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Dr. Ravindra Singh Yadav
Associate Professor,
Department of Chemistry,
M.M.H. College, Ghaziabad,
Uttar Pradesh, India

Analytical study of polyaniline-copper (II) oxide nano composite by wet chemical route

Dr. Ravindra Singh Yadav

Abstract

This paper presents the structural, conductivity, and photoluminescence properties of synthesized polyaniline copper (II) oxide (PAni-CuO) nanocomposite by chemical oxidation polymerization method with ammonium persulfate as an oxidant in aqueous hydrochloric acid under constant stirring at 0-2 °C in presence of N₂-atmosphere. CuO nanoparticles were synthesized by chemical co-precipitation method. Different weight percentage of CuO in PAni constitutes different PAni-CuO composite material were synthesized and characterized by X-ray diffraction, infrared, ultraviolet, scanning electron microscopy, transmission electron microscopy, photoluminescence and electrical conductivity methods.

Keywords: Polyaniline, copper (II) oxide, nano composite, photoluminescence, conductivity

Introduction

In recent years, researchers focused on synthesizing metal nanoparticles, 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 ^[1].

In addition, the properties of the composite materials depend on the morphology of the phases, which has to be controlled over several length scales. Therefore, the development of such materials is a "land of multidisciplinary" ^[2], where chemists, physicists, material scientists, and engineers have to work closely together. Semiconductor nanoparticles have drawn a significant interest because of their special properties such as a large surface to volume ratio, increased activity, special electronic properties, and unique optical properties ^[3, 4]. The oxides of transition metals are an important class of semiconductors having applications in multiple technical fields like solar energy transformation, magnetic storage media, electronics, and catalysis among the oxide of transition metals. Copper oxide (CuO) nanoparticles are of special interest because of their efficiency as nanofluids in heat transfer application ^[5].

Second, it is the basis of several high-T_c superconductors ^[6]. CuO is a semiconducting material with a narrow band gap and used for photoconductive and photothermal applications ^[7], opposite to n-type semiconducting metal oxides, CuO is p-type semiconductor with a band gap of 1.2-1.9 eV. New approach on conducting polymer composite material integrates the technology of conducting polymeric materials.

Polyaniline (PAni) 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. In this paper, we describe the synthesis of PAni and CuO dispersed PAni composite materials through in situ polymerization method. The prepared samples were characterized using X-ray diffraction (XRD), IR, ultraviolet (UV), scanning electron microscopy (SEM), transmission electron microscopy (TEM), photoluminescence (PL), and electrical conductivity studies.

2. Experimental

2.1 Materials

All the chemicals and reagents used were of analytical grade, copper (II) nitrate, aniline, ammonium persulfate (NH₄)₂S₂O₈, acetone, ethanol, ammonia solution was purchased from Merck Ltd, and Conc. HCl from SD Fine Chemicals. Double distilled water was used throughout this work.

Correspondence Author;
Dr. Ravindra Singh Yadav
Associate Professor,
Department of Chemistry,
M.M.H. College, Ghaziabad,
Uttar Pradesh, India

2.2 Synthesis of Nanocrystalline CuO

The sample of pure CuO compound was prepared by chemical co-precipitation method. The solution of 0.2 M of copper (II) nitrate was prepared in distilled water and to this solution ammonia was added dropwise, copper hydroxide gel thus formed was continuously stirred for 6 h at 85 °C. The block CuO powder thus obtained was filtered and oven dried.

2.3 Synthesis of Nanocomposites

Five samples of different weight percent of PANiCuO nanocomposite were prepared by adding known weight of CuO to aniline prepared in aqueous hydrochloric acid and stirred for ½ h. To this solution, ammonium persulfate as an oxidant was added drop-wise for ½ h under constant stirring at 0-2 °C in N₂ atmosphere for 8 h. Finally, the polymer was dried in air and then in an oven at 80°C for 15 h. Table 1 shows the composition of 5%, 10%, 15%, 20%, and 25% weight of PANi-CuO nanocomposites and named as A1, A2, A3, A4, and A5 respectively.

3. Results and Discussion

3.1 XRD Studies

Figures 1 and 2 show XRD patterns of CuO nanoparticles and A1-A5 PANi-CuO nanocomposites, respectively. On comparison with the JCPDS data (041-0254) reveals a fairly well-matched monoclinic structure for pure CuO particles [8], and JCPDS data (039-1840, 027-1977, 028-1946, and 032-1501) reveals a well-matched orthorhombic structure for prepared nanocomposite.

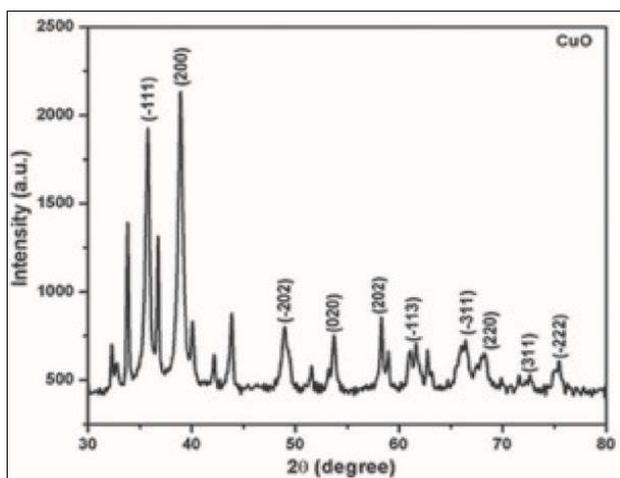


Fig 1: X-ray Diffraction Pattern of Pure Copper Oxide Sample

Average particle size D for different specimens was obtained from the main peaks using debye-scherrer equation-1 for peak width broadening as a function of the size of the particles.

$$D = \frac{0.89\lambda}{\beta \cos\theta} \quad (1)$$

The values observed for pure CuO and prepared PANi-CuO samples are shown in Table 2. The average size of the composite particle observed is found to be between 7.0 and 9.0 nm, and the average size of pure CuO particles are found to be ~16.3 nm. This clearly confirms the formation of CuO dispersed PANi nano composite.

Table 1: Weight % of PANi-CuO nano composite

Sample Name	Nano Composite	%Wt of CuO Nano particles
A1	PAni-CuO	5
A2	PAni-CuO	10
A3	PAni-CuO	15
A4	PAni-CuO	20
A5	PAni-CuO	25

PAni-CuO=Polyaniline-copper (II) oxide

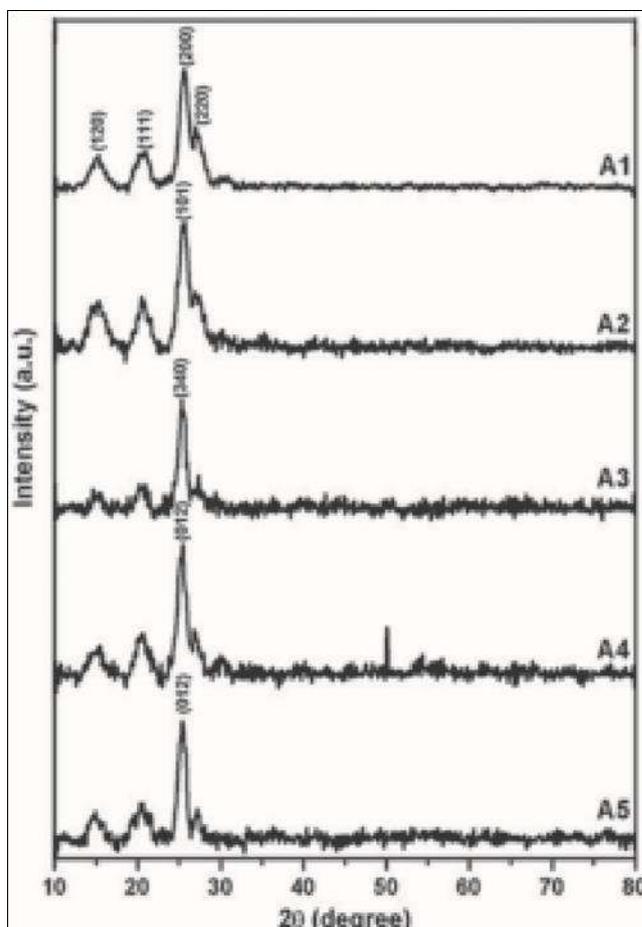


Fig 2: X-Ray Diffraction Pattern of A1-A5 Nano composites

Table 2: XRD data of pure CuO and PANi-CuO nanocomposites

Sample name	Average size D nm	d (Å)	2θ
CuO	16.30	2.3123	38.9175
A1	7.56	3.4729	25.6295
A2	7.28	3.5068	25.3778
A3	7.06	3.5141	25.3239
A4	7.49	3.5006	25.4234
A5	7.03	3.5087	25.3638

XRD=X-ray diffraction, PANi-CuO = Polyanilinecopper (II) Oxide.

3.2 Fourier Transform Infrared (FT- IR) Spectroscopic Analysis

FT-IR spectra of the CuO and all the nanocomposites were recorded using KBr. Figures 3 and 4a-e show the IR spectrum of pure CuO and PANiCuO nanocomposites, respectively. The band at 1560 cm⁻¹ and 1498 cm⁻¹ is attributed to C=N and C=C stretching mode of vibration for the quinonoid and benzenoid unit of PANi. The peaks around 1300 cm⁻¹ are assigned to C-N stretching mode of benzenoid ring. The peak at 1249 cm⁻¹ is the characteristic of the conducting protonated form of PANi [9, 10].

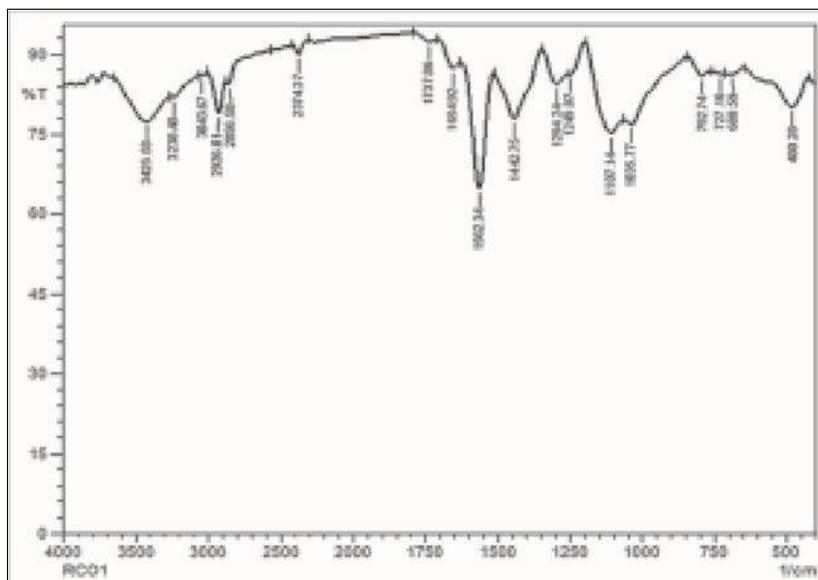


Fig 3: X-Ray Diffraction Pattern of A1-A5 Nanocomposites

The bands in the region $480\text{-}510\text{ cm}^{-1}$ are due to the presence of CuO in the nanocomposite. For the PANi-CuO composites, its IR-spectrum is almost identical to that of the pure PANi but all band shifts slightly towards the red side,

and the intensity ratio of quinonoid band has also changed. These results indicate that some interactions exist between PANi and CuO nanoparticles.

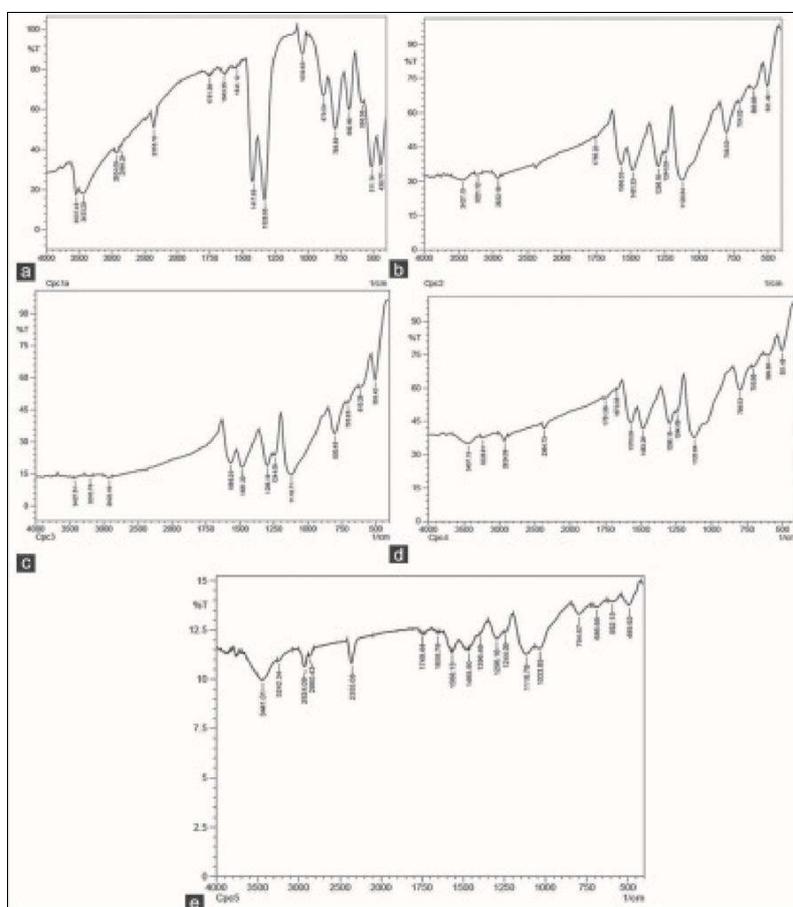


Fig 4: (a) Fourier Transform Infrared (FT-IR) Spectrum of A1, (b) FT-IR Spectrum of A2, (c) FT-IR Spectrum of A3, (d) FT-IR Spectrum of A4, (e) FT-IR Spectrum of A5

3.3. UV-visible Spectroscopic Analysis

UV-Visible spectra of all the nanocomposites were recorded using water as the solvent dissolved by ultra sonicator bath. Figure 5 shows the optical absorption spectra of PANi-CuO nanocomposites. The spectra reveal a characteristic two

absorption peaks of composite material at 350 nm and 442 nm correspond to $\pi\pi^*$ transition of C=N and polaron- π^* transition of C-N⁺. The absorbance increases in the higher wavelength side indicating the role of CuO nanoparticles. The peak around 440nm is shifted to higher wavelength

from A1 to A5. This shows the decreasing nanoparticle size of CuO as the weight % increases. The band can be assigned to charge transfer from oxygen to the metal center, one can expect to see the ligand field transitions in these cases [11, 12].

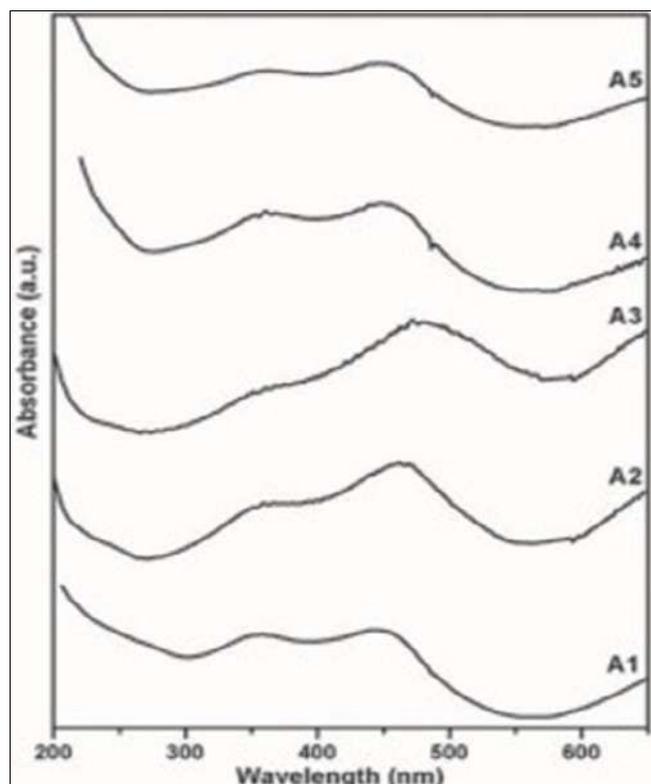


Fig 5: Ultraviolet-visible spectrum of A1-A5

3.4 SEM

The SEM of PANi-CuO nanocomposite (A3) sample at low to high magnifications is shown in Figure 6a.c. The fine flakes of CuO particles are well dispersed in the PANi matrix form clusters morphology; some smooth solid blocks are due to the presence of oxide particles, which increases the crystallinity of composite materials.

3.5 TEM

Figure 7a-c shows the TEM photograph of the sample (A3) PANi-CuO nanocomposite particles. From the image, we can see the ultra-fine particles of the transition metal oxides with a particle size distribution ~ 7.8 nm and this value is in good agreement with the values obtained from XRD data.

3.6. PL Spectra Study

The optical property of PANi-CuO nanocomposite was studied. The transfer of electron and hole from electronic level of CuO leads to emission. The PL spectra of nanocomposite samples excited at 383 nm are shown in Figure 8a-e at different weight % of CuO. It was observed from the figures, that the spectra were having only one emission band range at 441 nm (blue emission) is due to artifact [13], with increases in concentration of CuO the intensity of emission increases which could have been due to incorporation of CuO into PANi lattice and the excited states are subjected to electronic changes upon binding to the nanoparticles and due to changes of the molecular orbital symmetries of the PANi in the presence of CuO nanoparticles [14].

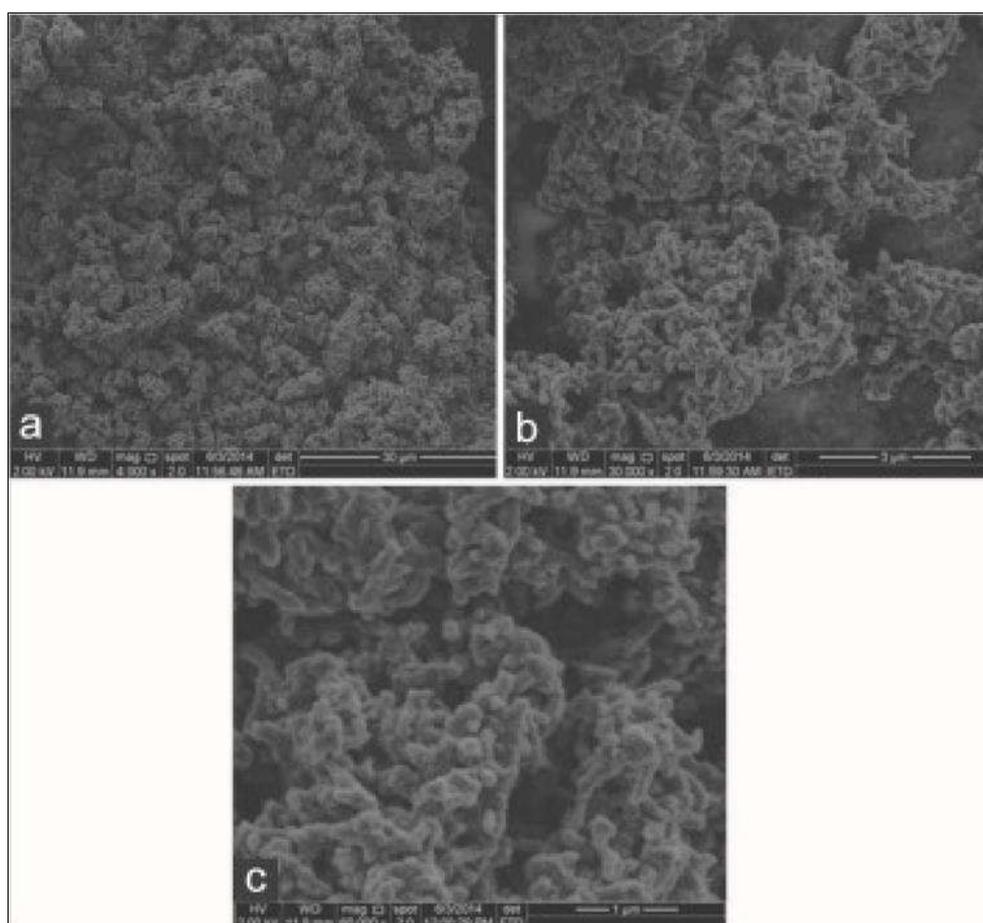


Fig 6: (a-c) Scanning Electron Microscopy Image of A3 Nanocomposite

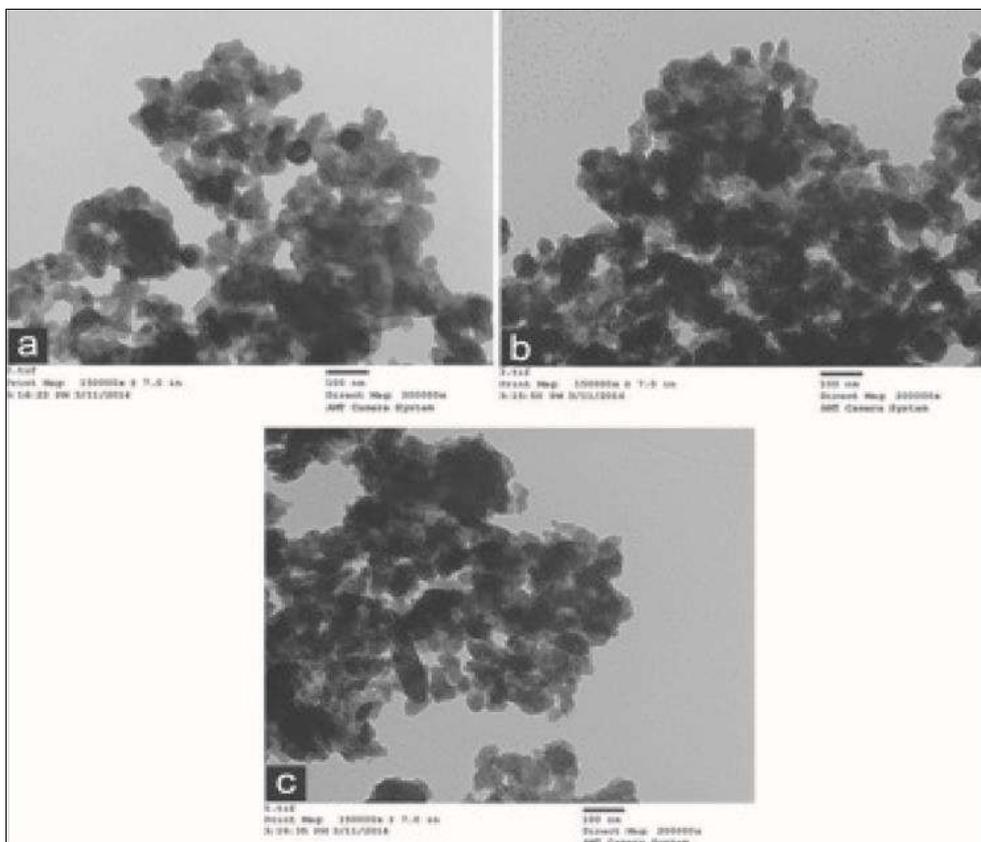


Fig 7: (a-c) Transmission Electron Microscopy Image of A3 Nanocomposite

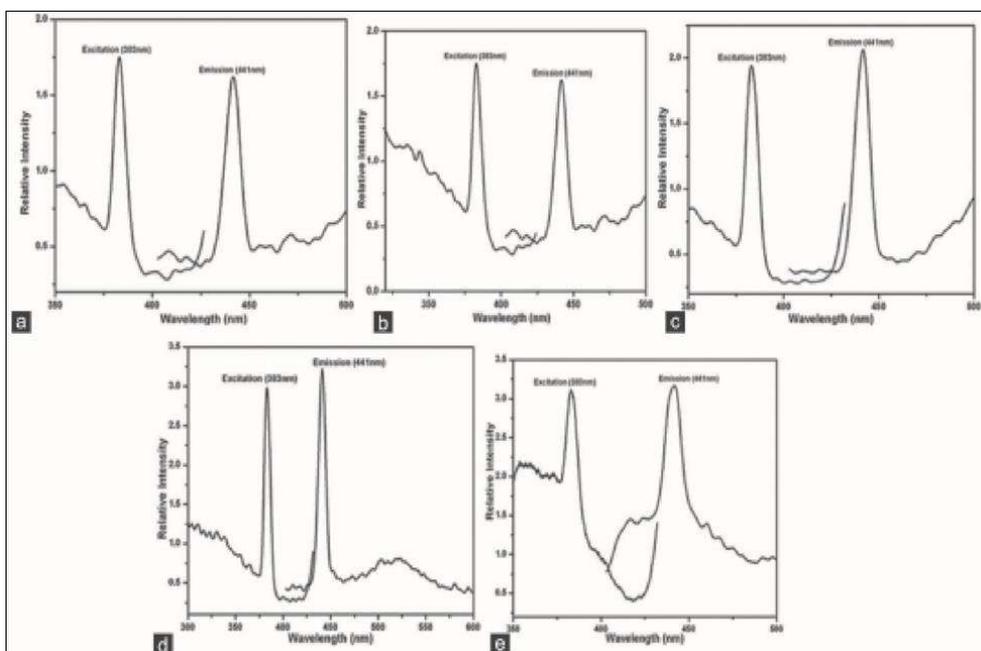


Fig 8: (a) Photoluminescence (PL) Spectrum of A1 Nanocomposite, (b) PL Spectrum of A2 Nanocomposite, (c) PL Spectrum of A3 Nanocomposite, (d) PL Spectrum of A4 Nanocomposite, (e) PL Spectrum of A5 Nanocomposite

Table 3: Calculated Band Gap Energy E_g Values of PANi-CuO Nanocomposites

Sample Name	E_g Values (eV)	
	At High T	At Low T
A1	0.550	0.130
A2	0.300	0.130
A3	0.560	0.110
A4	0.230	0.058
A5	0.330	0.120

PANi-CuO=Polyaniline-copper (II)oxide

3.7 DC Conductivity (Four Probe Method)

Figure 9a-e shows the variation of DC conductivity of A1-A5 nanocomposite with temperature. The calculated band gap energy values of different composites are given in Table 3. The temperature dependence of the electrical resistivity of PANi-CuO nanocomposite showing the metal to semiconductor transition.

Band gap energy E_g for different nanocomposites was

obtained from the slope using equation-2, thus a graph between \log of resistivity ($\log_{10}\rho$) and reciprocal of the temperature shown in Figure 9a-e. \log_{10}

$$E_g = \frac{\log_{10}\rho}{T^{-1}} \times 2k \quad (2)$$

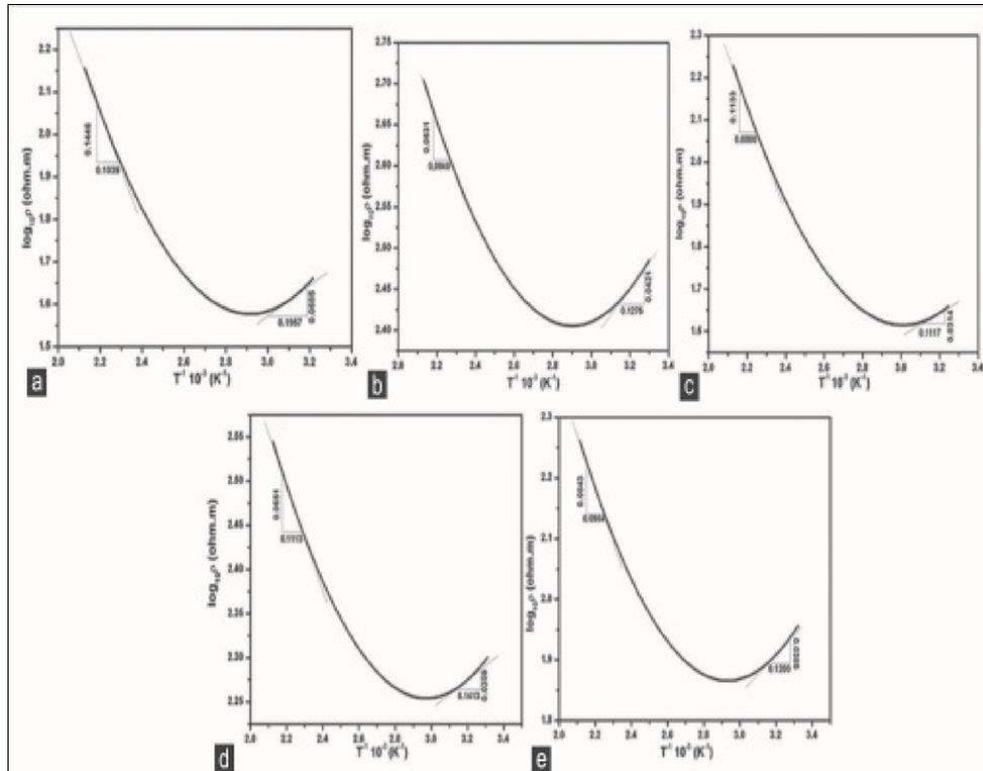


Fig 9: (a) Graph between $\text{Log}_{10}\rho$ Versus T^{-1} for A1, (b) graph between $\text{Log}_{10}\rho$ Versus T^{-1} for A2, (c) Graph between $\text{Log}_{10}\rho$ Versus T^{-1} for A3, (d) graph between $\text{Log}_{10}\rho$ Versus T^{-1} for A4, (e) graph between $\text{Log}_{10}\rho$ Versus T^{-1} for A5

Here

E_g = Band gap energy

T=Temperature

ρ = Resistivity

k = Boltzmann's constant

$$(8.617 \times 10^{-5} \text{ eVK}^{-1})$$

It is clearly seen that resistivity of the particles increases as the temperature increases. The conductivity of the sample A1-A5 decreases with rise in temperature^[15]. This confirms the metallic nature of the prepared PANi-CuO nanocomposite.

Conclusion

PAni-CuO nanocomposites were successfully prepared by chemical co-precipitation method. According to the results obtained, all the prepared nanocomposites have orthorhombic structure which is confirmed by XRD data. The SEM micrograph clearly reveals the dispersion of CuO nanoparticles in PANi matrix, and the particle size of nanocomposite obtained from TEM is around 7-8 nm which is good agreement with the values obtained from XRD data. IR and UV spectrum indicating the role of nano CuO particles and PL spectra shows some electronic changes occur in composite, so that the PANi-CuO nanocomposite

exhibit metallic property with orthorhombic structure. Because of these properties, PANi-CuO nanocomposite may find application in microwave frequencies as absorbing and shielding materials.

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