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Synthesis and Characterization of Conducting Polyaniline/Copper Selenide Nanocomposites

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ABSTRACT

The copper selenide (Cu_2Se)/polyaniline (PANI) nanocomposite was synthesized successfully by in situ polymerization through a simple and harmless technique. The structural characterization was carried out using Brucker D2 phase XRD. The optical measurements were made from UV-Visible spectrometer at normal incidence light wavelength in the range of 330-1100nm. Fourier transform infrared (FTIR) spectrograph confirmed the presence of functional groups and also the interaction between the polymer chains and Cu_2Se nanoparticles. The characteristic peaks in FT-IR and UV-Visible spectra were found shifted to higher wave numbers, which is attributed to the above said interaction. XRD pattern revealed the orderly arrangement of the polymer composite. Results obtained supports the prepared nanocomposite may be used as a multifunctional material for different nanoelectronic devices.

Keywords: *Copper selenide, PANI, Nanocomposite, Conducting Polymer*

1. INTRODUCTION

Extensive attention has been paid to the conductive polymers mainly due to their scientific importance and wide applications. A polymer to become electrically conductive, it must imitate a metal, which means that electrons in polymers must be free to move. The study of electrical property of polymeric materials has become interesting area of research because these materials have great potential application [1–3]. Most of the polymeric materials are poor conductors of electricity because they don't have free electrons to participate in the conduction process [4]. Polymers have poly-conjugated structures with poor electrical conductivity, but when treated with an oxidizing or a reducing agent, conductivity is enhanced reasonably. Among conjugated polymers, polyaniline (PANI) that has been widely studied for electronic and optical applications. The nanostructures of PANI also important due to the potential advantages as an organic conductor that exhibits low dimensionality and their wide applications [5,6]. Recently, polymers containing a chalcogenide, selenium, have exhibited promising properties as organic superconductors. Tetraselenesulfalene and other Se containing organic compounds have displayed metal to semiconductor transitions at low temperatures [7]. Various dopants have been used elswhare [8-13] in order to enhance the conductivity of PANI. However, studies on polyaniline doped with chalcogenides like Selenium (Se) [14] and its compounds are less. Among chalcogens selenium is of importance because of its applications in electronics, in photovolataics, and as superconductors [14,15].

In our present study, polyaniline was synthesized by conventional method and doped with copper selenide by in situ polymerization technique which is hitherto not reported. The as-prepared samples were characterized by Fourier Transform Infra Red (FTIR), using Agilent carry 660 and XRD with a CuKα radiation source (1.5418A°) operated at 30 kV and 80 mA. The optical measurements were made from UV-Visible spectrometer, Shimadzu UV-1800, at normal incidence light wave length in the range of 300-1100nm.

2. EXPERIMENTAL

Materials such as Ammonium persulphate (APS), Hydrochloric acid (HCl) (SDF), Sodium Hydroxide (NaOH), Cuppric Nitrate ($Cu(NO_3)_2.3H_2O$) (all are LR grade) and Metal Selenium were used as received. Aniline (AR grade, Ranbaxy) is double distilled before use.

2.1. Synthesis of PANI

The technique adopted here was an oxidative coupling involving the oxidation of monomers, to form a cation radical followed by coupling to form di-cation and the repetition leads to a polymer [16]. Polyaniline was synthesized by the polymerization of aniline in the presence of HCl (acts as a catalyst)

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using ammonium per sulphate (APS) (acts as an oxidizing agent) by chemical oxidative polymerization method. Aniline (2ml) was added to 50ml of 1.0M HCl taken in a 250 ml beaker. APS (5g) dissolved in 50 ml of 1.0M HCl and added in to the above aniline solution with vigorous stirring. The reaction temperature was maintained at ~0^0C. After the polymerization reaction, the resultant mixture was filtered and washed successively using 1.0M HCl followed by double distilled water, several times until the washings become colorless. Finally the residue was washed with acetone and dried at 60^0C.

2.2.Synthesis of Nanocrystalline Copper Selenide

Nanocrystalline Copper Selinide was synthesized [17] by a sol–gel process in which cupric nitrate ($Cu(NO_3)_2.3H_2O$) and selenium metal were used as source for Cu^{2+} and Se respectively. In the first step 5.0 g of NaOH was dissolved in 20ml of distilled water, 0.15g of Se powder was added to the solution and heated with constant stirring (~80^0C) using magnetic stirrer. After complete dissolution of the Se powder the alkaline solution turns to deep red. At this stage, 1.5ml of 0.5M $Cu(NO_3)_2$ was added, and heated to dryness at 140^0C for 5 h. Later, the product was washed with hot distilled water and ethanol, successively for several times, and dried in air for 1h.

2.3 Synthesis of Polyaniline - Copper Selenide Composite

The nanocomposite was prepared by dispersing the synthesized Copper selenide nanoparticles in the mixture of HCl (50ml, 1M) and aniline (2ml). The solution was stirred for 15-20min. later APS solution was added drop wise, till the solution turns black colour indicated the initiation of polymerization reaction. The stirring was continued for another 6hrs in order to complete the polymerization reaction. The precipitate so obtained was filtered and washed repeatedly with 1M HCl solution until filtrate becomes colorless and later washed with ethanol. The synthesized nanocomposite of PANI-Cu_2Se was dried in an oven at 60^0C for 1hr.

3. RESULTS AND DISCUSSION

3.1 Structural characterization by X-ray Diffractometer

The crystal structures of the synthesized nanoparticles were investigated by powder X-ray diffraction (XRD). Figure.1(a-c) shows the XRD pattern of PANI, Copper selenide and doped PANI respectively. The XRD spectrum of pure PANI as shown in fig.1(a) has a peak at 20.06 and 25.18, indicates its crystalline nature [18]. This characteristic peak of PANI is ascribed to the periodicity in parallel and perpendicular directions of the polymer chain. In fig. 1(b) the peaks observed for at 2θ angle at 26.68°, 44.74°, 54.18°, 64.71° and 82.92° confirms the formation of Copper selenide and it is crystalline in nature [19]. The obtain 2θ values corresponds to the Cu_2Se phase. However, the XRD patterns of PANI/Cu_2Se composites (Fig. 1c) exhibit the characteristic peak of PANI along with the crystalline peaks of Cu_2Se, owing to the systematic alignment of polymer chain. The increase in ordering of polymer composite with the addition of Cu_2Se nanoparticles indicates that the structure of PANI is strongly influenced by the nanoparticles.

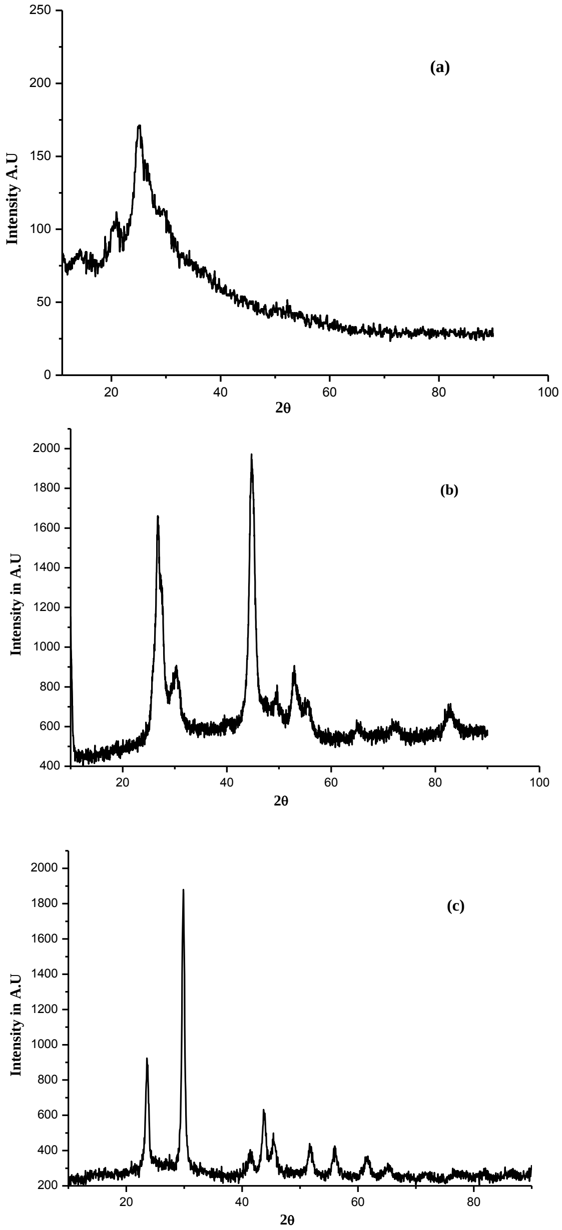

Figure 1: X-ray diffractogram of images of (a) PANI, (b) Copper selenide and (C) doped PANI

The increase in degree of regularity in arrangement or ordering of polymer chain is due to the strong interfacial interaction between the polymer and nanoparticles. Hence, the orientation of conducting polymer nanocomposites is of much interest, due to more highly ordered polymer matrix it could display a conductive property as in metals.

Presence of copper selenide peaks are observed in the PANI-Cu_2Se composite spectrum. This Cu_2Se peaks in the composite pattern confirms the formation of dispersed copper selenide in polyaniline and the same is also observed in the X-ray diffractogram of composite that the 2θ values of copper selenide is shifted.

The average size of the Cu_2Se and doped PANI nanoparticles are calculated from the full width of half maximum (FWHM) values of the diffraction peaks using Debye-Scherrer formula (cf. Table.1).

$$D = \frac{0.94\lambda}{\beta\cos\theta} \qquad (1)$$

Where, D is the average crystallite size, λ is the x-ray wavelength of CuK_α radiation (0.154nm), θ the diffraction angle, and β the FWHM.

Table 1: Average crystalline size of Cu_2Se and doped PANI

Sl. No	Nanoparticles	2θ	AverageParticle size (nm)
1	Cu_2Se	26.76 44.27	15.63
2	PANI-Cu_2Se	23.24 29.84	22.80

3.2 FT-IR characterization

The IR investigation was aimed to ascertain the formation of the PANI, Copper selenide and its composite. Figure.2 shows the FT-IR spectra, in the range 400-4000 cm^{-1} of KBr pressed pellets of PANI and its composite. In the spectrum, (cf.fig 2(a)) the bands at 1490 and 1563cm^{-1} show the characteristic C=N and C=C stretching of the quinoid and benzoid rings, respectively which is in good agreement with reported results [20]. The peaks at 1288 and 882cm^{-1} can be assigned to the C-N stretching of the secondary aromatic amine and an aromatic C-H out-of-plane bending vibration on 1,4-ring. The peak at 3462 cm^{-1} can be attributed to the N-H stretching mode. The in-plane bending vibration of the C-H on 1, 4-ring is observed at about 1132 cm^{-1} which was formed during protonation.

From the spectra (cf fig. (2b)), for doped PANI, the splitting of the bands are not observed after doping. The incorporation of copper selenide in the polymer leads to small shifts of some peaks of PANI viz. quinoid, benzoid and N-H stretching modes. It is also evident from the figure. 2(b) that the incorporation of nanoparticle to PANI causes some observable changes in the spectrum of the nanocomposite. Fourier transform infrared (FTIR) spectrograph confirms the presence of functional groups and also the interaction between the polymer chains with the Cu_2Se nanoparticles. Furthermore, the observed spectral features also reflect physical ordering and aligned conformation of the nanostructured polymer matrix [21], which is in correlation with the XRD and UV studies. The ordering of nanostructured molecular chains results in an ordered regularity in polymer composite, leads to shifting and sharpening of spectral bands [21].

3.3 Absorption spectra

UV-Vis spectroscopy is a powerful technique to characterize interfacial interaction between the PANI and Cu_2Se. Figure.3(b) shows that three distinctive peaks of polyaniline at 329, 432, 913nm, which are attributed to π–π*, polaron-π* and π-polaron transition [22,23] respectively. It was found that all the three absorption peaks (figure.3(a)) for PANI-Cu_2Se are shifted to the right compare to those of PANI film, indicates the red shift. The intensity of the PANI-Cu_2Se peak at 329 and 913nm is decreased significantly. The red shift of the polaron peak of the composite suggested that the polymer chains are existed in more expanded coil like conformation. The observed red shift in the composite indicates the insertion of nanoparticles-Cu_2Se to polymer chain.

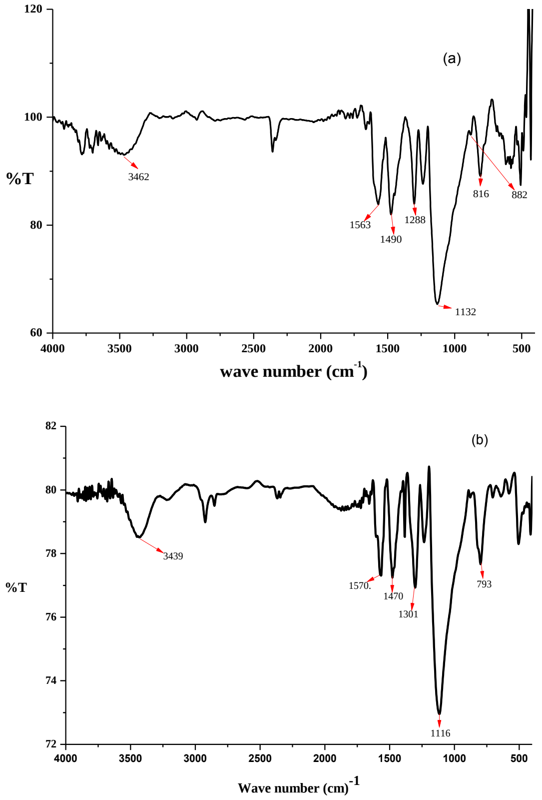

Figure 2: FT-IR spectra of (a) pure PANI and (b) doped PANI

The doping of nanoparticles with the polyaniline leads to an interaction at the interface of polyanilline and nanoparticles.

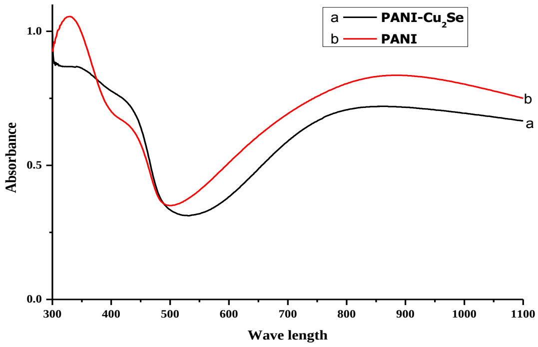

Figure 3: UV-Visible absorption spectra of (a) PANI-Cu_2Se, (b) PANI

4. CONCLUSION

PANI/Cu_2Se nanocomposite was synthesized successfully by in situ polymerization through a simple and environmental friendly technique. The XRD studies confirm the formation of copper selenide nanoparticles and its composite. The XRD pattern indicates that PANI/Cu_2Se nanocomposite has an orderly arrangement of the polymer chain, whereas synthesized PANI is slightly crystalline in nature. Particle size of the prepared Copper selenide and its composite are 15.63nm and 22.80nm respectively. The FTIR spectrum confirms the presence of chemical interaction between the nanoparticles and PANI, also supports the structural changes of PANI after doping and also confirms the incorporation of copper selenide in the polymeric chain. UV–Visible spectroscopy also supports the formation of a nanocomposite and the also composite material shows red shift. From the above studies it is confirmed the formation of a nanocomposite. Based on its optical properties and it may be used as a multifunctional material for nanoelectronic devices.

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***Bibliographical Sketch**

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