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SYNTHESIS, CHARACTERIZATION AND PHOTOLUMINESCENCE PROPERTIES OF CONDUCTING POLY (*O, M, P-* AMINOTHIOPHENOL)/CuO NANOCOMPOSITES

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ABSTRACT

The poly (o,m,p-aminothiophenol)/CuO nanocomposites were synthesized by in situ chemical oxidative polymerization method using ammonium persulphate as an oxidant in an aqueous HCl. The synthesized polymer nanocomposites were characterized using FTIR, UV-VIS, XRD, SEM and TEM. The thermal stabilities of the synthesized polymer CuO nanocomposites were determined from TGA/DTA studies. The electrical conductivity and photoluminescence studies were carried out for the synthesized Poly (o,m,p-aminothiophenol)/CuO nanocomposites. The study of electrical conductivities of the synthesized poly (o,m,p-aminothiophenol)/CuO nanocomposites showed that they were semiconducting in nature and the conductivites were in the order of $\times 10^{-4}$*. The results of photoluminescence studies of poly (o,m,p-aminothiophenol)/CuO showed that they can act as blue light emitters and hence they can be used in the light emitting diodes.*

KEY WORDS

Conducting polymers, nanocomposites, aminothiophenol, electrical conductivity, photoluminescence study.

1. INTRODUCTION

Nanocomposites are a special class of materials having unique properties and wide applications in diverse areas. [1-4] In recent years, researchers focused on synthesizing polymer metal nanocomposites, due to their unique electronic, optical, mechanical, magnetic, and chemical properties. Important aspects of the chemistry involved in the formation of these systems are uniformity, phase continuity, domain sizes, and the molecular mixing at the phase boundaries, which all have a direct influence on optical, physical, and mechanical properties.[5] Copper oxide (CuO) generally has the characteristics of stable oxides of copper, but its nanocomposite has change in its physical, chemical and magnetic properties.[6] It has many spectrums of applications such as electro optical properties, catalysis, sensors, solar cells and conducting film.

Polyaniline has received much attention because of its high electrical conductivity and ease of preparation at low cost. Metal oxides dispersed polymer composites have attracted a great deal of interest from researchers, because they frequently exhibit unexpected hybrid properties synergistically derived from both components. A derivative of polyaniline, aminothio phenols (ATP) are interesting electrochemical materials since thiol and amine have different reactivities, [7-9] the effective use of this molecular assembly may give rise to unique morphologies leading to multi-purpose chemical strategies. Moreover, the aromatic (conjugated π-electron system) ring of ATP intensifies the electrical coupling. Therefore, they can show electrochemical behavior resembling anilines and phenols. In recent years, electrical, optical, and dielectric properties of conducting polymers like polyaniline and substituted polyaniline synthesized by chemical oxidation polymerization have been studied in great detail.

In the present work, poly(*o,m,p*-aminothiophenol)/CuO nanocomposites were synthesized and characterized using FTIR, UV-VIS, XRD, SEM and TEM. An attempt has been made to investigate the electrical conductivity and photoluminescence properties of poly(*o*-aminothiophenol) / CuO (PoATP / CuO), poly(*m*-aminothiophenol) / CuO (PmATP / CuO) and poly(p-aminothiophenol) / CuO (PpATP/ CuO) nanocomposites.

2. EXPERIMENTAL METHODS

2.1. Synthesis of Polymer Nanocomposites

Ortho Aminothiophenol (monomer), Ammonium per sulphate (oxidant) and Copper oxide (CuO) were taken in the ratio of 1:2:1. The monomer was dissolved in 1M Hydrochloric acid. Copper oxide nanoparticle is added to the above solution with vigorous stirring in order to keep the CuO suspended in the solution. The aqueous solution of the oxidising agent was slowly added into monomer and metal salt solution. The solution was kept stirring for about 5 h at room temperature, after which the brownish black powder obtained as residue. The resultant polymer nanocomposite poly(*o*-aminothiophenol)/CuO was washed with distilled water until the filtrate was colorless then with acetone and with methanol to remove excess initiator and oligomers. Finally, the resultant precipitate was dried at room temperature for 24 hours. [10] Same procedure was adopted for the synthesis of poly (*m*-aminothio phenol)/CuO and, poly (p-aminothio phenol)/CuO.

2.2. Characterization Techniques

The FT-IR spectra of the synthesized poly (*o,m,p*-aminothio phenol)/CuO nanocomposites were performed using Perkin Elmer 1750 FTIR Spectrophotometer at room temperature. UV-VIS spectra were recorded from 200-800 nm using SHIMADZU model UV-2450 spectrophotometer by dissolving the polymer nanocomposites in DMSO as a solvent. TGA/DTA was recorded using Perkin Elmer Diamond under a nitrogen atmosphere up to 700°C at the heating rate of 20°C/min. X-ray diffraction (XRD) was recorded with Bruker AXS D8 Advance diffractometer at room temperature at 2θ angle ranging from 0̊ to 80̊. The morphological study of the synthesized polymer and its nano composite was carried out using Scanning Electron Microscopy, model: Jeol 6390 LV with accelerating voltage of 0.5 kV to 30 kV. Transmission electron microscopy, model Tecnai T20 G2 S-TWIN was used to investigate the dispersion of PATP/CuO nanocomposites. Photochemical measurements were carried out on a CHI608E electrochemical workstation and a 100 W Xe arc lamp (OSRAM, Germany) was used as the light source. Fluorescence Spectrophotometer of model Varian- Cary Eclipse was used to measure the photoluminescence property for the synthesized polymer CuO nanocomposites using Xenon flash lamp as source and the detector used was PMT.

3. RESULTS AND DISCUSSION

3.1. UV-VIS Spectroscopy

The UV-VIS absorption spectra of poly(*o,m,p*-aminothiophenol) / CuO nanocomposites dissolved in DMSO were shown in Figure 1. The spectra of all the polymer nanocomposites consist of two major absorption peaks; the first peak at 250–265nm was assigned to the π-π^* transition of the the benzenoid rings in the polymer chain. The intensity of the π-π^* absorption maxima were comparable for all the three polymer CuO nanocomposites. The second absorption peak at 300-350nm was due to n-π^* transition due to the quinonoid rings. [11,12]

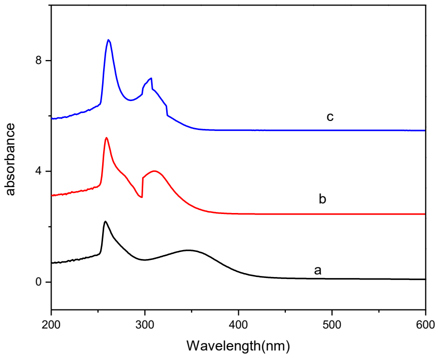

Figure 1: UV-VIS spectra of (a) PoATP/CuO, (b) PmATP/CuO and, (c) PpATP/CuO

3.2. FT-IR analysis

The FTIR spectra of PoATP/CuO, PmATP/CuO and PpATP/CuO nanocomposites were given in Figure 2 and from the spectra it was clear that the bands at 1477 and 1612 cm^{-1} were assigned to C=C stretching vibrations of the quinonoid and benzenoid ring present in the polymer nanocomposites. The participation of N–H stretching vibration was confirmed by the single peak around 3363 cm^{-1} in all the polymer CuO nanocomposites. [13] The peaks at 1249 and 1307cm^{-1} were associated with C–N–C stretching in the benzenoid and quinonoid imine units. The peak at 2366 cm^{-1} corresponds to S-H stretching. Furthermore, the bands at 823 and 752cm^{-1} were the characteristic of C–H out of plane bending vibrations of benzene nuclei. The strong peak at 1101 cm^{-1} was considered to be stemmed from delocalization of electrons in polymer backbone. [14]

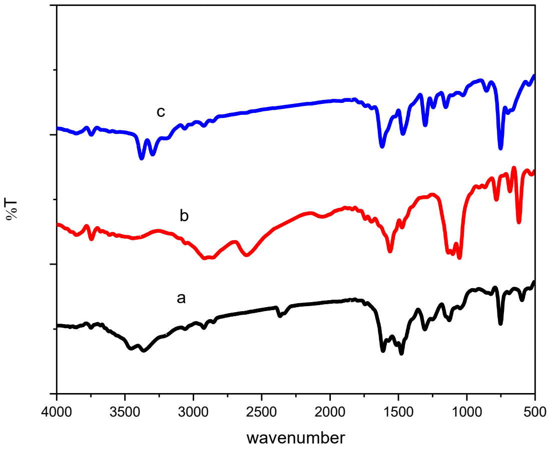

Figure 2: FT-IR spectra of (a) PoATP/CuO, (b) PmATP/CuO and, (c) PpATP/CuO

3.3. X-Ray Diffraction Studies

The XRD patterns of poly (aminothiophenol)/CuO nanocomposites were compared in Figure 3. The diffraction patterns were typical of crystalline/amorphous nature. The X-ray diffraction peaks (broad) around 2θ = 7° and 26° due to the characteristic peaks of emeraldine salt structure. [15] This also substantiates the absorption in the IR spectrum at 1128 cm^{-1} which was the electrical conductivity peak due to the emeraldine salt structure. In Figure 3, the nature of prepared polymer CuO nanocomposites were observed by the various sharp crystalline peaks in the XRD pattern. This observation from the XRD data endorses the uniform molecular level dispersion of CuO nanoparticles into the poly (aminothiol phenol) chain.

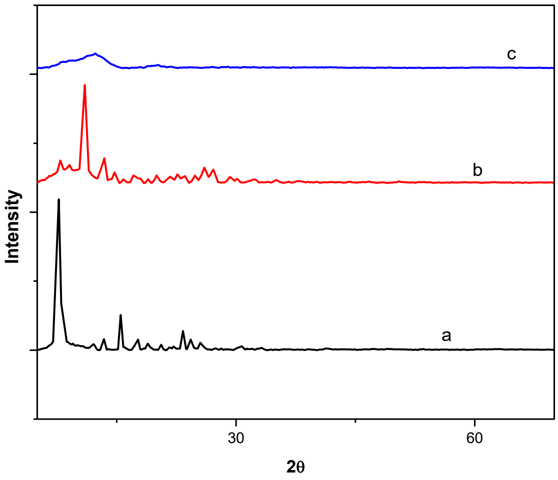

Figure 3: XRD pattern of (a) PoATP/CuO, (b) PmATP/CuO and, (c) PpATP/CuO

3.4. Thermogravimetric Analysis

thermal stability of the three polymer nanocomposites PoATP/CuO, PmATP/ CuO and PpATP/ CuO were evaluated using thermogravimetric analysis and shown in Figure 4. The thermal behaviour of the synthesized polymer nanocomposites were similar and exhibited a three-stage decomposition pattern. The first weight loss step corresponded to the loss of free acids, and volatile molecules in polymer matrix.[16] The second step was in the TGA curve because of loss of dopant, sublimation, and removal of low molecular weight polymer/oligomer from the polymer matrix.[17] While the third weight loss step was due to the complete degradation and decomposition of the polymer backbone.[18]

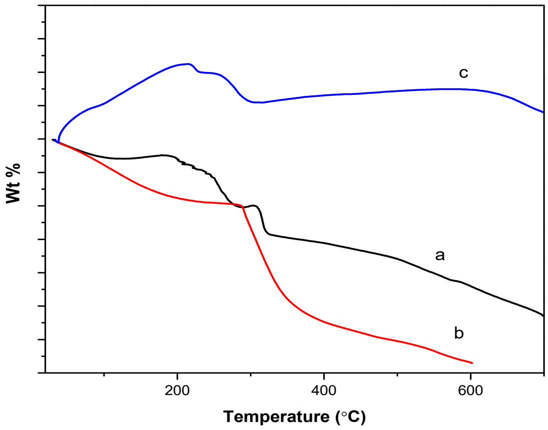

Figure 4:TGA of (a) PoATP/CuO, (b) PmATP/CuO and, (c) PpATP/CuO

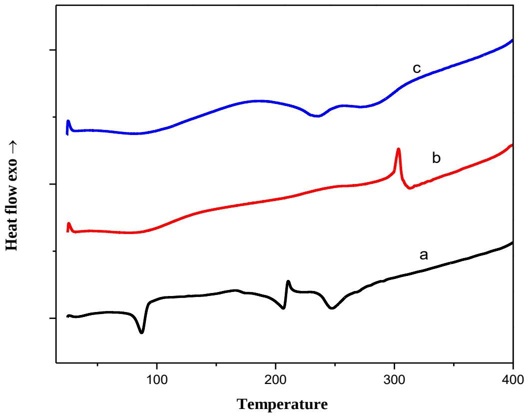

Figure 5: DTA of (a) PoATP/CuO, (b) PmATP/CuO and, (c) PpATP/CuO

The DTA curves of PATP/CuO nanocomposites in Figure 5 exhibited a main exothermic peak in the range of 200-500°C which were attributed to the transformation or degradation of polymeric backbone, thus proving the char residue at the end of the process. [19] Thus the TGA and DTA study confirmed that the synthesized polymer CuO nanocomposites possess good thermal stability.

3.5. Scanning Electron Microscopy

The Scanning Electron Microscopy (SEM) analysis was carried out to study the morphology of the chemically synthesized poly(o,m,p-aminothiophenol)/CuO nanocomposites. The poly(o-aminothiophenol)/CuO showed an agglomerated structure where poly(m-aminothiophenol)/CuO and poly(p-aminothiophenol)/CuO were exhibiting pollen grain form. [20] The SEM images of embedded CuO nanoparticle in the polymer matrix were shown in figure

6-8. The SEM pictures obviously revealed that the CuO nanoparticles were embedded in the polymer matrix.

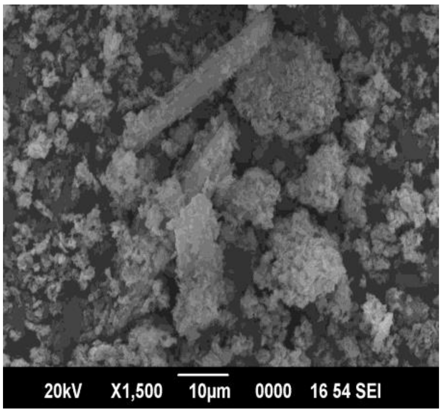

Figure 6: SEM image of PoATP/CuO

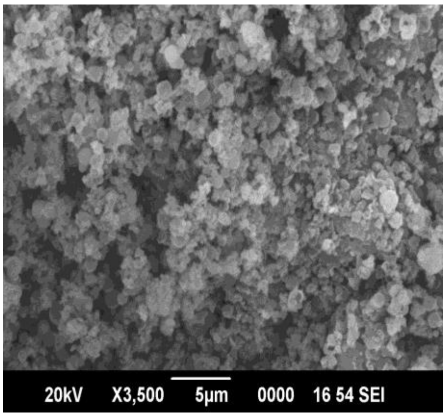

Figure 7: SEM image of PmATP/CuO

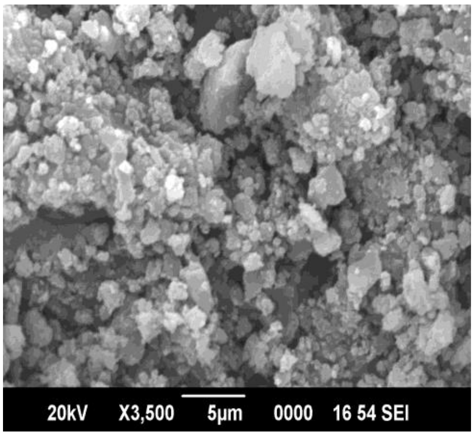

Figure 8: SEM image of PpATP/CuO

3.6. Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) images of polymer CuO nanocomposites taken at different angles were given in figure 9-11. The micrographs of polymer nanocomposites exhibited smooth surfaces. The TEM images of PATP/CuO exhibited both dark (metal) and light coloured region (polymer) which was indicating that more of CuO was incorporated. The nanocomposites were found to be homogeneous and were uniformly distributed. The CuO nanoparticles in the PATP/CuO nanocomposites indicated that the surface of nanoparticles had the interaction with PATP. [21]

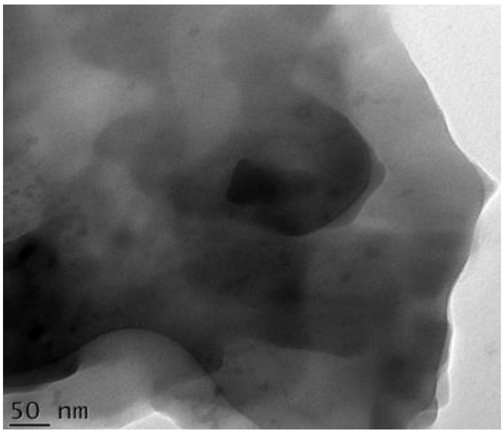

Figure 9: TEM image of PoATP/CuO

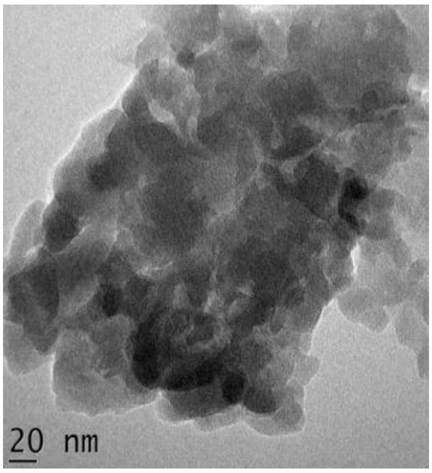

Figure 10: TEM image of PmATP/CuO

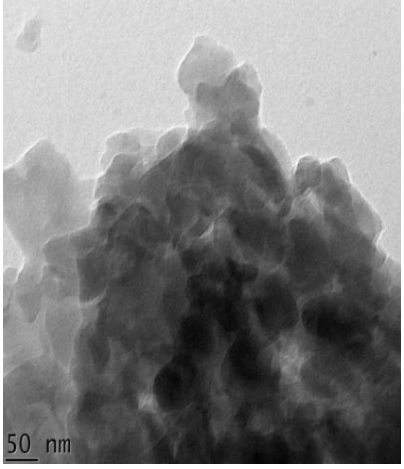

Figure 11: TEM image of PpATP/CuO

3.7. Conductivity

Photochemical measurements were carried out on a CHI608E electrochemical workstation and a 100 W Xe arc lamp (OSRAM, Germany) was used as the light source. In the present study, standard three electrode cell, with a Pt-wire was used as counter electrode, Ag/AgCl in saturated KCl as a reference electrode, the polymer CuO nanocomposite material were used as a working electrode and an aqueous solution of 0.1 M Na_2SO_4 was used as an electrolyte. The ionic conductivity σ is calculated using the equation. [22]

$$\sigma = t / (R_bA)$$

Where σ is the ionic conductivity, t is the thickness of the sample, R_b is the bulk resistance obtained from the intercept on the real axis at the high frequency end of the Nyquist plot and A is the most common area covered by the electrodes in contact with the sample.[23] The conductivity of the synthesized poly (o, m, p-aminothiophenol) were of semiconducting in nature and fall in the range of 10^{-4} S/cm.

3.8. Photoluminescence

Photoluminescence (PL) involves the process of photon excitation followed by photoemission. Most of the molecules occupy the lowest vibrational level of the ground state, and on absorption of light, they are elevated to produce excited state. From this level, the molecule can return to any of the vibrational levels of the ground state, emitting its energy in the form of fluorescence. The Photoluminescence properties of PoATP / CuO, PmATP / CuO, and PpATP / CuO nanocomposites synthesized were studied by varying the concentrations. The Photoluminescence spectra of PATP / CuO nanocomposites were shown in figure 12-14. The PL pattern has a strong emission bands around 340-430 nm and this region falls under the blue light emission. [24] The Photoluminescence results show that the emission intensity of poly (o, m, p-aminothiophenol) /CuO nanocomposites were lower at their highest concentration 1000 ppm and attains the highest emission intensity at their lowest concentration 50 ppm.

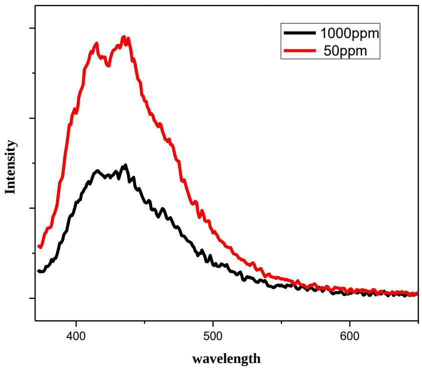

Figure 12:PL spectra of PoATP/CuO nanocomposite

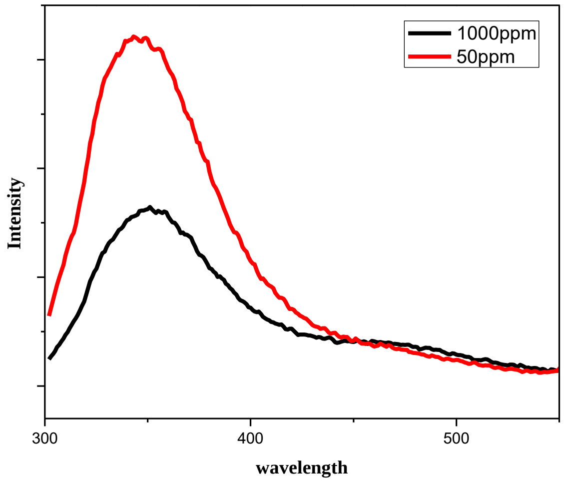

Figure 13:PL spectra of PmATP/CuO nanocomposite

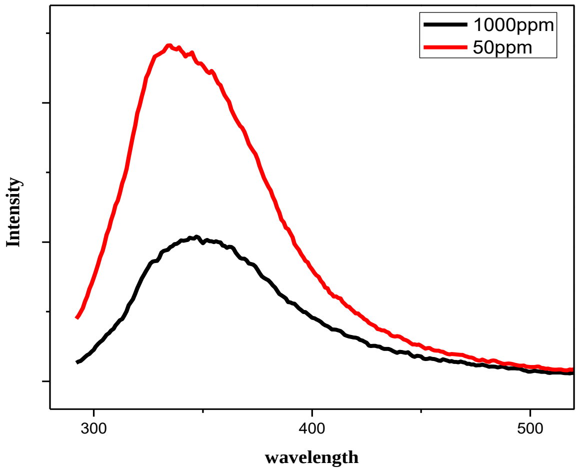

Figure 14: PL spectra of PpATP / CuO nanocomposite

4. CONCLUSION

The poly (o-aminothio phenol) / CuO, poly (m-aminothiophenol) / CuO and poly(p-aminothiophenol) /CuO have been successfully synthesized by chemical oxidative polymerization method and characterized by different spectroscopic techniques like FT-IR, UV-VIS, XRD, SEM and TEM. The characterization by UV-VIS, FT-IR suggested the formation of quinonoid and benzenoid rings which confirmed the formation of polymer nanocomposites. The thermal properties of the polymer were studied using thermo gravimetric analysis. The X-ray diffraction showed that the polymer CuO nanocomposites were crystalline/amorphous in nature and the morphology of the PoATP / CuO shows agglomerated form where PmATP/CuO and PpATP/CuO shows pollen grain like structure. The formation of polymer nanocomposites was confirmed by TEM analysis. The conductivity of the polymer nanocomposites was recorded, and the results showed that they were semiconducting in nature. The poly(o,m,p-aminothiophenol) exhibited very good fluorescence property which can be applied in different fields.

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