Synthesis and characterization of ZnO/CuO nanocomposite for humidity sensor application

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Abstract

Metal oxide nanomaterials shows variety of applications in the field of optoelectronics, semiconductors, catalysis, coatings, solar cells, ceramics, spintronic, biological and sensors. Present paper deals with ZnO/CuO nanocomposite material synthesis, characterization and humidity sensor application. Novelty of this work is to know the high sensitivity of two conjugated n and p type semiconductor metal oxide nanocomposite at various temperatures. Nanocomposite materials are synthesized by microwave-assisted method with the help of room temperature ionic liquid (RTIL). Zinc acetate, Copper acetate, Sodium hydroxide and 1-butyl-3-methyl-imidazolium-tetrafluoroborate ([BMIM]BF_4) were used as initial precursors. The obtained nanocomposite materials were annealed at different temperatures such as 500 °C, 600 °C, 700 °C and 800 °C. These annealed nanocomposite materials have been characterized by X-ray diffractometer (XRD), Particle size analyzer (PSA), Scanning electron microscope (SEM), Energy dispersive x-ray spectrometer (EDS) and Thermo gravimetric and differential thermal analyzer (TG/DTA) for analyze crystal structure, average particle size, surface morphology, elemental analysis and weight loss respectively. The humidity sensor application was predicted by controlled humidity chamber, hygrometer and digital multi meter. The resistance of the sensing element measured with respect to relative humidity from 10% to 98%. The sensitivity of the nanocomposite material increased from 1.7 % to 2.3 % along with increasing of annealing temperature 500 °C to 800 °C. ZnO/CuO nanocomposite annealed at 800 °C shows high sensitivity means it is also having good response and recovery times.

Keywords: ZnO/CuO nanocomposite; microwave-assisted method, XRD, SEM, humidity sensor application.

Introduction

The water vapour content in air or gas is called as Humidity; it affects many chemical, physical and biological processes [**1**]. A physical or chemical or biological parameter converted into electrical signal by the use of Sensor. Humidity sensor is used for the accurate control and reliable estimate of water vapours content in atmosphere. If the electrical signal converted by physical parameters it is known as physical sensor, if it is due to chemical and biological it is known as chemical sensor and biological sensor respectively [**2**]. The chemical sensor importance was increased day-by-day in the applications of environmental monitoring, air quality detection, packaging industry, security purposes in life comforts instruments, defence and health care [**3**]. Nanostructured metal oxides were shown extremely advanced properties in the area of chemical, magnetic, mechanical, optical, electronic and biomedical owing to its high surface to volume ratio and dimensionality. Generally, many metal oxide nano materials are available such as ZnO, CuO, TiO_2, SnO_2, WO_3 and In_2O_3 [**4**]. ZnO (Zinc oxide) is a wide band gap n-type semiconductor material with 3.3 eV energy gap and high excitation binding energy of 60 meV, due to this reason the different morphologies of the material was possible like nano rings, nano tubes, nano rods, nano sheets and nano wires [**5, 6**]. CuO (Copper oxide) is an inorganic p-type semiconductor material having 1.85 eV direct band gap [**7**]. The combination of ZnO/CuO semiconductor nano materials forms p-n heterojunction means that, electron donor-acceptor pairs observed in between n-type metal oxide and p-type metal oxide [**8**]. It can be used in various applications because of the improvement in the field emission within the devices and simultaneously increase the charge carrier separation [**9-11**]. Various synthesis techniques were available to prepare metal oxide nano materials like sol-gel [**12**], hydrothermal [**13**], chemical precipitation [**14**], chemical vapour deposition [**15**], microwave-assisted [**16, 17**] electrochemical [**18**]. Among all those methods microwave-assisted method is selected for synthesis of ZnO and CuO nano materials, because it is a very simple and fast technique which is performed under atmospheric pressures [**19**]. During the synthesis process, room temperature ionic liquid ([BMIM]BF_4) is added along with stirring, the reason behind this is to control the size and obtained different shapes [**20**].

This present paper, deals with the ZnO/CuO metal oxide nanocomposite synthesis, characterization and humidity sensor application. The novelty of this current study is to know the high sensitivity response of two conjugated n and p type semiconductor metal oxides at various temperatures. The 1:1 ratio of ZnO and CuO weight percentages taken and make ZnO/CuO nanocomposite using mechanical milling. The as synthesized ZnO/CuO nanocomposite materials were annealed at different temperatures such as 500 °C, 600 °C, 700 °C and 800 °C [**21**]. The obtained ZnO/CuO nanocomposite materials were characterized by X-ray diffractometer, Particle size analyser, Scanning electron microscope, Energy dispersive x-ray spectrometer and Thermo gravimetric & differential thermal analyser. The humidity sensor application of ZnO/CuO nanocomposites was investigated by hygrometer, sinometer (Digital Multi Meter-VC-9808^+) and controlled humidity chamber.

Experimental

Materials

Zinc acetate (98% purity), copper acetate (98% purity), 1 – butyle – 3 – methyle - imidazolium tetrafluoroborate [BMIM]BF_4) (97% purity) and sodium hydroxide (99% purity) all are purchased from Sigma Aldrich.

Material synthesis

ZnO and CuO nano materials were prepared individually and mixed with mechanical milling method. Zinc acetate (0.1 M) taken into 100 mL distilled water and mixed NaOH (0.1 M) with vigorous stirring. After 30 min of stirring [BMIM] BF_4 (0.9 mL) added to the above solution along with continuous stirring. This above solution kept in microwave-oven and irradiated for 10 min. Then cooled it to room temperature, centrifuged and collect the ZnO nano material. Copper acetate (0.1 M) taken into 100 mL distilled water and mixed NaOH (0.1 M) with vigorous stirring. The [BMIM]BF_4 (0.9 mL) added to the above solution along with continuous stirring after 30 min. This above solution kept in microwave - oven and irradiated for 10 min. Then cooled it to room temperature, centrifuged and collect the CuO nano material. The 1:1 weight percentage of ZnO and CuO nano materials mechanically milled using mortar and pestle for 60 min and prepared ZnO/CuO nanocomposite. The obtained nanocomposites characterized by various characterization techniques after heat treated at 500 °C, 600 °C, 700 °C and 800 °C temperatures.

Characterizations

The crystal structure and average crystal size was measured by BRUKER D8 Advanced X-ray diffractometer using CuKα_1 radiation (0.154 nm). The average particle size was obtained by HORIBA SZ-100 particle size analyzer. Surface morphology and elemental analysis observed using ZEISS scanning electron microscope. The weight loss of the material was calculated by EXSTRAR-6300 thermo gravimetric analyzer. The humidity sensor application was investigated by controlled humidity chamber, hygrometer and sinometer (DMM-VC-9808^+).

Results and discussion

X-ray diffractometer

The XRD pattern of nanocomposite at different annealing temperatures was shown in figure 1. ZC-5, ZC-6, ZC-7 and ZC-8 signified the annealing temperatures 500 °C, 600 °C, 700 °C and 800 °C respectively. The formation of ZnO/CuO nanocomposite was confirmed by the peaks which were obtained in the pattern. The symbols @ and # were used to represented ZnO and CuO peaks respectively. The XRD pattern matched with the JCPDS cards 36-1451 and 89-5899 for ZnO (hexagonal) and CuO (monoclinic) respectively.

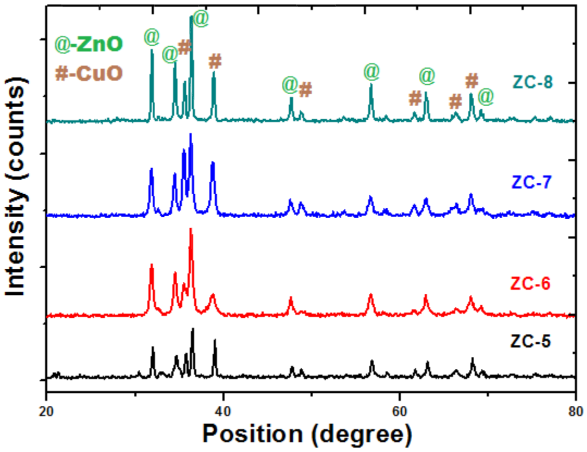

Fig.1 XRD pattern of ZnO/CuO nanocomposite.

There is no phase transformations occurred in the nanocomposite materials. The miller indices of the nanocomposite were observed as (1 0 0), (0 0 2), $(\bar{1}\,1\,1)$, (1 0 1), (1 1 1), (1 0 2), $(\bar{2}\,0\,2)$, (0 2 1), $(\bar{1}\,1\,3)$, (1 0 3), (2 0 0), (2 2 0) and (2 0 1) for 31°, 34°, 35°, 36°, 38°, 47°, 48°, 56°, 61°, 62°, 66°, 68° and 69° respectively. The bar which is indicated in the miller indices had shown the negative direction of plane.

The average crystallite was measured by Debye-Scherrer's equation:

$$D = {}^{K.\lambda}\!/_{\beta cos\theta} \qquad (1)$$

where, K-Debye-Scherrer's constant (0.9), λ-wavelength of the radiation (for $CuK\alpha_1$=0.154 nm), β-full width half maximum of the particular peak, θ-Bragg's angle.

The measured average crystallite sizes were 19 nm, 22 nm, 27 nm and 31 nm for ZC-5, ZC-6, ZC-7 and ZC-8 respectively [**21**].

Particle size analyzer

The average particle size of the nanocomposite was measured by particle size analyzer. The ND-YAG laser light source (wavelength 532 nm) is used in particle size analyzer. The nanocomposite was dispersed in ethanol for 15 min using ultra sonicator. The dispersed solution was taken into cuvette and observed the distribution of particles. If the particles motion is slow-the size of the particles is more, if it is fast- size of the particles is less. Based on this the histogram of the ZnO/CuO nanocomposite was formed. The mean value of the histogram is taken as average particle size. The average particle size of the ZnO/CuO nanocomposite was 25 nm, 29 nm, 32 nm and 38 nm for ZC-5, ZC-6, ZC-7 and ZC-8 respectively **[22]**.

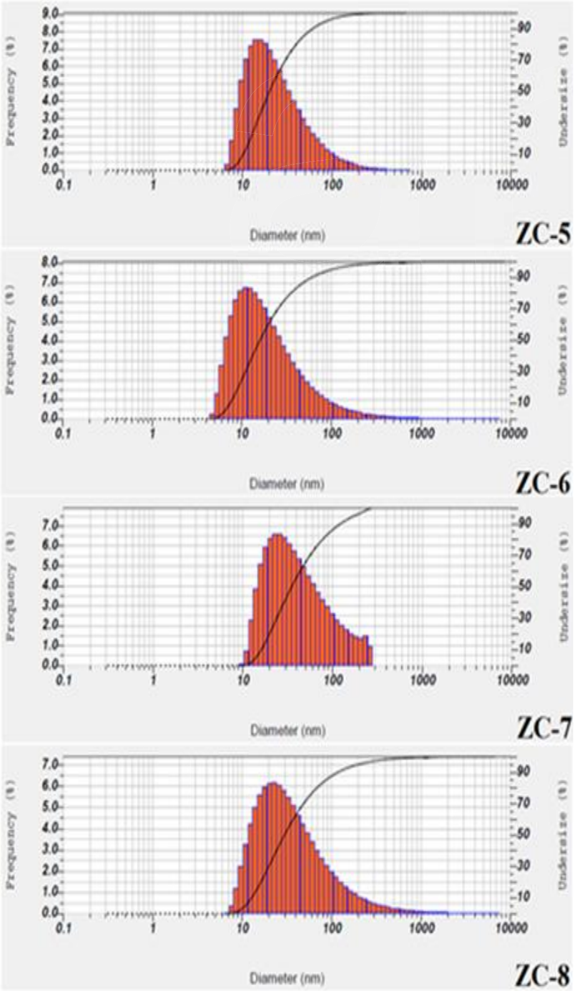

Fig. 2 XRD pattern of ZnO/CuO nanocomposite.

Scanning electron microscope and Energy dispersive x-ray spectroscope

Fig. 3 was shown that the ZnO/CuO nanocomposite SEM images at various annealing temperatures and the EDS spectrum of ZnO/CuO nanocomposite. The 1 µm SEM images inferred that the porous nature of the nanocomposite increased along with increasing of annealing temperature. This was happened due to the agglomeration of the nanocomposite. Depending on the agglomeration the particle size is increases, it causes increase the porosity of nanocomposite.

The porosity of the nanocomposite measured by the equation,

$$P\ (\%) = \frac{(\rho_{th} - \rho_a)}{\rho_{th}}\ X\ 100 \qquad (2)$$

where ρ_{th}-theoretical density and ρ_a-actual density.
The nanocomposite materials were showing spherical balls with chain like structures.

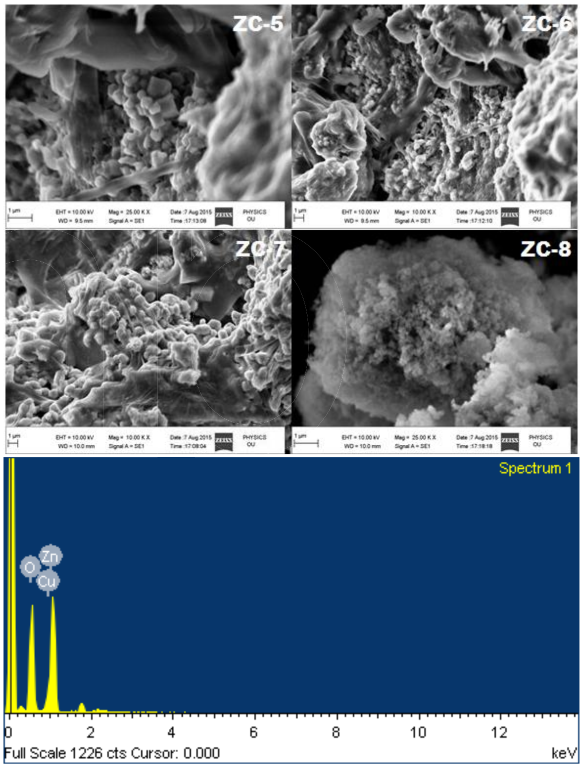

Fig. 3 SEM images and EDS spectra of ZnO/CuO nanocomposite.

The size range of the spherical shaped structures is 500 nm to 800 nm. The porosity of the ZnO/CuO nanocomposite is 3.364 %, 3.812 %, 4.258 % and 4.728 % for ZC-5, ZC-6, ZC-7 and ZC-8 respectively (The theoretical density of ZnO/CuO composite is 4.7476 gr/cc). Because of the above reason the nanocomposite is used in humidity sensor application.

The elemental analysis of the nanocomposite was explained by EDS spectrum. Zinc (Zn), Copper (Cu) and Oxygen (O) elements which were presented in the ZnO/CuO nanocomposite as shown in **Fig. 3**. The atomic percentages (Zn-23.24 %, Cu-22.39 % and O-55.37 %) also supported the formation of ZnO/CuO nanocomposite [**23, 24**].

Thermo gravimetric analysis

The ZnO/CuO nanocomposite weight loss was measured by thermo gravimetric analysis which is shown in **Fig. 4**. The weight loss and stability of the composite material observed from room temperature to 800 °C. From room temperature to 120 °C weight loss caused by the evaporation of water molecules. The organic materials evaporation was given the weight loss from 120 °C to 350 °C. From 350 °C to 800 °C the weight loss observed due to the evaporation of inorganic materials which were involved in the chemical reaction. The total weight loss was obtained as 2.1 %, 1.9 %, 1.8 % and 1.5 % for ZC-5, ZC-6, ZC-7 and ZC-8 respectively. The ZC-8 is having high stability compared with remaining three **[25]**

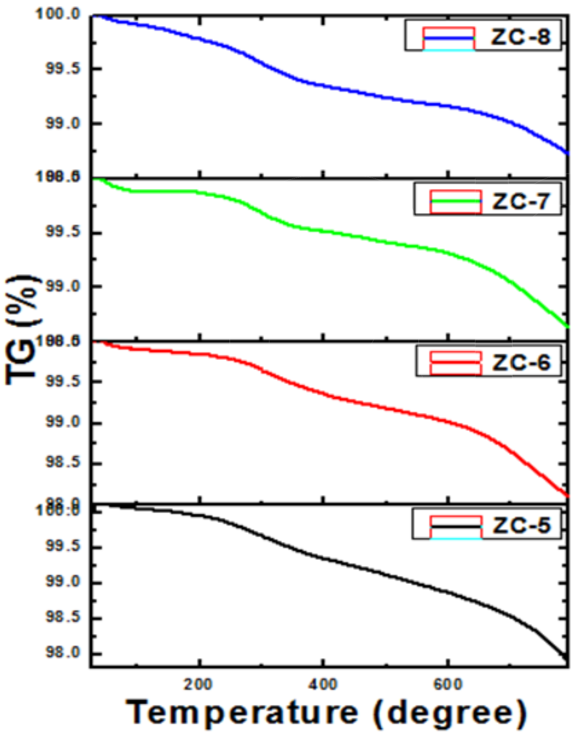

Fig. 4 TGA curves of ZnO/CuO nanocomposite.

Humidity sensor application

The ZnO/CuO nanocomposite is made as a pellet and investigated humidity sensor application. The controlled humidity chamber was used to create the humidity, the hygrometer is used to measure the relative humidity and the resistance was measured by digital multi meter. The resistance of the sensing element (pellet) observed with respect to relative humidity (RH) 10% to 98%. When the RH (%) increased the resistance was decreased. When the humidity of sensing element increases, more number of electrons is ejected and it causes the high conductance means resistance decreased. The resistance was decreased from 1342 MΩ to 1069 MΩ, 1374 MΩ to 1087 MΩ, 1401 MΩ to 1090 MΩ and 1430 MΩ to 1093 MΩ for ZC-5, ZC-6, ZC-7 and ZC-8 respectively. The resistance in terms of relative humidity was shown in **table 1** and resistance with respect to relative humidity shown in **Fig. 5**.

Table 1. Resistance in terms of relative humidity

RH (%)	CT-5	Error ±(2%)	CT-6	Error ±(2%)	CT-7	Error ± (2%)	CT-8	Error ±(2%)
10	1342	26.84	1374	27.48	1401	28.02	1430	28.6
20	1325	26.5	1356	27.12	1381	27.62	1407	28.14
30	1307	26.14	1337	26.74	1360	27.2	1382	27.64
40	1287	25.74	1316	26.32	1337	26.74	1356	27.12
50	1264	25.28	1292	25.84	1312	26.24	1328	26.56
60	1239	24.78	1266	25.32	1284	25.68	1298	25.96
70	1211	24.22	1237	24.74	1252	25.04	1264	25.28
80	1180	23.6	1204	24.08	1217	24.34	1226	24.52
90	1146	22.92	1168	23.36	1179	23.58	1185	23.7
95	1109	22.18	1129	22.58	1136	22.72	1141	22.82
98	1069	21.38	1087	21.74	1090	21.8	1093	21.86

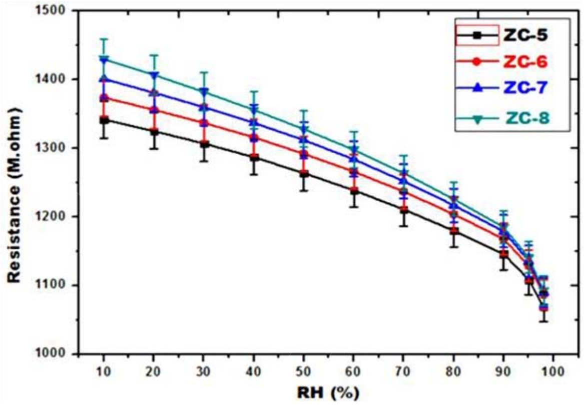

Fig. 5 Resistance with respect to Relative Humidity

The above data also inferred that the resistance value was increased with increasing of temperature. The sensitivity of the sensing element was measured by the following equation

$$S = {}^{\Delta R}/_{\Delta RH} \tag{3}$$

where, ΔR-is the change in resistance and ΔRH-is the change in relative humidity.

Table 2. Sensitivity in terms of relative humidity

RH (%)	CT-5	Error ±(2%)	CT-6	Error ±(2%)	CT-7	Error ±(2%)	CT-8	Error ±(2%)
15	1.7	0.034	1.8	0.036	2	0.04	2.3	0.046
25	1.8	0.036	1.9	0.038	2.1	0.042	2.5	0.05
35	2	0.04	2.1	0.042	2.3	0.046	2.6	0.052
45	2.3	0.046	2.4	0.048	2.5	0.05	2.8	0.056
55	2.5	0.05	2.6	0.052	2.8	0.056	3	0.06
65	2.8	0.056	2.9	0.058	3.2	0.064	3.4	0.068
75	3.1	0.062	3.3	0.066	3.5	0.07	3.8	0.076
85	3.4	0.068	3.6	0.072	3.8	0.076	4.1	0.082
95	3.7	0.074	3.9	0.078	4.3	0.086	4.4	0.088
98	4	0.08	4.2	0.084	4.6	0.092	4.8	0.096
Average	1.7	0.034	1.8	0.036	2	0.04	2.3	0.046

The sensitivity of the sensing element was increased with increasing of relative humidity from 15% to 98%. The sensitivity of the sensing element increased from 1.7 to 4.0, 1.8 to 4.2, 2.0 to 4.6 and 2.3 to 4.8 for ZC-5, ZC-6, ZC-7 and ZC-8 respectively. The sensitivity in terms of relative humidity was shown in **table 2** and sensitivity with respect to relative humidity was shown in **Fig. 6**.

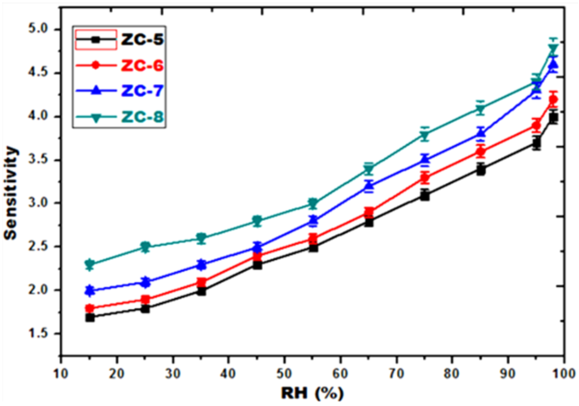

Fig. 6 Sensitivity with respect to Relative Humidity

Conclusion

ZnO/CuO nanocomposite materials were successfully synthesized by microwave-assisted technique using room temperature ionic liquids. The obtained materials heat treated at different annealing temperatures. XRD and EDS confirmed the formation of ZnO/CuO nanocomposite material. The ZnO (hexagonal) and CuO (monoclinic) structures were observed in XRD and the average crystallite was obtained within the nano range. The average particle size was greater than the average crystallite size. The porosity of the composite materials increased with increasing of annealed temperature, it was found in SEM images. The stability was increased with increasing of annealed temperature suggested by TGA. The resistance decreased with increasing of relative humidity and the humidity sensitivity was increased with annealed temperatures. Due to this reason the high annealed temperature sensing elements were used in humidity sensor fabrication.

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