Novel method to synthesize and characterize Zinc Sulfide nanoparticles

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doi: 10.6088/ijaser.0020101029

Abstract: Zinc sulfide nanoparticles were fabricated by solvent evaporation method with and without using capping agent, Hexa decyltrimethyl ammonium bromide (CTAB) at room temperature. The product was received in powder form. The structure and composition of the resultant product was characterized by means of UV and FTIR spectrophotometric studies. FTIR analysis showed peaks at 352.02 cm\(^{-1}\) and 611.46 cm\(^{-1}\) for Zinc Sulfide with CTAB, corresponding to Zinc and Sulfide stretching. For Zinc Sulfide without CTAB, the same stretching frequencies were observed at 315.10 cm\(^{-1}\) and 615.32 cm\(^{-1}\). UV spectrophotometer study determined the band gap of nanocrystalline Zinc Sulfide (with and without CTAB) as 5.48 eV and 5.99 eV, respectively. The optical absorption edge exhibited a blue shift with respect to that of the bulk sample. The blue shift with the decrease in crystalline size was attributed to the quantum size effects. When ZnS was prepared without CTAB, there was decrease in the size of the nanoparticle than when it was prepared with CTAB. Even though no capping agent (CTAB) was used in preparing ZnS, the particle size was well reduced. It was achieved by stirring the solutions during preparation. No agglomeration of nanoparticles was detected.

Keywords: Zinc Sulfide, nanoparticles, solvent evaporation, Hexa decyltrimethyl ammonium bromide (CTAB), Band gap, Blue shift.

1. Introduction

Among various nanomaterials, II-VI class inorganic semiconductor nanomaterials like CdS, ZnS, CdSe, ZnSe are proved to be versatile materials because of their applications in optoelectronic devices due to large variation of band gap as a function of particle size. Zinc sulfide has attracted much attention owing to its wide applications, including UV light emitting diodes, efficient phosphors in flat-panel displays, and photo catalysis. ZnS nanoparticles have the capabilities for applications in areas such as non-linear optical devices and fast optical switches and they have been studied extensively (Jayalakshmi and Rao, 2006).

Nano structured ZnS such as nanocrystals, nanowires, and nano belts exhibits excellent optical and electronic performances, which differ much from the bulk ZnS material due to the three-dimensional electrons and holes confinement in a small volume. The surface of a nano particle is more important than the bulk because nano particle have larger surface to volume ratios, surface atoms are bound by weaker forces because of missing neighbours, which leads to high surface reactivity (Behboudnia et al., 2005).

ZnS has a direct wide band gap (for the bulk cubic and hexagonal phases of ZnS, \(E_g = 3.68\) eV and 3.80 eV, respectively). Semiconductor has also been widely used as a phosphor in luminescent devices due to its emission in the visible range (Zhang et al., 2005). Their optical property, due to quantum confinement effect, dramatically changes and in most cases improves as compared with their bulk counter parts.

ZnS crystal usually exhibits a polymorphism of two phases with different stacking sequences of close packed planes to each structure: one is the cubic phase with a zinc blende structure (C–ZnS) and the other is the hexagonal phase with a wurtzite structure (H–ZnS) (Wei et al., 2005). At atmospheric pressure, C-ZnS is more stable at low temperatures and transformed to H–ZnS only at > 1,023 oC. Since the inherent
crystal structures of ZnS play an important role in its physical and chemical properties, the preparation of ZnS nano crystals with controllable phase is vital to develop them as building blocks in constructing the future nanoscale up to electronic devices. The novel and low cost method without any capping agent through eco-friendly path was utilized for synthesizing ZnS nanoparticles in this work.

2. Experimental studies

2.1 Chemicals

1-Hexane, 1-Pentanol, Zinc Chloride, Sodium sulfide, CTAB (hexa decyltrimethyl ammonium bromide), a surfactant molecule. The water used was deionized.

2.2 Synthesis

ZnCl$_2$ (solution A) and Na$_2$S (solution B) were taken in two 100 ml beakers. Solution A was prepared by combining 12 ml of hexane, 3.0 ml of 1–pentanol and 0.60 gm of CTAB. Solution B was also prepared in the same way. The solutions A and B were continuously stirred during preparation using a magnetic stirrer. Solution A and B were cloudy owing to the low solubility of CTAB. Then 0.6 ml of 0.012 M ZnCl$_2$ stock solution was added to solution A and 0.6 ml of 0.012 M Na$_2$S stock solution to solution B. Upon the addition of the aqueous component, the cloudy mixtures became colorless and transparent. The bulk ZnS particles formed by mixing solutions A and B together to form a slightly cloudy white solution. The white color indicated the formation of ZnS nanoparticles (Kurt Winkelmann et al., 2007).

$$
\text{ZnCl}_2 + \text{Na}_2\text{S} \rightarrow \text{ZnS} + 2\text{NaCl}
$$

Zinc Sulfide nanoparticles were also prepared by the same method without adding CTAB.

3. Instrumentation

Characterization of the above mentioned nanoparticles has been carried out using different techniques: FTIR spectroscopy and UV-VIS absorption spectroscopy. Samples for FTIR analysis were prepared in the form of pellets. Powder samples of nanoparticles were mixed with KBr powder and pellets were formed. Shimadzu Fourier Transform Infrared Spectrometer (IR Affinity-1) was used to record the spectra. The sample was analyzed using Shimadzu UV-1800 Spectrophotometer.

4. Results and Discussion

Nanoparticles of semiconductors have been investigated for a longtime for their optical properties. FTIR spectral analysis showed peaks at 352.02 cm$^{-1}$ and 611.46 cm$^{-1}$ for zinc sulfide with CTAB corresponding to Zinc and sulfide stretching. There were few absorption peaks between 400-4000 cm$^{-1}$, indicating that the prepared nano–ZnS was a nicer infrared-transmittance material (Aneeqa Sabah et al., 2010). For zinc sulfide without CTAB, the same stretching frequencies were observed at 350.10 cm$^{-1}$, 615.32 cm$^{-1}$ and also some peaks around 400-4000 cm$^{-1}$. It indicated the formation of Zinc sulfide nanoparticles. The FTIR spectrum is given in figures 1 and figure 2. UV Spectrometric analysis showed that as particle size is reduced below the Bohr size of exciton, the energy gap increases and can be observed as shift in the absorption edge (Bangal and Ashtaputre, 2005). Band gaps for Zinc Sulfide (with and without CTAB) were 5.48 eV and 5.99 eV, respectively which was much increased from band gap for bulk ZnS (3.68 eV). From figures 3 and 4 the absorption spectra for Zinc Sulfide (with and without CTAB) and nanoparticles was found to be well shifted from their bulk value. The well defined excitonic peaks for Zinc Sulfide at room temperature were observed since ZnS was in the form of nanoparticles.
Novel method to synthesize and characterize Zinc Sulfide nanoparticles R K

**Figure 1:** FTIR Spectrum of ZnS with CTAB

**Figure 2:** FTIR Spectrum of ZnS without CTAB

**Figure 3:** UV Spectrum of ZnS with CTAB
In all the cases, the optical absorption edge exhibited a blue shift with respect to that of bulk samples. The blue shift with the decrease in crystalline size should be attributed to the quantum size effects (Xu et al., 1998). When ZnS was prepared without CTAB, there was decrease in the size of the nanoparticle than when it was prepared with CTAB. Even though no capping agent, CTAB, was used in preparing ZnS, the particle size was well reduced. It was achieved by stirring the solutions during preparation. No agglomeration of Zinc Sulfide at room temperature were observed since ZnS was in the form of nanoparticles.

**Table 1: Synthesis of ZnS nanoparticles**

<table>
<thead>
<tr>
<th>ZnS</th>
<th>BAND GAP OF BULK (eV)</th>
<th>BAND GAP OF NANOPARTICLE (eV)</th>
<th>PARTICLE SIZE (nm)</th>
<th>ABSORPTION PEAK (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>With CTAB</td>
<td>3.68</td>
<td>5.48</td>
<td>1.57</td>
<td>227.30</td>
</tr>
<tr>
<td>Without CTAB</td>
<td>5.99</td>
<td>1.39</td>
<td>207.51</td>
<td></td>
</tr>
</tbody>
</table>
5. Conclusions

Zinc sulfide has band gap energy of 3.6 eV and is also most widely used nanomaterials in solar cells, electroluminescent devices for the cathode ray tube, field emission display, lasers, sensors, infrared windows, displays, photo conductors etc. A novel method was used to synthesize ZnS semiconductor nanoparticle. This work provided simple route for synthesizing nanoparticles without any capping agent (CTAB). It was a novel one, prepared without any capping agent, through eco-friendly path. The FTIR and UV-Spectrometric results confirmed that the particles were nanometric in size. This method would be utilized because of its advantages of simplicity and low cost as well as the better quality of production. Similar nanoparticles may also be prepared using this method.

6. References