV-visible absorption spectrum was recorded on UV-visible spectrophotometer (Shimadzu, UV-1201) after sonicating a very small amount of the sample in approximately 10 mL isopropanol on a ultrasonic bath for 20 minutes.

**Results and discussion**

XRD pattern obtained for synthesized ZnS nanoparticles (Fig. 1) revealed that the peaks located at \(d\)-values of 3.11(100), 2.71(9), 1.90 (45) and 1.63 (30) match well with standard JCPDS power diffraction data (File No. 5-0566) for \(\beta\) ZnS (3C-type) sphalerite with cubic structure\(^\text{13}\). The mineral name sphalerite is given for single cubic 3C modification as it occurs widely and can be identified easily. The synthesised ZnS nanoparticles were stable under most of the conditions on earth. The diffraction peaks were broadened indicating that nanoparticles are small in size (size in the range of 27.7 nm. to 49.5 nm)\(^\text{14,15}\). No peaks were detected for impurities in the sample confirming the phase purity of the synthesized ZnS nanoparticles.

The size and shape of the synthesized nanoparticles and their chemical composition were examined using FESEM (Fig. 2) and EDX (Fig. 3) respectively. The FESEM image showed that particles are almost spherical in shape. The size varies in the range of 27.7 to 49.5 nm. The EDX spectra revealed the predominance of carbon, zinc, oxygen and sulphur with their composition (wt.%) 67.79%, 17.69%, 8.11% and 6.40% respectively. The presence of oxygen atom in the nanostructure was due to the ethylene glycol used in the synthesis. The results of XRD were further confirmed by EDX spectrum which also showed that ZnS nanoparticles were of high purity.

The FTIR spectra of the synthesized ZnS nanoparticles has been compared with reported values for different stretching and bending vibrations modes in standard references\(^\text{16,17}\) (Supplementary data, Fig. S1). The broad band observed around 3386 cm\(^{-1}\) is ascribed to O-H stretching vibrations due to the absorption of moisture on the surface of ZnS. The
bands centered at 2942 and 2880 cm\(^{-1}\) may be due to the C-H-stretching vibrations, bands observed at 1084 and 1258 cm\(^{-1}\) may be due to C-N stretching vibrations and those at 1636 and 1566 cm\(^{-1}\) may be ascribed to N-H stretching vibrations. The bands present at 1205 and at 1041 cm\(^{-1}\) were due to C-C and C-O stretching vibrations respectively. The bands due to C-H bending vibrations were observed at 879, 1339 and 1409 cm\(^{-1}\). The characteristic band of Zn-S stretching vibrations was observed around 675 cm\(^{-1}\), which is in good agreement with the earlier value reported by Salavati et al\(^{18}\) for characteristic stretching vibrations of ZnS bond at 671 cm\(^{-1}\).

The TGA and DSC curves of synthesized ZnS particles were studied (Supplementary data, Fig. S2). The TGA curve indicates weight losses in two stages. In the first stage, 30.44% weight loss was observed (at around 125 °C) due to desorption of moisture and in the second stage around 5.57% weight loss was observed (at around 340 °C) due to decomposition of organic matter\(^{19}\). DSC results show endothermic peaks in the temperature range of 125.14–169.80 °C associated with 3611 mJ (100.40 J) of energy. These peaks of DSC can be correlated with the TGA peaks representing 30.44% weight loss in the sample.

UV visible absorption spectrum of the ZnS nanoparticles shows absorption peak at 249 nm (Supplementary data, Fig. S3) unlike that of bulk\(^{20}\) at 320 nm. The blue shift of peak indicates widening of bandgap\(^{21}\).

TEM micrograph of the ZnS nanoparticles is shown in Fig. 4. It exhibits the formation of more or less spherical shaped nanoparticles with variation of size in the range of 5–8 nm.

In the present study, zinc sulphide nanoparticles were synthesized successfully by solvothermal approach and characterized. XRD pattern confirms the formation of phase pure nanoparticles of \(\beta\) ZnS

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-K</td>
<td>67.79</td>
<td>85.24</td>
</tr>
<tr>
<td>O-K</td>
<td>8.11</td>
<td>7.66</td>
</tr>
<tr>
<td>S-K</td>
<td>6.40</td>
<td>3.02</td>
</tr>
<tr>
<td>Zn-L</td>
<td>17.69</td>
<td>4.09</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>99.9</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

Supplementary data
Supplementary data associated with this article, viz., Figs S1-S3, are available in the electronic form.
References
