Effect of Addition of Polyaniline (PANI) on the properties of copper (II) Oxide nanoparticles

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Abstract
High resistivity (or low electrical conductance values) materials have found their applicational foot in those domains of electrical-electronical where resistors, heat filaments, space heaters, shunt resistors electric irons and etc. are broadly exercised on. This paper investigates the effect of addition of polyaniline (PANI) on the properties of copper (II) oxide (CuO) nanoparticles. Sol-Gel method was used to synthesize CuO nanoparticles while PANI was obtained by oxidative polymerization process. The structural characterizations of the composite material and the effect of PANI on the CuO nanoparticles are studied through FESEM, XRD, FTIR and Raman Spectroscopy. XRD confirmed the formation of CuO without the presence of CuO₂. FESEM showed the clear formation monoclinic structure of CuO. EDX revealed that Cu and O atoms are in stoichiometry, thus confirming the formation of CuO bond and peaks of C, N and O are also obtained depicting the PANI formation. The characteristic peaks are obtained for both CuO (402.99-678.74 cm⁻¹) and PANI (1109.94-1568.54 cm⁻¹ and 3058.81-3436.21 cm⁻¹) through FTIR. The Raman analysis of CuO sample showed 3 peaks (290.01 cm⁻¹, 333.51 cm⁻¹ and 624.81 cm⁻¹) and while PANI showed peaks in the range from 1166.48 cm⁻¹ – 1582.81 cm⁻¹. The dielectric properties were investigated using Maxwell-Wagner model and Koop’s phenomenological theory. The fore-mentioned composite material can also be considered to be devised in a resistor.

Keywords: Copper Oxide, Sol-Gel Auto Combustion method, Oxidative polymerization method, Polyaniline, Dielectric Properties, Resistors.

1. Introduction

The sphere of nanomaterial science has been studied extensively. They have many structural and surface morphological merits as compared to their counterpart, Bulk Materials. The one standing out the most, being higher surface to volume ratio. The worth of the device is counted if the material used in the fabrication of the device exhibits superior surface & physical nature as it is one of the predominant point in determining the chemical, thermal, electrical and magnetic aspects. The primary reactions take place on the surface of the material which influences the mechanisms of the device and thus controls the applicational facet of it. More the surface/ volume ratio, better will be the adsorption/ absorption process and thus more the preferable outputs.

The Transition Metal Oxides or commonly used with the acronym MO’s, they belong to a peculiar bracket of nanomaterial domain. They have been garnishing ample recognitions all because of their outstanding structural nature. The physical/ chemical characteristics of MOs strongly rely on compositions, sizes, shapes and structures of the nanopowders. Also a notable change in the surface
energy of the material is observed when the MOs are brought down to nanoscale dimension. These influential outputs led to new learnings in terms of physical and chemical aspects that are not workable for bulk materials. Thence preparation of superior quality of nanopowders with defined and controllable size and morphology, chemical compositions, and structures via manoeuvring the fabrication process became a salient need. Numerous methods are employed to synthesise the MOs; chemical, physicochemical, hydrothermal, sol gel auto-combustion etc. The physical morphology and thermal-electrical characteristics of transition MOs have made them a prominent candidate for both theoretical learnings and practical utilizations[1] [2].

Oxygen reacts with copper atom forming two different crystal structures; Cupric Oxide, CuO and Cuprous Oxide, Cu2O. Both the structures have been studied and researched on thoroughly, showing favourable results in certain aspects as per needs. But Cu2O is unstable form as compared to CuO which gives the latter mentioned metal oxide an upper hand. Copper (II) oxide (CuO) is an inorganic, intrinsic p-type semiconductor because of vacancies of Cu-atoms. It has monoclinic crystal formation which occurs in tenorite mineral form having bandgap of 1.2-1.9 eV and work function of 5.3 eV. They have admirable features like, strong thermal and electrical conductivity, high stability, photovoltaic properties, and antimicrobial activity. They share their usages in various fields; commercial sectors, industrial and domestic domains. They hold a strong foot in miscellaneous regions. They are used in removal of inorganic pollutants, gas sensors, magnetic phase transitions, bio-sensors, catalysts, superconductors, photodetectors, high efficiency thermal conducting material, magnetic recording media and many more to name. They are also considered favourable materials for the production of solar cells due to their high solar absorbance, excellent electrical properties, low thermal emittance, high carrier concentration etc. The credit for their numerous applications is not only because of their physical-chemical nature but also depending upon their high theoretical capacity, safety, environmental friendliness, cheap, easy fabrication [3][4].

MO’s are the class of materials that exhibit enhanced behaviours in terms of electrical-thermal conductivity, when doped/ mixed with other metals or materials of such sort. Conducting Polymers are one of the studied aspirants. Their interference in the structural world of the host material, strengthens the intrinsic properties thus amplifying the electrical-thermal conductivity of the whole composite mixture as compared to the individual material thus giving better results. Conducting polymers as Polypyrrole (PVP), Polyaniline (PANI) and Polythiophene (PTs) have couple benefits as; (I) They can be fabricated/ operated at room temperature (II) They exhibit high sensitivity towards gases and humidity because of their porous nature (III) They are light weight (IV) They show flexibility (V) They are low cost. The decrease in resistivity (or increase in conductivity) is noticed and that is attributed to the H-bonds forming between H2O-molecules and the N-centre of the polymer backbone. This promotes the proton exchanges that leads to increased doping level of the conducting polymer and therefore results in expanding of charge carriers which accommodates the increased conductivity[5] [6].

PANI, is one of the known conducting homo-polymer. Its molecular structure accommodates the formation of benzenoid or quinonoid state, though both of them can show their respective existences in different oxidation states. The ‘benzenoid (B)’ state is where the H-atoms are coupled to the N-atoms; it is the completely reduced leucoemeraldine state, whereas the ‘quinonoid (Q)’ state has no H-atoms attached to N-atoms, this is the fully oxidized permigraniline state. PANI is used in different sectors; commercial, industrial gains, based on its applicational requirement. They are now also considered as gas and humidity sensing materials because of their good physical properties, simple and accommodable fabrication method, chemical & environmental stability, cheap & easy availability of aniline monomer, high sensitivity etc[7][8].

In this work, we are studying the effect of mixing polyaniline with copper (II) oxide nanopowders and how it interferes with its structural nature and changes the surface morphology. The electrical nature of the composite mixture is being studied through dielectric analysis, and how the substituted polymer influences the behaviour of the composite material. The composite mixture is obtained by mixing CuO
nanopowders with PANI nanopowders and is studied via 3 varied samples; C1(CuO), C2(CuO + PANI, 4:1) and C3(CuO + PANI, 1:1). Sol-gel auto-combustion method is employed to synthesise the CuO metal oxide whereas PANI is synthesised by oxidative polymerization process.

2. Experimental Details

2.1 Reagents & Chemicals used

CuO (Cupric oxide): Copper (II) nitrate trihydrate Cu(NO$_3$)$_2$.3H$_2$O (AR/ACS grade, CDH company), Polyvinyl Alcohol (AR grade, Loba Chemie Pvt. Ltd). PANI(Polyaniline): Hydrochloric Acid HCl (AR grade, Loba Chemie Pvt. Ltd), Aniline Monomer (AR, 99.5% pure, MOLYCHEM), Ammonium per sulphate NH$_4$S$_2$O$_8$ (AR, Central Drug House (P) Ltd).

2.2 Preparation Methods

Sol- Gel auto-combustion method was used to obtain CuO nanopowders. Saturated and aqueous diluted solutions of CuO and polyvinyl alcohol were concocted individually and then were blended using a specific ratio. The suspension was then stirred for 3-4 hours at room temperature. And afterwards, the suspension was then heated at higher temperature with continuous stirring up to complete water evaporation and till the initiation of auto-combustion takes place. The powder acquired after the complete self-ignition process, were called the ‘precursor powders’ and they were calcinated at temperature 600°C for 3 hours under normal atmospheric conditions to obtain the desired metal nitrate nanopowders[4]. PANI was synthesised through ‘Oxidative Polymerization Method’. Two separate solutions were prepared; NH$_3$-Solution (in ice bath) and APS- Solution. After stirring the solutions for 1 hour, APS-solution was then slowly poured into NH$_3$-Solution (in ice bath) and the mixture was then again stirred for 1 hour before adding HCl in the above mixture (in ice bath). The whole solution was then stirred for half an hour and then was filtered to get the needed product.

3. Characterization techniques

The morphology of the composite mixture was studied with the help of structural and electrical characterizations. The crystal structure and phase was studied through X-Ray Powder Diffraction (XRD) (Bruker D8 Advance, CuKα 1.54Å). And, the particle size was calculated from Scherrer’s equation i.e. $D = \frac{k \lambda}{\beta \cos \theta}$ where; $k=0.9$ called space factor, $\lambda=$ wavelength, $\beta=$ full width at half maximum (FWHM) of the peak and $\cos \theta =$ Bragg angle. Fourier Transform Infrared Spectroscopy (FTIR), (Nicolet FTIR interferometer IR prestige-21 (model 8400S)) was used to understand the surface morphology of the nanopowders. The vibrational modes analysis was studied through Raman Spectroscopy (Confocal Micro-Raman spectrometer (STR 500) AIRIS Japan using the solid state laser having the excitation wavelength 532 nm). The elemental information was obtained by Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-Ray (EDX) Mapping ((FEI Nova NanoSEM 450 FE-SEM) which is being operated at 15 kV voltage). And Dielectric properties were analysed with the help of Impedance Analyser (Wayne Kerr 6500B) having bias voltage in the range from 0 to $\pm$40V DC and the DC bias current ranging from 0 to 100 mA and frequency in the range of 20 Hz–120 MHz using sample pellets being coated with silver paste having thickness 0.5cm.

4. Results & Discussions

4.1 XRD Analysis

The structural phase and crystal morphology of CuO and composite mixture nanopowders were interpreted using XRD. The obtained diffraction peaks confirm the formation of ‘monoclinic CuO’ in
‘tenorite phase’. The XRD analysis compromises of ten diffraction peaks for the value of $2\theta$ (°) = 32.5°, 35.5°, 38.7°, 48.7°, 53.4°, 58.2°, 61.4°, 65.7°, 66.1° and 67.9° and corresponding peaks (hkl-values) were = (1 1 0), (1 1 -1), (2 0 0), (2 0 -2), (0 2 0), (2 0 2), (-1 1 3), (0 2 2), (3 1 0) and (2 2 0) respectively. All the obtained peaks were in accordance with the JCPDS Card No: 48-1548. The values of the lattice parameter were: a= 4.7 Å, b= 3.4 Å and c= 5.1 Å. Using Debye–Scherrer’s equation, the particle size value was obtained to be D= 34.9 nm, with the formulae, $D = \frac{k \lambda}{\beta^* \cos \theta}$, where; $D=$ particle size, $k=0.9$, shape factor, $\lambda=$ X-ray wavelength, $\beta^*= $ Full Width Half Maximum and $\cos \theta= $ Bragg angle[9][10][11][12][13][14].

Table 1. Lattice Parameters (a, b, c), Crystallite Size (D), FWHM ($\beta^*$), Braggs Angle (2$\theta$) and Volume (V) of C1 (CuO), C2 (CuO + PANI, 25% wt CuO) & C3(CuO + PANI, 50% wt CuO).

|     | a (Å) | b (Å) | c (Å) | D (nm) | $\beta^*$ | 2$\theta$ | V (Å$^3$) |
|-----|-------|-------|-------|--------|----------|----------|-----------|
| C1  | 4.41  | 3.42  | 5.11  | 34.90  | 4.39 x 10$^{-3}$ | 38.72    | 82.53     |
| C2  | 4.41  | 3.42  | 5.11  | 31.52  | 4.86 x 10$^{-3}$ | 38.73    | 82.57     |
| C3  | 4.71  | 3.42  | 5.10  | 34.90  | 4.39 x 10$^{-3}$ | 38.72    | 82.52     |

Fig 1. XRD Analysis of C1 (CuO), C2 (CuO + PANI, 4:1) and C3 (CuO + PANI, 1:1).

4.2 FTIR Analysis
FTIR analysis is used to identify/study the functional groups present in a molecule. Every respective chemical bond has a distinctive energy band, which further facilitates in providing the information for the structure, strength & type of bond present in a compound. To obtain pure CuO, higher the temperature the nanopowders are calcinated at, lower will be the possibility for the formation of Cu2O or any other compound. For C1 (CuO), the standard Cu-O peaks were obtained at: 413.8 cm⁻¹, 435.4 cm⁻¹, 470.5 cm⁻¹, 528.8 cm⁻¹, 590.7 cm⁻¹ and 678.7 cm⁻¹, which occurs because of strong absorption between the molecules. The peaks from 1350 cm⁻¹ to 1680 cm⁻¹ were designated to C=O bonds present due to CO2 in the air. The peaks within the range 2800 cm⁻¹ to 3500 cm⁻¹ were the O-H bonds of water molecules. For C2 (CuO + PANI, 4:1), the peaks at values; 402.9 cm⁻¹, 433.8 cm⁻¹, 475.5 cm⁻¹, 508.4 cm⁻¹, 586.3 cm⁻¹ and 644.4 cm⁻¹ were of Cu-O molecule and peaks at 1373 cm⁻¹, 1523 cm⁻¹ and 1682 cm⁻¹ were C=O bonds. PANI peaks were obtained as: 819.1 cm⁻¹ & 891.8 cm⁻¹ for C-H bonds. 1123.8 cm⁻¹ for C-H bond. 1250.6 cm⁻¹ & 1300.9 cm⁻¹ were C-N stretching of PANI. Peaks at 1487.3 cm⁻¹ & 1560 cm⁻¹ were the benzoid ‘B’ and quinonoid ‘Q’- attachments of PANI respectively. N-H stretching of PANI was obtained at 3322.5 cm⁻¹ and 3436.2 cm⁻¹. 3500 cm⁻¹ to 3900 cm⁻¹ range of peaks were the due to O-H bond formation. For C3 (CuO + PANI, 1:1), 415.5 cm⁻¹, 439.1 cm⁻¹, 507.8 cm⁻¹ and 583 cm⁻¹ were the standard Cu-O peak values and 1373.6 cm⁻¹, 1523.6 cm⁻¹ and 1677.5 cm⁻¹ were the peaks of C=O bond. 833 cm⁻¹, 891.8 cm⁻¹ were C-H bonds. 1109.9 cm⁻¹ is In-Plane C-H bond. 1246 cm⁻¹ & 1300.9 cm⁻¹ were PANI C-N stretching peaks. The benzoid ‘B’ and quinonoid ‘Q’- units of PANI were given by peaks 1482.7 cm⁻¹ and 1568.5 cm⁻¹ respectively. 3177.1 cm⁻¹, 3327.1 cm⁻¹ and 3436.2 cm⁻¹ were the PANI N-H stretching peak values. O-H bonds formed due to water molecules falls within the range of 3500 cm⁻¹ to 3900 cm⁻¹. No peaks were obtained in the range 605 cm⁻¹ to 640 cm⁻¹, which indicates the absence of Cu2O[15][16][17][18][19][20][21][22][23][24][25][26][27][28].

Fig 2. FTIR Analysis of C1 (CuO), C2 (CuO + PANI, 4:1) and C3 (CuO + PANI, 1:1).

4.3 Raman Analysis
Raman spectroscopy is the “fingerprint” range of a molecule as the ‘Raman Shift’ gives data regarding the vibrational, rotational and the other additional low frequency transitions that takes place in the molecules. For C1 (CuO), CuO is associated with $C_{6}$ space group i.e. 2 molecules are present per each primitive cell. Now because there are 4 atoms present in a primitive cell therefore it consists of 12 phonon branches. The zone-centre optical-phonon modes are $\Gamma \frac{1}{4} A_{g} + 2 B_{g} + 4 A_{u} + 5 B_{u}$. Amidst of them, 9 optical modes are present out of which, there are 3- $(A_{g} + 2 B_{g})$ Raman active modes, 6- $(3 A_{u} + 3 B_{u})$ Infrared active modes and 3- $(A_{u} + 2 B_{u})$ symmetry Acoustic modes. The standard peaks were obtained for CuO at the values of: 293.5 cm$^{-1}$ allocated to $A_{g}$ mode and 341.1 cm$^{-1}$ & 627.2 cm$^{-1}$ to $B_{1g}$ mode and $B_{2g}$ modes respectively. For C2 (CuO + PANI, 4:1), the 413.8 cm$^{-1}$ peak was for $A_{g}$ mode and 520.5 cm$^{-1}$ & 781.9 cm$^{-1}$ peaks were for $B_{1g}$ mode and $B_{2g}$ modes respectively for CuO structure. For PANI, 1585.8 cm$^{-1}$ peak value was of C=C bond of quinonoid ‘Q’ unit. 1556.4 cm$^{-1}$ for N-H stretching. 1490.3 cm$^{-1}$ for the C-C bond of benzoid ‘B’ unit. 1415.7 cm$^{-1}$ was of C=N stretching. A C$\equiv$N$^+$ bond formation was also observed at 1322.5 cm$^{-1}$ peak value. The 1218.1 cm$^{-1}$ peak was for C-N bond. The C-H bond was observed at 1165.5 cm$^{-1}$. For C3 (CuO + PANI, 1:1), the peaks obtained for CuO were: 418.4 cm$^{-1}$ ($A_{g}$ mode) and 520.5 cm$^{-1}$ ($B_{1g}$ mode) & 777.3 cm$^{-1}$ ($B_{2g}$ mode). And for PANI; 1585.8 cm$^{-1}$ (C=C bond of quinonoid ‘Q’ unit), 1558.7 cm$^{-1}$ (N-H stretching), 1488.4 cm$^{-1}$ (C-C bond of benzoid ‘B’ unit), 1415.7 cm$^{-1}$ (C=N stretching), 1331.4 cm$^{-1}$ (C$\equiv$N$^+$ bond formation), 1218.1 cm$^{-1}$ (C-N bond) and 1165.5 cm$^{-1}$ (C-H bond). A drastic shift was obtained in CuO peaks in C2 and C3 as compared to C1, that could be because the formation of PANI may have interfered in CuO structure [29][30][31][32][33][34][35].

![Raman Spectroscopy Graph](image)

Fig 3. RAMAN Analysis of C1 (CuO), C2 (CuO + PANI, 4:1) and C3 (CuO + PANI, 1:1).

### 4.4 FESEM Analysis
FESEM uses the interaction with the electrons instead of light interaction and is availed regarding the detailed topographic statistics for the surface or the complete or the fractioned objects. For C1 (CuO), the SEM analysis of CuO exhibited an image of properly formed monoclinic crystal structure of the mentioned metal oxide as observed in fig (a), which was in accordance with the theoretical results as well. The EDX Mapping of the sample shows the emergence of Cu and O peaks which concludes the formation of the metal oxide CuO. The atomic wt % ratio of Cu-atom and O-atom is 1.6. Also the average particle size obtained was 24.9 nm. CuO nanoparticles displayed a uniform size distribution with respect to few of the compact structures. For C2 (CuO + PANI, 4:1), the peaks for Cu-atom, O-atom, N-atom and C-atom were obtained which shows the formation for both CuO & PANI in the composite mixture. In fig (b), no proper structure formation for CuO is seen, and so the distorted structure showed that PANI has interfered with the structure of the host material and thence concludes that the bond formation has taken place[36][37].

![Image](image_url)

**Fig 4.** FESEM and EDX mapping Analysis of (a). C1 (CuO) and (b). C2 (CuO + PANI, 4:1).

### 4.5 Dielectric & Impedance Analysis

The impact of temperature and frequency on the occurrence of conduction whether in bulk or nanostructured materials is learned through Dielectric Studies. The dielectric behaviour of the matter is attributed to the ionic, electronic and dipolar properties. The dielectric evaluation is done to understand the electrical mechanisms happening inside the materials. In Fig 5(a). the dielectric constant was decreasing continuously with the increase in the value of frequencies, with C3 giving the lowest values among the three samples. The high dielectric constant values at lower frequencies and then it being continually decreasing w.r.t increase in temperature can be interpreted as; the dipole becomes free with the raising temperature and they react to the electric field that is being applied. Therefore, leading to the increase in polarization and hence the values of dielectric constant. The dielectric loss, Fig 5(b). was exhibiting similar pattern as that of dielectric constant. The reason for such behaviour can be because of lattice defect. The pure CuO was showing different nature with its loss value showing an increase after a certain frequency value with increase in temperature. The AC Conductivity was studied through Fig...
The pure CuO showed the highest value for electrical conductivity and as the amount of PANI was increased, the conductivity showed decreased values with C3 showing the least values. Fig 5(d), (e), are the real ($Z'$) and the imaginary ($Z''$) part of the complex impedance. These types of plots including Fig 5(f) were known as the Nyquist plots of Impedance. This graphical plot was comprised of three semi-circles; left-side semi-circle (at higher frequencies) for contribution of grain, middle semi-circle (at intermediate frequencies) for contribution of grain boundaries and right-side semi-circle (lower frequencies) for the contribution of interface. In Fig 5(f), C3 was exhibiting strange behavior with minute zig-zag orientation which could be because of the increased amount of polymer present in CuO[38][39].
5. Conclusion

The composite mixture of CuO and PANI was studied through three varying samples C1 (CuO), C2 (CuO + PANI, 4:1) and C3 (CuO + PANI, 1:1), with CuO and PANI synthesised through ‘Sol Gel Auto-Combustion’ and ‘Oxidative Polymerization’ respectively. X-ray analysis affirmed the CuO formation having the space group of $C_{6h}$. FTIR showed the characteristic peaks for CuO (402.99-678.74 cm$^{-1}$) and PANI (1109.94-1568.54 cm$^{-1}$ and 3058.81-3436.21 cm$^{-1}$). The addition of PANI increased the resistivity of CuO drastically (i.e. decreased the conductivity values as compared to standard values) which makes the composite mixture an emerging candidate material for resistors and such devices.

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