

Influence of Ultrasonically Stabilized ZnS Nanoparticles on Structural Properties of Polyaniline

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Abstract: *Ultrasonically stabilized Zinc Sulfide (ZnS) nanoparticles have been incorporated in the polymeric chain of polyaniline by in-situ chemical oxidation method. ZnS nanoparticles have been synthesized by wet chemical precipitation method using DMF as a stabilizing agent. Composites of polyaniline with ZnS nanoparticles have been synthesized by varying weight percentage of ZnS nanoparticles with aniline monomer. Composites were subjected for structural and morphological studies in terms of XRD, UV-VIS, SEM and TEM. Broad peaks in XRD pattern of ZnS reveals the formation of nanosized particles of average diameter 10 nm which is also confirmed from TEM image. Homogeneous distribution of ZnS nanoparticles in PANI matrix was observed in SEM image. Measurement of DC conductivity shows enhanced conductivity for 10 % composite as compared to pure PANI and other composites.*

Keywords: Zinc Sulfide nanoparticles, nanocomposites, polyaniline, electrical conductivity.

1. Introduction

An organic polymer that possesses the electrical, electronic, magnetic and optical properties of a metal while retaining the mechanical properties, processability etc. associated with a conventional polymer is termed as 'Intrinsically Conducting Polymer' also known as Synthetic metal [1]. Their relative large conductivity, flexibility, low cost and light weight make conducting polymers much more desirable than metals in many applications. Among various conducting polymers discovered, polyaniline (PANI) is the forefront of research due to its easy processability, stability in ambient atmosphere and low cost with advanced electrical, optical and electrochemical properties [2]. As compared to saturated polymers (in which all of the four valence electrons of carbon are used up in covalent bonds), in conjugated polymers, the electronic configuration is fundamentally different. In conjugated polymers, the chemical bonding leads to one unpaired electron (π electron) per carbon atom. The electron delocalization provides the "highway" for charge mobility along the polymer chain. The conductivity of these polymers depends on the level of doping and the alignment of chains. Consequently doped conjugated polymers are good conductors.

Zinc Sulfide (ZnS) is the most studied and widely used II-VI class inorganic compound semiconductor due to its applications as fluorescent material and in photonic research [3,4]. ZnS has been synthesized as quantum dots, nanowires, nanobelts and nanocombs [5]. It is a wide band gap (3.68 eV) semiconductor having conductivity in the range 10^{-5} - 10^{-6} S/cm. PANI is regarded as amorphous or polycrystalline with electrical conductivity in the metallic regime. When conducting polymers are combined with inorganic

semiconductor nanoparticles, they show dramatic changes in their properties. Therefore it is thought worthwhile to synthesis composites of PANI with ZnS nanoparticles to study their structural and electrical transport properties, the knowledge of which would be useful in various applications.

2. Experimental

Cost effective and simple chemical precipitation method was used to synthesis ZnS nanoparticles using Zinc precursor and DMF (N, N Dimethyl formamide) as a stabilizing agent. Na_2S was used as a source of Sulphur ions. Nanosized ZnS powder was obtained by filtering, washing and drying the precipitate as usual. Being unstable; synthesized Nanoparticles was sonicated for 3 hrs. to ensure the uniform size distribution. Polyaniline have been synthesized by in-situ chemical oxidation polymerization method in acidic aqueous medium. [6] Ammonium persulphate was used as oxidizing agent. In-situ polymerization of the monomer (aniline) was initiated by the dropwise addition of persulphate with constant stirring at room temperature. During this stirring for one hour, synthesized ZnS powder was added in different amount with aniline monomer for composite synthesis. After continuous stirring for 2 hours, the precipitate was left for overnight. Then it is filtered, washed with 1 M H_2SO_4 and distilled water and then methanol until the filtrate was colourless to ensure the complete removal of oligomers and impurities. Precipitate was then dried in vacuum oven for 12 hours at 80 °C to obtain dried greenish powder of polyaniline and its composites.

Synthesized ZnS nanoparticles, PANI and PANI-ZnS nanocomposites were subjected for characterization. X-ray

diffraction pattern were recorded on Philips-PW-700 automatic X-ray diffractometer using $\text{CuK}\alpha$ radiation of wavelength $\lambda=0.1540 \text{ \AA}$ and a continuous scan of $2^\circ/\text{min}$. at 35 Kv and 20 ma. UV-VIS spectra were recorded on UV-1800 Shimadhu double beam spectrophotometer in DMF. Morphological study was done using SEM technique by JSM-6380A Scanning Electron Microscope having resolution of 3.0 nm and TEM analysis with Transmission Electron Microscope PHILIPS model- CM200 with resolution 2.4 \AA . The dry powder was made in to pellet using hydraulic press. Electrical conductivity was measured using four probe method within the temperature range 303K-398K

3. Results and Discussion

Crystalline nature and diffraction pattern of ZnS, PANI and their composites (10%) is in figure 1. Diffraction pattern of ZnS shows broad peaks at 2θ values of 28.66° , 47.56° and 56° corresponding to the reflections from (111), (220) and (311) planes. The broadness of peaks indicates the formation of nanostructured ZnS. The particle size was calculated using Scherrer's equation [7] which is around 8.7 nm. PANI salt shows two peaks around $2\theta = 20^\circ$ and 26° which are attributed to the periodicity perpendicular and parallel to the polymer chain [8, 9]. Polyaniline is polycrystalline and reported to have orthorhombic crystal structure [10]. However the variation in polymerization condition by the addition of ZnS powder has promoted some rearrangement of the polymer chain observed in the XRD spectra of composite.

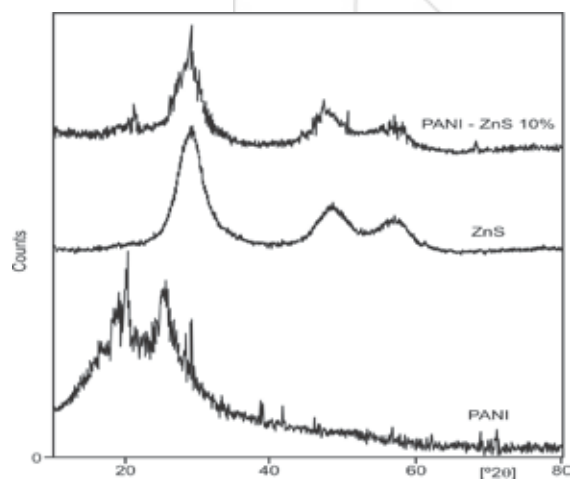


Figure 1: XRD pattern of PANI, ZnS and PANI-ZnS -10% nanocomposite

It is observed that introduction of ZnS in the PANI matrix has increased crystallinity and shows corresponding peaks of ZnS over the pure PANI. Also it was observed that as the weight % of ZnS increases, the peaks due to PANI has been reduced significantly and crystalline nature of ZnS starts dominating. This indicates the ordered structure of composites as compare to PANI and strong interfacial interaction of nanosized ZnS with PANI matrix. Hence such composites possess dual advantages of low dimension and ordered organic conductor may be useful in fabrication of nanoelectronic devices.

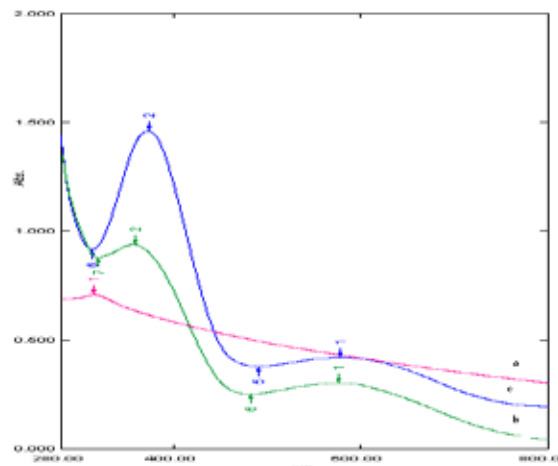


Figure 2: UV-VIS spectra of (a) ZnS, (b) PANI and (c) PANI-ZnS 10% nanocomposites.

UV-VIS absorption spectra of ZnS, PANI and PANI-ZNS 10% nanocomposites are shown in figure 2. The maximum in absorption spectra observed at 310 nm for synthesized ZnS indicates the blue shift in absorption maxima as compare to bulk. (337 nm). The blue shift in absorption maxima and increased band gap energy up to 4.01 eV also confirms the formation of nanosized ZnS particles. The spectrum of PANI shows the presence of two absorption bands, one in the UV region and other in the visible region. The band at 330 nm in the UV region corresponds to $\pi-\pi^*$ transition (from the valence band to the conduction band) and the band in the visible region at 585 nm corresponds to inter ring charge transfer associated with excitation from benzenoid to quinoid moieties [6]. The incorporation of the ZnS nanoparticles in the PANI matrix have a large influence on the absorption spectra. The intensities and the positions of these absorption peaks depends on the length of the conjugated systems, the longer such a system, the longer the wavelength. The increased absorption intensity in case of composite indicates the formation of more number of polaron and bipolarons which are the charge carriers in conducting polymers as compare to pure PANI which is in consistent with the increased value of electrical conductivity for composite containing 10% filler particles.

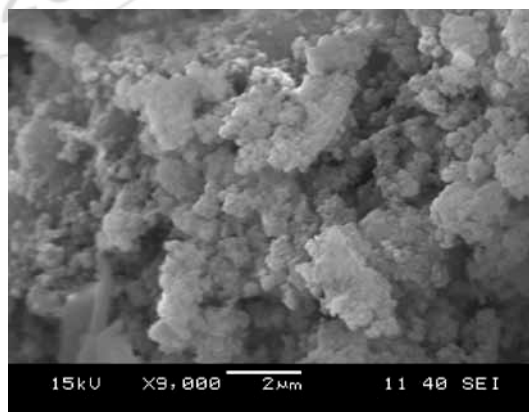


Figure 3: SEM image of PANI-ZnS nanocomposites.

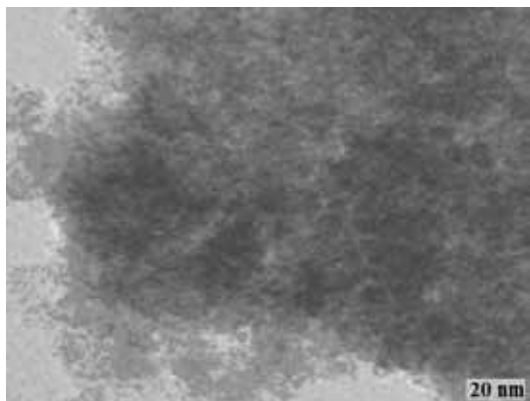


Figure 4: TEM image of ZnS

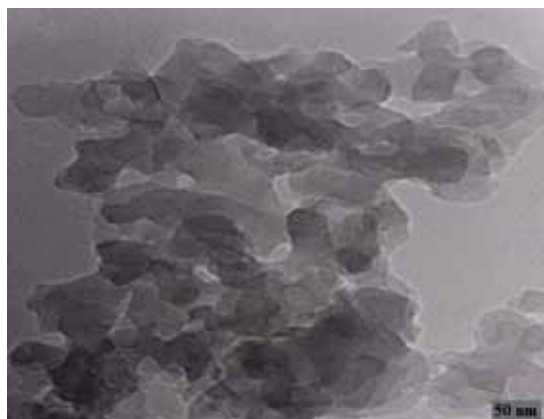


Figure 4: TEM image of PANI-ZnS nanocomposites

Morphological study in terms of Scanning Electron Microscopy of the composite shows the homogeneous distribution of ZnS particles in the PANI matrix as shown in figure 3. A TEM image (fig.4) of composite reveals the nanosized ZnS particle covered with PANI. To study the charge transport mechanism and to find the transport parameters, temperature dependent electrical conductivity of PANI and all composites have been studied. Figure 5 shows the thermal conductivity behavior of PANI and composites.

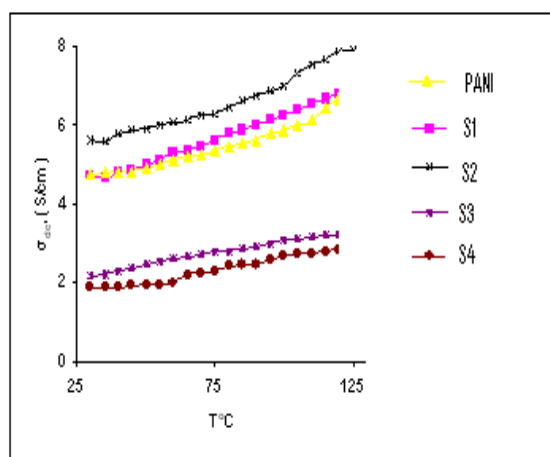


Figure 5: Variation of conductivity with temperature (S1=PANI-ZnS 5%, S2=PANI-ZnS 10%, S3=PANI-ZnS 15%, S4=PANI-ZnS 20%)

It is observed that conductivity increases exponentially with rise in temperature which is similar to semiconducting nature of the materials. Also it is found that, though the observed conductivity of the ZnS is very low (4.7×10^{-5}

S/cm) as compare to PANI (fig.6), a composite containing 5% and 10% ZnS nanoparticle shows higher electrical conductivity as compared to pure PANI. Thereafter conductivity decreases as the filler concentration increases up to 20%. The sudden increase in the conductivity for a particular concentration of nanofillers (here 10%) could have been explained by percolation threshold [11, 12] which predicts that at a certain amount of concentration of filler, a full conducting path is formed for the flow of current and conductivity rises. We may conclude that, this concentration of nano filler is favorable for the formation of large number of polarons and bipolarons which in turn increases the conductivity. The linear graphs between $\log \sigma$ Vs temperature implies that conduction in PANI and composites is carried out predominantly by hopping mechanism i.e. polarons acts as charge carriers hopping from state to state.

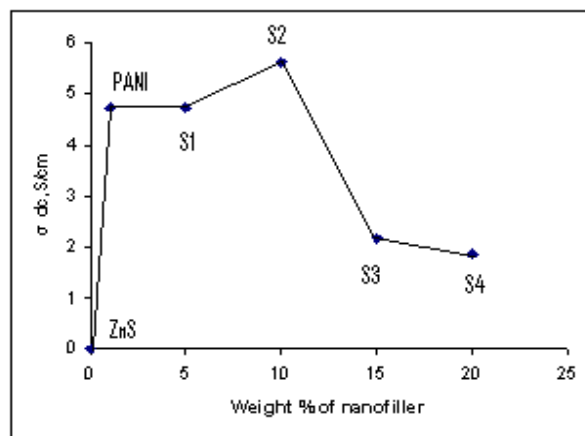


Figure 6: Plot of dc conductivity of composites versus weight % of ZnS nanofillers

4. Conclusions

Nanosized ZnS particles have been synthesized by precipitation method. Polyaniline and a series of PANI-ZnS nanocomposites with different weight % have been synthesized by in-situ polymerization method. The study of X-ray diffraction and UV-VIS absorption spectroscopy reveals the well incorporation of the nano sized ZnS in the PANI matrix and effects the structural and optical properties of polyaniline. The enhanced electrical conductivity for the composites of 5% and 10% with ordered structure compared to pure PANI may be applicable in the nanoelectronic devices which have the dual advantages of low dimension and organic conductor. The analysis of conductivity variation with temperature suggests that the charge transport mechanism in PANI and all composites can be explained by variable range hopping model.

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