Synthesis, Characterization, Conductivity and Gas Sensing Performance of Copolymer Nanocomposites Based on Copper Alumina and Poly(aniline-co-pyrrole)

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Research Article

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Abstract

Poly (aniline-co-pyrrole) (PANI-co-PPy) with variable loadings of copper alumina (Cu-Al$_2$O$_3$) nanoparticles were synthesized by benign in-situ chemical oxidation polymerization. The structural, thermal transition and morphological interpretations were made with Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), differential scanning calorimetry (DSC) and high-resolution transmission electron microscope (HR-TEM). The electrical properties such as AC conductivity and dielectric measurements were performed at room temperature to verify their application in developing new electronic devices. The arrangement of nanoparticles in the copolymer and the synergistic interaction in the polymer matrix was deduced from FT-IR and XRD. HR-TEM indicates the nanosized uniform dispersion of filler in the copolymer. DSC revealed a reduction in the flexibility of polymer with an increase in glass transition temperature of copolymer composites. AC conductivity measurement manifested an increased hopping of charge carriers in nanocomposites when compared with pristine PANI-co-PPy. Dielectric properties were maximum for copolymer with 5wt.% Cu-Al$_2$O$_3$. The increase in dielectric properties of copolymer nanocomposites confirmed the efficient packing density of nanofiller within the polymer. Excellent gas sensing traits were observed for copolymer nanocomposites due to the electron transfers existing between PANI-co-PPy and ammonia gas. The magnificent material properties make (PANI-co-PPy)/Cu-Al$_2$O$_3$ nanocomposites, a promising contender for developing nano-electronic devices.

Introduction

In the recent era, usage of energy is increasing exponentially while energy storage is always a challenge. Conducting polymers with excellent electrical and dielectric properties is a solution for the energy storage crisis. The conducting polymers are widely used in electronics, batteries, supercapacitors and EMI shields [1–4]. Polyaniline (PANI) and polypyrrole (PPy) are extensively used conducting polymers as they are easily prepared, have excellent electrical properties and chemical as well as environmental stability [5–7]. Contrastingly the insoluble nature and lack of processability are the demerits of PANI and PPy [8]. Synthesis of polymer nanocomposites and copolymers can be utilized to resolve these paucities [9, 10]. Thus, the ideology behind the synthesis of copolymer nanocomposites is that they possess excellent properties by removing discrepancy of properties of individual polymers. The inference made out of numerous research work is that the incorporation of metal oxide nanoparticles enhances the electrical, magnetic and thermal properties of the polymer [11]. The aforementioned enhancement arises due to the unique chemical and physical properties of metal oxide nanoparticles.

Cu-Al$_2$O$_3$ is the best choice as nanofillers as they blend the principal characteristics of Cu (electrical and thermal properties) and alumina (mechanical properties and corrosion resistance) [12, 13]. Many works are published on the catalytic activities of Cu-Al$_2$O$_3$ in the synthesis of various organic compounds [14, 15]. In the previous work, we synthesized PANI/Cu-Al$_2$O$_3$ nanocomposite with excellent thermal, electrical and gas sensing properties than PANI [16]. The marginal enhancement in the properties is an account of
the interaction of Cu-Al$_2$O$_3$ nanomaterial with the PANI matrix. So, in the present work, we are curious in studying the effect of interaction between Cu-Al$_2$O$_3$ nanoparticles and PANI-co-PPy.

Conducting polymer or copolymer nanocomposites can be synthesized through two major modes: electrochemical method [17] and chemical method [18]. In electrochemical polymerization, a slight change in conditions may cause adverse effects on the properties of the materials. The most pronounced chemical method of synthesis is in-situ oxidation polymerization which involves simple procedures and uniform distribution of graphene oxide nanofillers into the polymeric abutment is guaranteed [19]. While other chemical modes of synthesis such as solution phase synthesis have several disadvantages. For example, the recovery of polymeric nanocomposites from solution can become a tedious task moreover, the solvent mainly used are harmful organic compounds. So, in an economic as well as a green chemistry point of view, the in-situ oxidation polymerization is the apt method for generating (PANI-co-PPy)/Cu-Al$_2$O$_3$ nanocomposites without compromising the quality of the material.

To the best of our knowledge, no works have been yet published on synthesis and property evaluation of Cu-Al$_2$O$_3$ nanoparticle reinforced (PANI-co-PPy). Hence the main objective of this work is the synthesis of (PANI-co-PPy)/Cu-Al$_2$O$_3$ nanocomposite by in-situ chemical oxidation method. The structural elucidation, degree of crystallinity and microscopic studies are performed by FT-IR, XRD and HR-TEM analysis. The effect of Cu-Al$_2$O$_3$ nanoparticles on the glass transition temperature of PANI-co-PPy has been evaluated by DSC. Further, the electrical and dielectric properties of the (PANI-co-PPy)/Cu-Al$_2$O$_3$ nanocomposites are studied in detail. Eventually, the ammonia gas sensing response of the synthesized nanocomposites are also evaluated with respect to different loading of nano-fillers

**Experimental**

**Materials and Methods**

Aniline, pyrrole, ferric chloride (FeCl$_3$), sodium dodecyl sulphate (SDS), copper nitrate (Cu (NO$_3$)$_2$), aluminum nitrate (Al (NO$_3$)$_3$), urea, HCl and methanol were acquired from Merck India. The pyrrole and aniline were purified by vacuum distillation and kept below 100°C ahead of usage.

**Synthesis of Cu-Al$_2$O$_3$ nanopowder**

Cu-Al$_2$O$_3$ nanopowder was prepared using solgel auto combustion technique [16]. In the aforementioned technique, an aqueous solution of Cu (NO$_3$)$_2$, Al (NO$_3$)$_3$ and urea were fused in 1:2:3 ratios. The appearance of the solution was converted to viscid nature when constantly stirred at 100°C. Finally, the solution is placed in a muffle furnace at 500°C. The nanoparticle produced was readily moved into a desiccator.

**Synthesis of poly (aniline-co-pyrrole) copolymer**
The copolymerization between aniline and pyrrole monomer was achieved by regular oxidation polymerization using ferric chloride as an oxidant. For this, 1.0 M solution of FeCl₃ was made in water in a three-neck flask. This oxidant solution was stirred for 15 min in an ice-cold condition. Simultaneously an acidic aqueous monomeric solutions were prepared by taking an equimolar concentration of aniline and pyrrole and this mixture was thoroughly homogenized using ultrasonicator. The homogenous monomer solutions were gently added to oxidant solution maintained at 0°C using a dropping funnel. Within a couple of minutes, the red colored FeCl₃ solution was transformed to blackish-green color. The color change was evidence of the polymerization reaction. The solution was kept at 0°C and continuously stirred for 8 h to ensure maximum polymerization. The excess monomers and oxidant left behind in copolymer were removed by thorough washing with water and methanol. The copolymer was finally dried at 60°C to get constant weight.

**Synthesis of poly(aniline-co-pyrrole)/Cu-Al₂O₃ nanocomposites**

The encapsulation of copper alumina within poly (aniline-co-pyrrole) matrix was achieved by in-situ polymerization. Like in the synthesis of pristine copolymer discussed in the previous session, for the synthesis of nanocomposites oxidizing agent employed as ferric chloride. The nanofluids with different compositions of Cu-Al₂O₃ nanoparticles (3, 5, and 7 wt. %) were prepared by dispersing in water using a surfactant (SDS). The precursor was made by transferring this nano-dispersion to monomer solution and the reaction mixture was ultrasonicated for half an hour. To the reaction mixture, FeCl₃ solution (1.0 M) was added dropwise with continuous stirring for half an hour. The ice-cold temperature and stirring were maintained for almost 8 h for polymerization of copolymer nanocomposites. The blackish green residue was filtered out and washed with distilled water and methanol, finally, the nanocomposites were dried in vacuum oven at 60°C for 24 h.

**Instrumentation**

The FTIR spectrum of Cu-Al₂O₃, PANI-co-PPy and their nanocomposites were recorded using JASCO 4100 FT-IR spectrometer. Bruker D8, Advance X Ray Diffractometer with CuKa (λ = 1.5407 Å) was employed to obtain X Ray diffraction (PANI-co-PPy)/Cu-Al₂O₃ in the range of 20 to 80° (scanning rate of 5°). The FESEM images of (PANI-co-PPy)/ Cu-Al₂O₃ nanocomposite were studied using the Carl Zeiss VP-500 model. HRTEM images of (PANI-co-PPy)/ Cu-Al₂O₃ nanocomposites were taken in JEOL, JEM–2100 HR, Japan. The temperature-induced phase transformation of (PANI-co-PPy)/Cu-Al₂O₃ nanocomposites was studied using Shimadzu DSC-50 (heat rate10 °C /min). The frequency-dependent AC conductivity, dielectric constant and dielectric loss parameters in the range of 10² to 10⁶ Hz of pelletized samples (0.5 mm thickness and 1.5 cm diameter) were measured with the help of Hioki 3570 Model. The gas sensing characteristics of copolymer with Cu-Al₂O₃ composites were measured by passing ammonia gas at room temperature. The pelletized composites were inserted into the glass chamber for passing ammonia gas. The ammonia gas (100 ppm) was passed into the glass chamber and the resistance of nanocomposites was measured as the sensitivity of the copolymer. The ammonia gas was removed from the glass.
chamber for each cycle and the sensor was placed in atmospheric air for recovery. The sensor response is defined as: Response (%) = [(Rg - Ra)/Ra] ×100, where Ra is the sensor resistance tested in air, and Rg is in the target gas.

Results And Discussion

FT-IR spectrum

The FT-IR spectrum of copolymer and its nanocomposite is illustrated in Figure 1. For pure copolymer, the absorption bands in the range of 3411 to 3107 cm⁻¹, corresponding to the vibration of the O N-H stretching. The sharp peak at 1586 cm⁻¹ is ascribed to the C=C stretch associated with quinoid moiety. The peak at 1492 cm⁻¹ is the benzenoid fractions of polyaniline present in the copolymer. Further CN, CH stretching and CH wagging vibrations of the copolymer are observed respectively at 1203 cm⁻¹, 1112 cm⁻¹ and 755 cm⁻¹. These inferences obviously indicated the successful copolymerization of aniline and pyrrole monomers. The major absorption bands in the FT-IR spectrum of CuAl₂O₃ nanoparticles are spotted at 544 cm⁻¹ (Cu-O stretching), 3334 cm⁻¹ (O-H stretch) and 1626 cm⁻¹ (O-H bend) [20]. The characteristic Cu-O band is clearly observed in the FT-IR spectrum of (PANI-co-PPy)/CuAl₂O₃ nanocomposite at 563 cm⁻¹ and which points towards the successful encapsulation of nanoparticles between polymeric layers. In addition to this, when compared with the FT-IR spectrum of the copolymer, the characteristic NH peak of the copolymer is significantly shifted to higher wavenumber (i.e., from 3235 to 3441 cm⁻¹). This shift absorption peak along with the appearance of new peak manifested the synergistic interaction between polar segments of PANI-co-PPy with the polar moiety of CuAl₂O₃ nanoparticles.

X-ray diffraction pattern (XRD)

The X-ray diffraction patterns of the synthesized nanoparticles and the copolymer with Cu-Al₂O₃ are shown in Figure 2. The XRD of PANI-co-PPy exhibited a broad and strong peak at 2θ value =23.37⁰. The broadness of this peak indicated the amorphous nature of synthesized copolymer. The crystalline nature of Cu-Al₂O₃ nanoparticles is evident from the distinct sharp peak present at 2θ = 25.35⁰, 32.52⁰, 35.35⁰, 38.67⁰, 43.35⁰, 48.68⁰, 52.50⁰, 57.64⁰, 60.73⁰, 66.09⁰ and 68.39⁰. These crystalline peaks are from the copper, copper oxide and alumina phases present in the Cu-Al₂O₃ nanoparticles. The spectra show that the synthesized copolymer nanocomposites exhibit the slight changes in the position of the broader peak of copolymer with the crystalline peaks of nanoparticles indicate the formation of a nano-crystalline structure due to the effective interaction between nanoparticles and the copolymer chain. Further, the amorphous nature of copolymer is found to diminish with the inclusion of Cu-Al₂O₃ nanoparticles. The intensity of the crystalline peaks in nanocomposites is enhanced at higher loading of nanoparticles. Thus, the XRD results reveal the successful inclusion of Cu-Al₂O₃ nanoparticles within the copolymeric material.
High resolution transmission electron microscopy (HR-TEM)

The structural and morphological analysis of (PANI-co-PPy)/Cu-Al$_2$O$_3$ nanocomposites is carried out by HR-TEM. Figure 3 (a) and (b) show the different contents of Cu-Al$_2$O$_3$ incorporated copolymer nanocomposites. It is clear that spherically shaped particles of Cu-Al$_2$O$_3$ nanofillers are uniformly distributed in the copolymer matrix. The unique coverture of Cu-Al$_2$O$_3$ nanomaterial in the copolymer is observed in 5 wt. % sample (Figure 3 (a)) is due to the effective interaction of the nano-filler with the copolymer. As shown in Figure 3 (b), the Cu-Al$_2$O$_3$ nanofillers are unevenly inserted and dispersed in the copolymer matrix. The interaction between Cu-Al$_2$O$_3$ and copolymer is poor at higher loading of nanofillers which results in an agglomerated morphology. The histogram image of the nanocomposite is given in Figure 4 and the average particle sizes of the copolymer nanocomposites are around 56 nm.

Differential scanning calorimetry (DSC)

The temperature-associated phase transition of PANI-co-PPy and their nanocomposites with Cu-Al$_2$O$_3$ nanofillers obtained from DSC is presented in Figure 5. Single glass transition temperature ($T_g$) is observed for pristine (PANI-co-PPy) at 107$^\circ$C and the single glass transition temperature in the DSC profile shows the effective copolymerization of aniline and pyrrole. The second endothermic dip occurred at 240 $^\circ$C, which is caused by the melting ($T_m$) of the copolymer. The copolymer with 3 and 7 wt. % composites showed the glass transition at 120$^\circ$C and 129 $^\circ$C respectively. This can be accounted to the diminishing of the amorphous nature of the polymer with the inclusion of Cu-Al$_2$O$_3$ nanoparticles [21]. More specifically, the compact network structure developed in the copolymer matrix reduces the segmental mobility of the copolymer chain. The $T_m$ values of the copolymer is also increased to 247$^\circ$C and 258$^\circ$C respectively for 3 and 7 wt. % composites. The increase in melting temperature of the nanocomposite indicates that the addition of nanoparticles enhances the crystallinity of copolymer nanocomposite.

AC conductivity

The plot of AC conductivity Vs frequency of (PANI-co-PPy)/Cu-Al$_2$O$_3$ nanocomposites are depicted in Figure 6. An exponential nature is observed in the graph for all the samples i.e., constant AC conductivity throughout the lower frequency range and invariable increase in conductivity at higher frequencies. From the plot, it is evident that the AC conductivity of (PANI-co-PPy)/Cu-Al$_2$O$_3$ nanocomposites is higher than bare copolymer. Generation of defects and shortening of polymeric chains are due to the formation of bond between PANI-co-PPy and Cu-Al$_2$O$_3$ can be ascribed for the enhancement in AC conductivity [22]. Among all samples under study, supreme conductivity is observed for (PANI-co-PPy)/5 wt.%Cu-Al$_2$O$_3$ nanocomposite. The consistent distribution of nanoparticles at this loading facilitates an effortless charge transport [16]. The conductivity of (PANI-co-PPy)/7 wt. % nanocomposite is poor when compared with 5 wt. % composite. The inconsistent distribution of inorganic filler particles within the copolymer matrix resulted in lumps which restricts the charge transport.
\textbf{Dielectric constant}

The amount of energy stored in a material is quantified by its dielectric constant. The dielectric constant of (PANI-co-PPy)/\(\text{Cu-Al}_2\text{O}_3\) nanocomposites is shown in Figure 7. An enrichment in dielectric constant values of (PANI-co-PPy)/\(\text{Cu-Al}_2\text{O}_3\) nanocomposites than PANI-co-PPy is due to the interfacial polarization and dipolar polarization. Unlike PANI-co-PPy, diversity of organic and inorganic counterparts in (PANI-co-PPy)/\(\text{Cu-Al}_2\text{O}_3\) influences the Maxwell-Wagner-Sillars polarization and hence an improvement in the magnitude of dielectric constant [23]. Moreover, the higher values of dielectric constant for (PANI-co-PPy)/\(\text{Cu-Al}_2\text{O}_3\) nanocomposites manifests their higher conductivity [26]. Maximum dielectric property is obtained for (PANI-co-PPy)/5 wt.% \(\text{Cu-Al}_2\text{O}_3\) nanocomposite. The uniform distribution of nanomaterial facilitated the Maxwell Wagner-Sillars polarization in the aforementioned nanocomposites. However, at higher loadings, the non-homogenous morphology restricted the orientation of dipoles and hence dielectric constant values are decreased.

\textbf{Dielectric loss tangent (Tan \(\delta\))}

Dielectric loss quantifies the energy dissipation in a material. Figure 8 evinced the plot of dielectric loss tangent of (PANI-co-PPy)/\(\text{Cu-Al}_2\text{O}_3\) nanocomposites. The dielectric loss of material usually depends upon the crystal structure, crystalline defects, dopant ions and grain boundaries. The \(\tan \delta\) value of (PANI-co-PPy)/\(\text{Cu-Al}_2\text{O}_3\) nanocomposites is higher than (PANI-co-PPy). The inclusion of nanofillers improved the long-range order and creates more bound charges thereby facilitating energy dissipation [24]. The maximum dielectric loss is observed for 5 wt.% composite. The effective alliance between the polar functionalities can be ascribed to their superb properties. While this association is found to diminish with a further filling of nanofillers and hence \(\tan \delta\) response in higher loaded samples decreases.

\textbf{Gas sensing properties}

The results from gas sensing studies of (PANI-co-PPy)/\(\text{Cu-Al}_2\text{O}_3\) nanocomposites are provided in Figure 9. The inflation in resistance with the passage of ammonia gas can be attributed to the electron transfer process that occurred between the sensor and \(\text{NH}_3\) gas. The maximum resistance after the passage of ammonia gas is observed for bare (PANI-co-PPy) due to deflation in a number of charge carriers in the macromolecular chain. The decrease in resistance value for nanocomposite indicates their better gas sensing toward ammonia gas. In copolymer nanocomposites, the electron transfer process between polymer and \(\text{NH}_3\) gas impeded due to the synchronizing effect of electron donating property of \(\text{Cu-Al}_2\text{O}_3\) nanofiller and electron withdrawing nature of copolymer [25]. The (PANI-co-PPy)/5 wt.%\(\text{Cu-Al}_2\text{O}_3\) nanocomposite is observed to have maximum sensing behavior towards ammonia gas due to greater surface area available for adsorption. The sensing property is diminished at higher loading due to the non-homogenous distribution of nanofillers within the copolymer. The non-homogenous distribution results in a poor surface area for \(\text{NH}_3\) gas adsorption [26]. The response of (PANI-co-PPy)/\(\text{Cu-Al}_2\text{O}_3\) nanocomposite sensors on subjection to \(\text{NH}_3\) gas at different time is depicted in Figure 10. From
the graph, concentration dependency of gas sensing response. The NH\textsubscript{3} gas sensing response of (PANI-co-PPy)/Cu-Al\textsubscript{2}O\textsubscript{3} nanocomposites is better than pure copolymer. The electronic changes that occurred within the polymeric material created more and more active sites for adsorption of NH\textsubscript{3} gas and hence improving the sensitivity. For polymer nanocomposites, up to 5wt. \% loading sensitivity is observed to improve with an increase in filler particles added. The limited active centers due to the lumping of nanomaterials in higher loading increased the enthalpy of adsorption of NH\textsubscript{3} gas.

**Conclusions**

This study is a methodical approach to analyze the structural, morphological, thermal, electrical and dielectric characteristics of (PANI-co-PPy)/Cu-Al\textsubscript{2}O\textsubscript{3} nanocomposites synthesized via in-situ chemical oxidation polymerization. FT-IR confirmed the perfect incorporation of Cu-Al\textsubscript{2}O\textsubscript{3} nanoparticles within the PANI-co-PPy matrix. XRD pointed to the existence of polymeric and Cu-Al\textsubscript{2}O\textsubscript{3} (crystalline) phase in the material which was already confirmed from the FT-IR spectrum. The formation of spheres in the polymer abutment was manifested by HR-TEM images. Further, a decrease in particle size of polymer with the inclusion of nanofillers was evident from microscopic images. The shift in glass transition temperature confirmed the alliance between heteroatoms of the copolymer and metallic components in the nanocomposites. AC conductivity studies manifested the generation of a conductive network with cushioning of nanofillers. Excellent charge storage ability was observed for (PANI-co-PPy)/Cu-Al\textsubscript{2}O\textsubscript{3} nanocomposites. The most favorable electric and dielectric properties were observed for (PANI-co-PPy)/5 wt.% Cu-Al\textsubscript{2}O\textsubscript{3} nanocomposites. The electronic changes occurring in a copolymer with the inclusion of Cu-Al\textsubscript{2}O\textsubscript{3} nanofillers is the reason for their improved sensitivity against NH\textsubscript{3} gas. The excellent properties suggest that (PANI-co-PPy)/Cu-Al\textsubscript{2}O\textsubscript{3} nanocomposite is a potential candidate for developing conductive coatings, gas sensing devices, batteries and resistors.

**Declarations**

The authors of this article have no conflict of interest to declare

**References**


Figures

Figure 1

FT-IR spectrum of Cu-Al$_2$O$_3$ and copolymer with Cu-Al$_2$O$_3$ nanoparticles
Figure 2

XRD of copolymer, Cu-Al$_2$O$_3$ and copolymer/ Cu-Al$_2$O$_3$ nanocomposites
Figure 3

HR-TEM photographs of copolymer with (a) 5wt.% Cu-Al$_2$O$_3$ and (b) 7wt.% Cu-Al$_2$O$_3$
Figure 4

Histogram of the particle size distribution of poly(aniline-co-pyrrole)/Cu-Al$_2$O$_3$
Figure 5

DSC profile of poly(aniline-co-pyrrrole) and poly(aniline-co-pyrrole)/Cu-Al$_2$O$_3$ nanocomposites
Figure 6

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Figure 7

Dielectric constant of copolymer and its nanocomposites
Figure 8

Tan δ of copolymer and its nanocomposites
Figure 9

Gas sensing response for ammonia gas of copolymer with various contents of Cu-Al$_2$O$_3$
Figure 10

Change in gas sensitivity of copolymer with different contents of Cu-Al$_2$O$_3$