**NiS/SnS Core-Shell Embedded Polyaniline Composite: Synthesis and Characterization**

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**Abstract**

Solar cell is a key topic of energy technology research. Recently, low dimensional nanostructure has brought up much attention to fabricate photovoltaic devices. Using nanostructure materials can improve not only efficiency but reduce the cost and size. The room temperature synthesis and characterization of the conducting polyaniline (Pani) films embedded with Co\(^{2+}\) doped, PVA capped NiS/SnS core-shell particles as photoluminescent boosters is reported. The photoluminescence intensity of the core-shell particles-Pani film had increased significantly. The scanning electron micrographs revealed core-shell structure and their periodic arrangement in the polymer matrix. The charge transfer resistance of the film was found to be 438 \(\Omega\). Periodic arrangement of the nanoclusters of the core-shell particles in the continuous conductive polymer matrix and high carrier density promise this material for the photovoltaic applications.

**Keywords:** Core-shell, Composite Materials, Polymers, Luminescence, Optical Properties.

**1. Introduction**

Semiconductor/polymer composites have been extensively investigated during the last decade due to their improved performance and potential applications. Composite materials made of conjugated polymer and metal sulphide quantum dots imparts unique opportunities for the fabrication of novel devices. The presence of conjugated \(\pi\) electrons along the backbone of the polymers provides them the ability to support positive as well as negative charge carriers with high mobility along the chain. Interesting and unique physical properties are expected when the delocalized carriers interact with the semiconductor quantum dots. Potential areas of application of composite materials include nanoelectronics, low voltage flat panel displays, sensors, etc\(^1\)\(^-\)\(^5\).

Pani is the most promising organic conducting polymer\(^6\) for electronic applications due to its combination of electrical conductivity and environmental stability\(^7\)\(^-\)\(^9\). Various metal chalcogenide/polymer nanocomposites with desired functions have been prepared via an in situ reaction, such as II–VI sulfide/polymer nanocomposites\(^10\)\(^,\)\(^11\). Compared to their individual constituents, the core-shell particles exhibit better physical and chemical properties thereby widening their applications range\(^12\). Significant efforts are devoted to fabricate core-shell colloidal sulphides with custom-specific structural, optical and surface properties\(^13\)\(^,\)\(^14\). Among the various metal sulphides, nickel sulphide is one of the promising candidates\(^15\)\(^-\)\(^18\). As the size and extent of aggregation of the particles play a significant role in the optical properties, stabilization of the particles in suitable matrix is essential. The large surface to volume ratio in nanocomposites enables an efficient separation of photo-induced charges which is important for photovoltaic applications\(^19\)\(^,\)\(^20\). Efficient harnessing of solar energy through photoelectrochemical route is a promising option to meet the increasing energy demands. Conducting and luminescent boosters in such systems will pave way for their enhanced efficiency. In this paper, we report a polymer-controlled growth strategy to prepare NiS/SnS...
core-shell particles embedded Pani composite films using polyvinyl alcohol (PVA) as the polymer-controller matrix by in situ method.

2. Experimental

Polyvinyl alcohol (Kemphasol Chemical Ltd.), nickel chloride (Fischer Ltd.), cobalt chloride (Fischer Ltd.), stannous chloride (Fischer Ltd.), aniline hydrochloride (Fischer Ltd.) and ammonium persulphate (Fischer Ltd.) were used for preparation without any further purification. All chemicals used were of AR grade. Hydrogen sulfide was prepared in laboratory using Kipp’s apparatus. Double distilled water was used for the preparation of the solutions. 20 ml of 0.1 M of nickel chloride was added to 10% PVA solution followed by the addition of 20 ml of 0.25% cobalt chloride solution, H₂S gas and 11.5 ml of 2% stannous chloride dehydrate under constant stirring conditions. The colloidal solution obtained was sonicated for 5 minutes and then added to 25ml of aniline hydrochloride (0.2M) solution. 25 ml of ammonium persulphate (0.25M) solution was added under constant stirring conditions. The solution was stirred for 30 minutes to allow the polymerization to complete. From this solution free standing films of the core-shell composites embedded in Pani were formed by casting. The films were rinsed with dilute hydrochloric acid for the purpose of doping Pani. Pani film was washed with acetone to remove the oligomers. The film was dried at 80 °C in an oven and used for further studies. The sequence of steps involved in the synthesis is given in flow chart (Figure 1).

3. Result and Discussion

3.1 UV Spectra

Figure 2 shows the optical absorption spectra of NiS, NiS:Co, NiS:Co/SnS core-shell colloids along with that of Pani and Pani loaded with the core-shell colloids. An increase in absorbance is observed for the Co²⁺ doped NiS colloidal particles (Figure 2a, 2b). With the outer coverage SnS, the absorbance increases further (Figure 3c). For bulk NiS, CoS and SnS, the absorption edges are at 350 nm, 347 nm and 954 nm respectively. Blue shift in the absorption edge for NiS (280 nm, Figure 3a) and NiS:Co (255 nm, Figure 3b), from the corresponding bulk values, implies the quantum confinement effect of the nanoscale particles²⁳. No other exciton peak or another steep edge in the UV region of the optical absorption spectra was observed indicating the absence of isolated SnS nanoparticles²⁴. The absorption spectra of NiS in Pani (Figure 2d), NiS:Co in Pani (Figure 2e) and NiS:Co/SnS in Pani (Figure 2f) are shown in Figure 2. The Pani-colloid composite shows a wide absorption spectrum (Figure 2f) in the UV-Visible and near IR regions, suitable for harvesting of solar energy. The absorption spectrum of Pani is also shown for comparison (Figure 2g). The role of NiS:Co/ SnS core-shell in increasing in the absorption intensity of Pani is evident from Figure 2f. In the absorption spectrum of Pani, the peak at 328nm is due to the π-π* transition within the benzenoid segment. The second shoulder-like absorption band at 450 nm is attributed to the doping level of Pani and the third absorption peak around 800 nm is related to the formation of localized polaron at the backbone of the polymer. The observed three characteristic peaks in absorption spectra indicate only pure Emeraldine Salt (ES) formed in the system without the formation of Emeraldine Base (EB) or Leucoemeraldine Base (LB) of Pani. The absorption peaks in core-shell composite embedded in Pani are due to the synergetic effects of polyaniline and the core-shell materials. The
core-shell composite embedded in Pani shows a wide absorption spectrum in the UV-Visible and near infrared regions, much favourable for the photoelectrochemical harvesting of solar energy.

Band gap energy and transition type was derived from mathematical treatment of the data obtained from the optical absorbance versus wavelength data with the following relationship for near-edge absorption:

\[ \alpha = \frac{k(h\nu - E_g)^{n/2}}{h\nu} \]  

where, \( \alpha \) is absorption coefficient (cm\(^{-1}\)), \( h \) is the Plank’s constant; \( \nu \) is the frequency of radiation (Hz), \( E_g \) is the energy band gap (eV) for direct band gap semiconductor, \( k \) equals a constant while \( n \) carries the value of either 1 or 4. The bandgap, \( E_g \), could be obtained from a straight line plot of \((\alpha h\nu)^{2/n}\) as a function of \( h\nu \). Extrapolation of the line to the base line, where the value of \((\alpha h\nu)^{2/n}\) is zero, will give \( E_g \)\(^2\). If a straight line graph is obtained for \( n = 1 \), it indicates a direct electron transition between the states of the semiconductor, whereas the transition is indirect if a straight line graph is obtained for \( n = 4 \). Figure 3 shows the Tauc plot for NiS:Co/SnS-Pani system. Extrapolation of the straight line portion of the graph to \( \alpha = 0 \) gives a band gap energy of 2.50 eV for NiS:Co/SnS-Pani. The straight line behaviour infers the direct transition between the states of the semiconductor composite.

Figure 2. UV-Visible absorption spectra of (a) NiS (b) NiS:Co (c) NiS:Co/SnS (d) NiS-Pani (e) NiS:Co-Pani (f) NiS:Co/SnS-Pani (g) Pani.

Figure 3. Tauc plot for NiS:Co/SnS-Pani.
3.2 Photoluminescence

The PL spectra for NiS, CoS, SnS, NiS:Co, NiS:Co/SnS core-shell particles and NiS:Co/SnS-Pani is shown in Figure 4 at an excitation wavelength of 300 nm. The PL spectrum of NiS (Figure 4a) shows the blue band at 431 nm (2.87 eV) due to the band-edge emission, with about 1.07 eV blue shift compared to the bulk crystal (1.8 eV) due to the quantum size effect. The PL spectra for CoS (Figure 4b) shows the near band edge intense emission at 404 nm and a weak emission at 808 nm while NiS:Co (Figure 4d) exhibits sharp emission peak at 500 nm. The PL spectrum of SnS shows peaks at 326 nm and 354 nm. The PL spectrum of NiS:Co/SnS (Figure 4e) exhibits strong and broad peak centered at about 523 nm with increased photoluminescence emission. For the physically mixed system of NiS and SnS, the PL intensity would register a decrease at their characteristic emission peaks whereas for the core-shell formation the PL intensity increases. While the doping of NiS with Co$^{2+}$ had red shifted the PL peak, shell formation with SnS has enormously increased the emission intensity over the visible range and hence acts as the booster for the incident visible light much preferred for the photoelectrochemical systems. Addition of Pani suppresses the photoluminescence (Figure 4f). The decrease in the PL intensity values at all wavelengths is due to fact that Pani is non-fluorescent and it disallows the recombination of photogenerated charges.

3.3 XRD Studies

X-ray powder diffraction (XRD) analysis was carried out to investigate the phase of the NiS:Co/SnS-Pani composite. A typical XRD pattern of the film is shown in Figure 5. Particle size of about 96 nm was evaluated by Scherrer equation. Peaks have been indexed and suggest that the core material formed was NiS with rhombohedral crystal structure with cell parameters $a = 9.620$ Å and $c = 3.149$ Å, which are close to the data in JCPDS card no. 12-0041 and also reported by Qingtao Pan et al. Separate peaks characteristic of CoS or SnS are not observed. The presence of a small foreign ion inclusion or a shell layer over the core does not affect the XRD peaks of the core particles.

3.4 SEM Analysis

Scanning electron microscopy is a convenient technique to study the microstructure of thin films. Figure 6 shows the scanning electron microscopic image of the NiS:Co/SnS-Pani film at three different magnifications. The
uniform distribution of the core/shell particles is well evident. The luminescence and the spatial arrangement facilitating multiple reflections are the factors responsible for the enhanced spectral response of the composite film. SEM provides evidence for the stabilization of the core/shell particles-Pani composite by its periodic arrangement. The particle size is about 300 nm whereas the rods are 4-5μm long and 300 nm wide. The contrast between the core and the shell are evident.

3.5 Mott-Schottky Plot

The Mott-Schottky plot was constructed of the inverse square of space charge layer capacitance measured at a fixed frequency of 10000 Hz as a function of potential. The paramagnetic characteristic of this composite material was also confirmed by the magnetic susceptibility measurement using Sherwood Auto MSB meter. The Mott-Schottky plot (Figure 7) shows a negative slope for the NiS:Co/SnS core-shell particles embedded Pani film indicating a typical p-type of the semiconductor. The flat-band potential, $E_{fb}$, is inferred from the intersection of the plot with the x-axis, as $E_{fb} = 3.55$ V. The carrier density is evaluated as $2.00 \times 10^{27}$.
3.6 AC Impedance

Features in the impedance spectra of electrochemical systems are related to physicochemical processes, occurring in the system when electric current passes through it\textsuperscript{33,34}. Charge Transfer resistance (Rct) is a characteristic quantity for an electrode reaction indicative of electron transfer kinetics. Thus a large charge-transfer resistance indicates a slow reaction. The curvature of the Nyquist plot in Figure 8 at high frequencies represents the double-layer capacitance in parallel with the charge transfer resistance. From the AC impedance spectrum (Figure 8), the charge transfer resistance of the film was found to be 438 $\Omega$.

3.7 Conductivity Measurement

Figure 9 shows the NiS:Co/SnS core-shell particles in PVA matrix (a) and NiS:Co/SnS core-shell particles in Pani matrix (b). The conductivity of the core-shell particles

![Mott Schottky plot of NiS:Co/SnS core/shell particles embedded Pani film.](image)

![Photographs of (a) NiS:Co/SnS core/shell particles in PVA matrix. (b) NiS:Co/SnS core/shell particles embedded Pani matrix.](image)

![AC Impedance spectrum of NiS:Co/SnS core/shell particles embedded Pani film (inset: Equivalent circuit).](image)
embedded Pani film was 0.48 S/cm as evaluated by the four probe method.

4. Conclusion

Room-temperature synthesis of p-type semiconductors materials based on core-shell structures in Pani matrix has been reported. The UV-Visible absorption and emission spectra of NiS:Co/SnS-Pani revealed the stepwise spectral modifications effected by the preparation method. The scanning electron micrographs revealed core-shell structure and their periodic arrangement in the polymer matrix. The conductivity and carrier density promise this material for the photoelectrochemical applications.

5. References


