Electrical and optical studies in polyaniline nanofibre–SnO₂ nanocomposites

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Abstract. Polyaniline nanofibre–tin oxide (PAni–SnO₂) nanocomposites are synthesized and mixed with polyvinyl alcohol (PVA) as stabilizer to cast free-standing films. Composite films are characterized by X-ray diffraction studies (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), photoluminescence spectroscopy (PL) and UV-visible spectroscopy. XRD confirms the formation of PAni nanofibre–SnO₂ nanocomposite. From TEM images, diameter of the polyaniline nanofibre and SnO₂ nanoparticles in the PAni–SnO₂ nanocomposite are found to be 20–60 nm. SEM results show fibrous morphology of the PAni nanofibre and spherical morphology of polyaniline–SnO₂ composites. The nanocomposites exhibit high relative photoluminescence intensity in violet as well as green–yellow region of visible spectrum. From electrical conductivity measurement, it is confirmed that PAni nanofibre–SnO₂ nanocomposite follows Mott's one-dimensional variable range hopping (VRH) model.

Keywords. Polyaniline nanofibres; tin oxide; nanocomposites; photoluminescence; TEM; UV-vis spectroscopy.

1. Introduction

Nanocomposites are a special class of materials originating from suitable combinations of two or more nanosized objects by some suitable techniques resulting in materials having unique physical properties and wide application potential in diverse areas (Gangopadhyay and De 2000). There is a growing interest in combining both organic and inorganic materials to synthesize nanocomposites for applications in electronics and photonics (Su and Kuramoto 2000). Preparation of composites of polyaniline (PAni) has been considered to improve the processibility of PAni. These composites have the ability to enhance their material properties with desirable mechanical and physical characteristics (Raghavendra *et al* 2003). PAni is an unique and one of the most technologically promising conducting polymers because of its ease of preparation, low cost, high environmental stability, relatively stable electrical conductivity and especially for its very simple acid doping and base de-doping chemistry. Since the conductivity of PAni depends on both the oxidation state of the main polymer chain as well as the degree of protonation of the imine sites (MacDiarmid 2001), any interaction with PAni that alters either of these processes will affect its conductivity. PAni has a great variety of potential applications including anticorrosion coatings, batteries, sensors, separation membranes and antistatic coating (Chandrasekhar 1999). It is reported that PAni shows photoluminescence indicating existence of multiple electronic states including polaron bands, defect bands and con-

duction bands (Sharma *et al* 2006). PAni–semiconductor nanocomposites have become increasingly popular materials for applications in sensors, EMI shielding and antistatic coating due to enhanced processibility and protection of the semiconductor nanocomposites and conducting nature of host polymer. PAni is a good candidate for serving as the host matrix for inorganic semiconductors in optoelectronic applications because of its hole-conducting ability, when combined with the electron-conducting inorganic semiconductors, can increase the radiative electron–hole recombination rate so as to improve the optoelectronic performance of the inorganic semiconductors (Gaponik *et al* 2000). Semiconducting nanocomposites of PAni with inorganic semiconductors like cadmium sulphide (Lu *et al* 2005), cadmium telluride (Gaponik *et al* 1999), zinc oxide (Zheng *et al* 2002), zinc sulphide (Pant *et al* 2006) and titanium dioxide (Ganesan and Gedanken 2008) have been reported for diverse applications in optoelectronics.

In recent years, functional metal oxides have received increasing attention due to their unique physical properties (Ge *et al* 2006). Functional oxides have two structural characteristics: cations with mixed valence states and anions with deficiencies (vacancies). By varying either or both of these characteristics, the electrical, optical, magnetic and chemical properties can be tuned, giving the possibility of fabricating smart devices that utilize the semiconductivity, superconductivity, ferroelectricity and/or magnetism offered by the oxides (Wang and Kang 1998). Among the technologically promising functional metal oxides, tin oxide (SnO₂) has received a great deal of attention as a transparent conductor due to its applications in various opto-electronic devices including flat panel displays, photoconductors and solar cells

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(Amin *et al* 2001). SnO_2 is a *n*-type semiconductor with a bandgap of 3.6 eV at 300 K, whereas PANi is a typical conductive polymer which is usually considered as a *p*-type material (Dey *et al* 2004).

In view of the foregoing, by synthesizing a nanocomposite of semiconducting material, SnO_2 and conducting polymer, PANi, the electrical, optical and stability of the system can be enhanced. In the present work, we report the development of organic–inorganic PANi nanofibre– SnO_2 hybrid nanocomposite in polyvinyl alcohol with a view to study its structural, electrical and optical properties.

2. Experimental

Aniline monomer (Sigma-Aldrich), ammonium peroxy disulphate (APS) (Merck), benzene (Sisco Research Lab), tin chloride dihydrate (Merck), ethanol (Changshu Yangyuan Chemical, China), tetrabutyl ammonium hydroxide (Merck), hydrochloric acid (HCl) (Qualigens Fine Chemicals) and polyvinyl alcohol (PVA) (BDH) (molecular weight = 11,000–31,000, degree of hydrolysis = 98–98.8%) were used as received. SnO_2 nanocolloids were prepared by a colloidal process described elsewhere (Dutta and De 2007). 0.1 M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 50 ml ethanol under constant magnetic stirring. 10 ml double distilled (DD) water was added drop wise to the ethanol solution to keep chemical homogeneity. Addition of 0.01 M tetrabutyl ammonium hydroxide as a surfactant to the above solution produced smaller SnO_2 colloidal particles. 0.1 M HCl was added to keep pH of the solution below 4.

Polyaniline nanofibre– SnO_2 nanocomposite was synthesized by interfacial polymerization technique. At first, 1M aniline was dissolved in 10 ml benzene. 0.25 M Ammonium peroxy disulphate (APS), 5 ml SnO_2 colloids and 1 M HCl were dissolved in 10 ml DD water. Both the solutions were added, in a glass vial to make an interface. As soon as the solutions were added, a green line appeared at the interface indicating the beginning of formation of PANi, which being hydrophilic moved into water allowing further polymerization at the interface and suppressing secondary growth (Huang 2006). PANi nanofibre– SnO_2 composite was washed with DD water, filtered with Whatman filter paper and dried. 10 Wt% of nanocomposite powder was added to 20 ml 4% PVA and stirred for 6 h at room temperature. Films were cast on clean glass plates and dried in a dessicator. PANi nanofibres without SnO_2 colloids were also prepared by interfacial polymerization technique and 10 wt% of PANi nanofibres were mixed with 20 ml 4% PVA to get PANi films.

XRD studies on PANi nanofibre, SnO_2 and PANi nanofibre– SnO_2 were carried out using Rigaku X-ray diffractometer (model MINIFLEX)-200. SEM micrograph was taken using JEOL–JSM 6390 LV scanning electron microscope. TEM images were taken using JEOL–TEM-100 CXII (carbon coated copper grids) in SAIF, Shillong. The UV-vis spectroscopic measurements were conducted on aqueous dispersion of PANi nanofibre, SnO_2 colloids and PANi

nanofibre– SnO_2 nanocomposite using UV-1700 spectrometer. The PL spectra were taken on films of SnO_2 , PANi nanofibre and PANi nanofibre– SnO_2 nanocomposite using Perkin Elmer LS-55 fluorescence spectrometer. Electrical conductivity was measured using four-probe technique.

3. Results and discussion

3.1 Structural and morphological studies

Figure 1 shows X-ray diffraction patterns of (a) PANi nanofibre, (b) PANi nanofibre– SnO_2 composite and (c) SnO_2 . In figure 1(a), the broad characteristic peak of polyaniline at 26° indicates the formation of nanofibres. In figure 1(c) all the diffraction lines are assigned to the tetragonal rutile crystalline phase of tin oxide with peak positions at $2\theta = 11.55^\circ$ (110), 23.52° (211), 35.48° (222), 47.97° (422). In figure 1(b), all the XRD peaks characteristics of SnO_2 and PANi are present, which confirm the formation of PANi nanofibre– SnO_2 nanocomposite.

The diameters of PANi nanofibres and SnO_2 nanoparticles were estimated using the Scherrer formula:

$$D = 0.9\lambda / \beta \cos \theta, \quad (1)$$

where λ , β and θ are the X-ray wavelength ($1.5405 \text{ \AA}$ for $\text{CuK}\alpha$), the full width at half maximum (FWHM) of the diffraction peak, and Bragg diffraction angle, respectively. The polyaniline nanofibre diameters are in the range of 40–60 nm and the particle size of SnO_2 particles is calculated to

Figure 1. XRD spectra of (a) PANi nanofibre, (b) PANi nanofibre– SnO_2 nanocomposite and (c) SnO_2 .

be in the range of 20–50 nm, which is quite consistent with TEM results.

The scanning electron micrograph of PANi nanofibre–SnO₂ composite is shown in figure 2. The micrograph shows porous microstructure in which SnO₂ nanoparticles are dispersed in fibrous PANi forming a nanocomposite. The transmission electron micrographs of PANi nanofibres and PANi–SnO₂ nanocomposite are shown in figure 3(a and b), respectively. Figure 3(a) shows that the diameters of PANi nanofibres synthesized by interfacial polymerization technique are in the range of 40–60 nm. In the PANi nanofibre–SnO₂ nanocomposite, polymerization of PANi takes place in the presence of spherical SnO₂ nanoparticles of size 30–50 nm entrapping them inside PANi nanofibre chains, thus forming true nanocomposites as observed in figure 3(b).

3.2 Optical properties

Figure 4(a) shows UV-vis absorption spectrum of PANi nanofibres. The PANi nanofibres which are synthesized in the emeraldine salt form, in their ‘compact coil’ conformation, exhibits three prominent peaks (Xia *et al* 1995). The absorption peak at around 300 nm is attributed to the $\pi - \pi^*$ band transitions. The peak at around 440 nm is due to π -polaron band transitions and the peak at 800 nm is due to the polaron band– π^* transitions. The absorption bands obtained from the UV-visible spectra are consistent with that reported in the literature (Xia *et al* 1995). Although theoretical calculations predict that the bipolaron state is energetically more favoured than the polaron (Angelopoulos *et al* 1988), it is widely agreed that polarons are the charge carriers responsible for high conductivity in PANi (Epstein *et al* 1987; Nakajima and Kawagoe 1989; Watanabe *et al* 1989). It has been proposed that the presence of coulombic interactions, dielectric screening and local disorder in the PANi lattice act to stabilize the delocalized polaron state (Bonnell and Angelopoulos 1989).

Figure 2. Scanning electron micrograph of PANi nanofibre–SnO₂ nanocomposite.

Figure 3. Transmission electron micrographs of (a) PANi nanofibre and (b) PANi nanofibre–SnO₂ nanocomposite.

In the UV-vis spectra of pure SnO₂ in figure 4(c), a strong peak is observed around 240 nm with a blue shift of energy of 0.83 eV with respect to bulk SnO₂ ($E_g = 3.6$ eV) indicating particle size of SnO₂ in the nanorange. In the UV-vis spectra of PANi nanofibre–SnO₂ nanocomposite in figure 4(b), all the peaks of PANi nanofibres as well as strong peak due to SnO₂ are observed indicating the formation of PANi nanofibre–SnO₂ nanocomposite.

Figure 5(a) shows PL spectrum of SnO₂ excited with an excitation wavelength of 228 nm. It shows a broad peak centred at 610 nm. This peak might be related to the crystalline defects introduced during the growth of SnO₂. The oxygen vacancies interact with interfacial tin vacancies leading to the formation of a considerable amount of trapped states within the bandgap, which results in a PL signal in SnO₂ (He *et al* 2006). The PL spectra for PANi nanofibre and PANi nanofibre–SnO₂ nanocomposite are shown in figures 5(b, c) with an excitation wavelength of 228 nm. The peak at 414 nm in figure 5(b) for PANi arises due to transitions from the polaronic band to the π -band (HOMO) band structures of PANi (Sharma *et al* 2006). In figure 5(c) photoluminescence peaks at 503, 511 and 528 nm are observed. Figure 5(b, c) shows that the PL intensity is increasing in the PANi nanofibre–SnO₂ nanocomposite in both violet and green–yellow region

Figure 4. UV-vis spectra of (a) PANi nanofibre, (b) PANi nanofibre-SnO₂ nanocomposite and (c) SnO₂.

of visible spectrum, which may be attributed to formation of more density of states in the energy band upon the addition of SnO₂. There are electron donating groups such as =NH in PANi and SnO₂ is an electron conducting semiconductor. This combination enhances the electron mobility in the composites. This in turn favours the formation of singlet excitons. The singlet exciton states so formed decay radiatively to the ground state resulting in enhanced photoluminescence (Wise *et al* 1998). The relative intensity of 610 nm SnO₂ PL peak is considerably lower as compared to the relative peak intensity of PANi nanofibres, so it is not prominent in the PANi nanofibre-SnO₂ nanocomposite. Stafstorm and co-workers predicted the existence of lower energy transitions (1.8 and 2.8 eV) due to the polaron bands and higher energy transitions (4.1 eV) from the upper defect band to the conduction band (Stafstorm *et al* 1987). Exact correlation with the results of Stafstorm is not possible in PANi nanofibre and PANi nanofibre-SnO₂ nanocomposite due to disorder within the PANi nanofibrous structure and presence of dopant can also affect the energetic positions involved in practical situation. The presence of distinct peaks in the PL spectra indicates the possibility of the existence of multiple electronic states participating in the photo-excitation process (Sharma *et al* 2006).

3.3 Electrical properties

The temperature dependence of d.c. conductivity for PANi nanofibre and PANi nanofibre-SnO₂ nanocomposite is shown in figure 6. The figure shows that both PANi nanofibres and PANi nanofibre-SnO₂ nanocomposite samples are semiconducting in nature and the conductivity is higher for PANi nanofibre-SnO₂ nanocomposite as compared to that for

Figure 5. PL spectra of (a) SnO₂, PL spectra of PANi nanofibre and PANi nanofibre-SnO₂ nanocomposite in (b) violet region and (c) green-yellow region.

PANi nanofibre. The room temperature d.c. conductivity for PANi nanofibre and PANi nanofibre-SnO₂ composite are calculated to be $7.19 \times 10^{-4} \text{ Scm}^{-1}$ and $1.22 \times 10^{-3} \text{ Scm}^{-1}$,

Figure 6. Temperature dependence of σ electrical conductivity ($\ln \sigma$ vs $10^3/T$) of PANi nanofibre and PANi nanofibre–SnO₂ nanocomposite.

respectively. Due to introduction of SnO₂, electronic density of states are increasing in the polaronic band between the π – π^* HOMO–LUMO structure of PANi at the PANi nanofibre–SnO₂ interface. This results in an increase in conductivity not only by increasing the carrier concentration but also by increasing the mobility which renders the interchain charge transport more efficient (Luthra *et al* 2003).

The temperature dependence of conductivity can be best fitted within the experimental error with one-dimensional phonon assisted Mott's variable range hopping (VRH) model:

$$\sigma = \sigma_0 \exp[-(T/T_0)^{1/2}], \quad (2)$$

where pre-exponential factor $\sigma_0 = e^2 N(E_F) R v_{ph}$, R the average hopping distance:

$$R = [8/9 \pi \alpha N(E_F) kT]^{-1/2} \text{ and } T_0 = 8^3 \alpha^3 / 9 \pi k N(E_F),$$

where $N(E_F)$ is the electronic density of states at the Fermi energy, α the inverse localization length (spatial extension of localized wave function), e the electronic charge, v_{ph} the typical frequency ($\approx 10^{13}$ Hz), T_0 the characteristic Mott temperature which corresponds to the hopping barrier for charge carriers (also known as the pseudo activation energy) and measures the degree of disorder (Mott and Davis 1979; Roth and Carroll 2004). From the linear curve fitting of $\ln \sigma$ vs $T^{-1/2}$, σ_0 and T_0 are found to be $4.197 \times 10^{-3} \text{ Scm}^{-1}$ and 78.14 K, respectively for PANi nanofibre and $4.279 \times 10^{-3} \text{ Scm}^{-1}$ and 41.25 K for PANi nanofibre–SnO₂ nanocomposite. The size of hopping barrier, T_0 , is smaller in the PANi nanofibre–SnO₂ nanocomposite as compared to PANi nanofibre. This enhances the hopping rate between adjacent localized states and leads to an increase in electrical conductivity in PANi nanofibre–SnO₂ nanocomposite (Mott and Davis 1979).

4. Conclusions

Polyaniline nanofibre–SnO₂ nanocomposites are synthesized by interfacial polymerization technique. XRD and TEM confirm the formation of nanocomposites with diameters of PANi nanofibre and SnO₂ nanoparticles in the range of 20–60 nm. PL spectra shows an increase in relative photoluminescence intensity in PANi nanofibre–SnO₂ nanocomposite in violet and green–yellow region of visible spectrum as compared to that for pure PANi nanofibre. Temperature dependence of electrical conductivity of the PANi nanofibre–SnO₂ nanocomposite fits the one-dimensional Mott's variable range hopping model. From this model, it can be concluded that the increase in electrical conductivity in the PANi nanofibre–SnO₂ nanocomposite is due to decrease of hopping barrier as a result of more number of density of states introduced by SnO₂ in the PANi nanofibre–SnO₂ interface. This nanocomposite can be used to fabricate optoelectronic devices with enhanced electrical and optical properties.

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