RESEARCH PAPER

Preparation and Characterisation of ZnO - SiO_2 and Bi_2O_3 – CuO Nanocomposites

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ABSTRACT

In the present work, ZnO - SiO_2 and Bi_2O_3 – CuO nanocomposites have been prepared by sol gel with alternate precursors existing in literature. They are characterised by XRD, SEM,UV, FTIR and photoluminescence spectra .The XRD results indicate a crystallite size of approximately 80 nm for both nanocomposites. SEM image shows a heterogeneous particle size for both samples. The band gap of ZnO- SiO_2 and Bi_2O_3– CuO obtained from Taucs plot is 4.1 eV and 2.85 eV, respectively. PL spectra show high intensity absorption for ZnO-SiO_2 in comparison to Bi_2O_3–CuO. The composites of Bi_2O_3–CuO is recommended for efficient optical coating against the coating made from Bi_2O_3

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INTRODUCTION

Nanocomposites are the 21st century materials which find application in aerospace, biomedical and automobile industries[1]. An appreciable property change is observed between the micro composite and nanocomposite of the same chemical composition. The size property correlation can further contribute to the property of nanocomposite. Among the various class of nanocomposites, oxide based composites have been investigated extensively due to their ease of preparation. Oxide composites are alternatives to silicon carbide composites owing to their low cost and improving thermal stability at high temperature [2]. Oxide–Oxide ceramic matrix composites have enabled wide spread industry adoption because of low cost fibre and development in fabric architectures [3]. A recent research demonstrates the major application of metal oxide composites as gas sensors [4]. ZnO - SiO_2 nanocomposites were investigated for their sensing properties by Mossad *et al.* [5]. ZnO - SiO_2 nanocomposites have also been studied and characterised by Panthohan *et al.* [6]. Mossad synthesised ZnO - SiO_2 nanocomposites from zinc acetate, TEOS, and SiO_2. Panthohan used rice husk as a source of silica source. ZnO- SiO_2 nanocomposites show UV, Visible and white light emissions with relatively small limiting threshold [7].In the present work, ZnO- SiO_2 nanocomposites have been synthesised from Zinc Sulphate and SiO_2 powder.

Bi_2O_3 nanoparticles were synthesised and investigated for their catalysis, optical coatings and gas sensors [8]. Bi_2O_3 nanoparticles of 50 nm were synthesised previously with bismuth nitrate, and urea [9].Nanocomposites of Bismuth oxide-zirconia, bismuth oxide- multi walled carbon nanotube, bismuth oxide-barium titanate, and bismuth oxide-polyaniline have been reported earlier[10-11]. Bismuth oxide nanocomposites

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have been used as electrolyte for low temperature fuel cells [10] and H_2O_2biosensors [11].CuO has a narrow band gap of 1.2eV and is used for sensors, solar cells and optoelectronic industries [12]. Synthesising nanocomposites of Bi_2O_3–CuO can contribute to the increase in thermal and electrical properties of Bi_2O_3.

EXPERIMENTALS

Preparation of ZnO - SiO_2 nanocomposites

3g of Zinc sulphate is dissolved in 50 ml distilled water along with 2 cc of ammonium hydroxide .The solution is stirred for 10 min. 1 g of SiO_2 powder is added to the solution while stirring for 30 min at room temperature. This is followed by simultaneously heating and stirring at 70 °C for four h. A paste of the precursors obtained is then heated at 500 °C for 2 h to get the desired nanocomposite.

Preparation of Bi_2O_3– CuO composites

3g of copper sulphate is added to 50 ml distilled water and stirred for 20 min. Similarly, 3g of bismuth sulphate is added to 50 ml distilled water and stirred for 20 min. Then, both solutions are mixed and 0.5 g NaOH is added to the solution during stirring. The solution is heated at 200 °C for 3 h and 600 °C for 2 h to get the desired nanocomposite. Colour changes were observed with addition of NaOH.

RESULT AND DISCUSSION

Characterization of the prepared nanocomposites

X-Ray diffraction: Powder diffraction pattern of the samples are collected from PANalytical X'Pert PRO powder X-ray Diffractometer with a step size of 0.05 and diffraction angles 20 ˚ to 80°. The scan step time is 10 sec and K alpha radiation is 1.54060A. A mixture of amorphous and crystalline morphology is observed from the XRD pattern of ZnO - SiO_2 nano composite as indicated in Fig 1. During preparation, the sample was calcined at 500 °C for two h. This could be the reason for the presence of crystalline phases of wurtzite ZnO observed at 2θ values of 30, 46 and 73. Similar results have been also reported for ZnO - SiO_2nano composite heated at 600 °C [6]. The peak obtained at 22 and 26 are indicative of SiO_2 phase. Since Zinc sulphate is taken in larger amount (3g) in comparison to SiO_2 (1g), there are more peaks for ZnO .This also indicates incomplete dispersion of the individual phases of composites.

The crystallite size is calculated by Debye Scherrer's equation i.e. $D=0.91\lambda/\beta.\cos\theta$ where,

D– Crystallite size in nm.

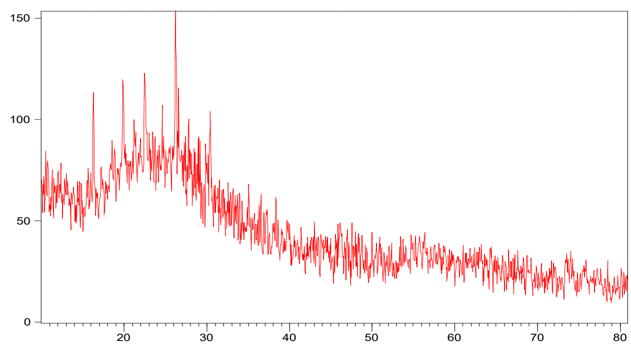

Fig. 1. XRD image of ZnO-SiO_2 nanocomposite

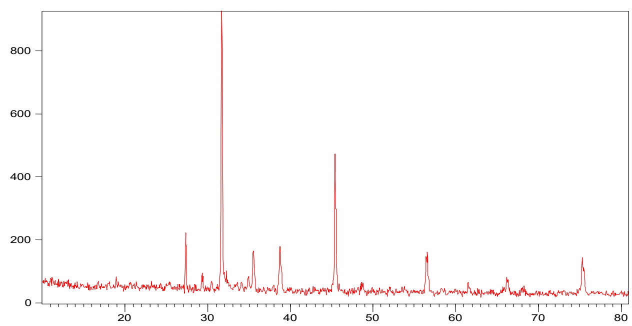

Fig. 2. XRD of Bi_2O_3– CuO nanocomposite

λ – Wave length of the X-ray radiation in nm^{-1},
β – Corrected full width at half maximum height,
θ – Diffraction angle in degrees.

The crystallie size for ZnO - SiO_2 nanocomposite is approximately 80 nm.

A crystalline morphology is observed from the XRD pattern of Bi_2O_3– CuO nanocomposite, as shown in Fig 2. The peaks observed at diffraction angles of 35-40 and 55, 63, and 75 confirm the presence of CuO, and peaks at 26 and 45 confirm the presence of Bi_2O_3. CuO is identified in its monoclinic tenorite phase and the results are in accordance with JCPDS 89-2531. Bi_2O_3 is identified in its monoclinic alpha phase [11].The crystallite size of the prepared Bi_2O_3– CuO nano composite was found to be 80 nm using the Debye Scherrer formulae.

SEM Characterisation

Fig. 3 shows the SEM image of ZnO-SiO_2 nanocomposite with inhomogenous grain size and high agglomeration. Fig. 4 shows the SEM image of Bi_2O_3– CuO with irregular shaped particles. A large volume fraction is seen in nano size varying from 100-250 nm.

UV Characterization

UV-Vis absorption spectrum of dispersed powders for both composites were recorded with UV-Vis-NIR spectrometer, Oceanoptics from 200-800 nm. Band gap is found by constructing Taucs plot for different energy values from transmission spectrum for both nanocomposites as shown in Figs. 5 and 6. The band gap for ZnO - SiO_2 and Bi_2O_3– CuO are approximately 4.05 eV and 2.85 eV. Amorphous silicon thin films have a band gap of 9.3 eV as reported by Weinberg [12]. Celabrese reported the band gap of α quartz as 6.3 eV [13]. For 3 nm particles the band gap of SiO_2 is 2.6 eV [14]. The band gap properties of semiconductors largely depend on the nanosize and percentage of crystallinity. The present work identifies the band gap for ZnO - SiO_2 as 4.05 eV for a size of 80 nm.The results depend on the nanosize, shape

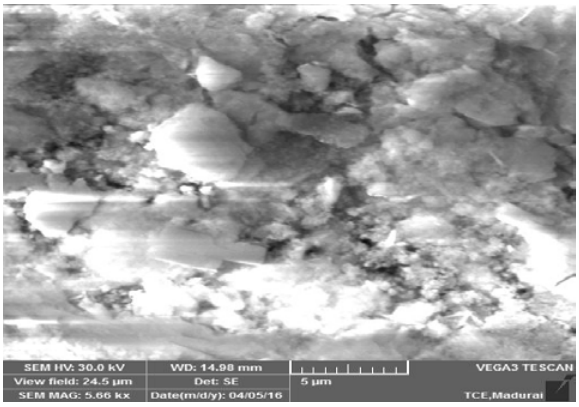

Fig. 3. SEM image of ZnO-SiO_2 nanocomposite

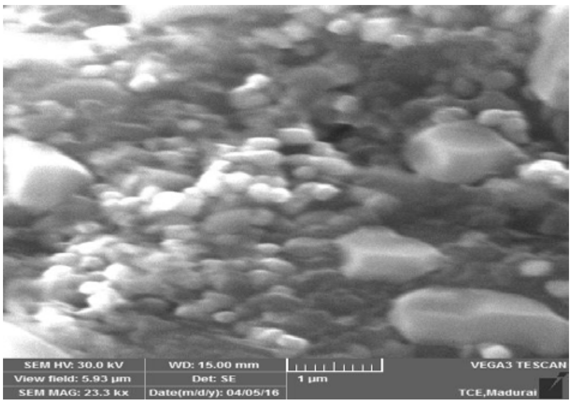

Fig. 4. SEM image of Bi_2O_3– CuO nanocomposite

and also volume fraction of individual phase and method of measurement of band gap. The band gap of monoclinic alpha phase of Bi_2O_3 is 2.85 eV [15] and monoclinic tenorite phase of CuO is 2.1eV .In the present work, the band gap of Bi_2O_3– CuO is the same as that of monclinc Bi_2O_3– CuO. Thus, the same optical properties of Bi_2O_3 can be obtained, however, the thermal conductivity of the composite can increase due to presence of CuO. Bi_2O_3–CuO can produce optical coatings with better heat transfer and cut down additional expenditure in cooling for optoelectronic devices.

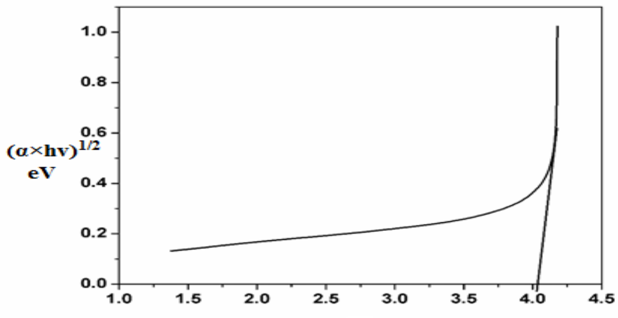

Fig 5. Taucs plot of ZnO - SiO_2

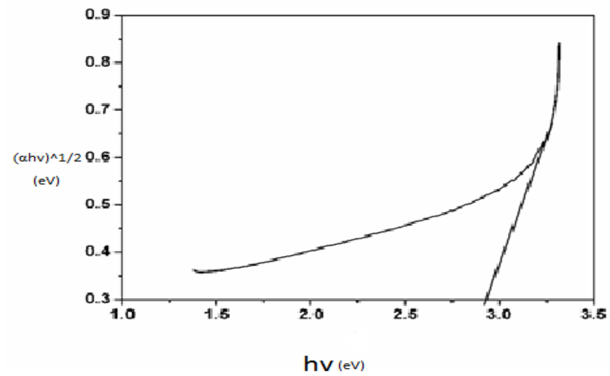

Fig. 6. Taucs plot of Bi_2O_3– CuO

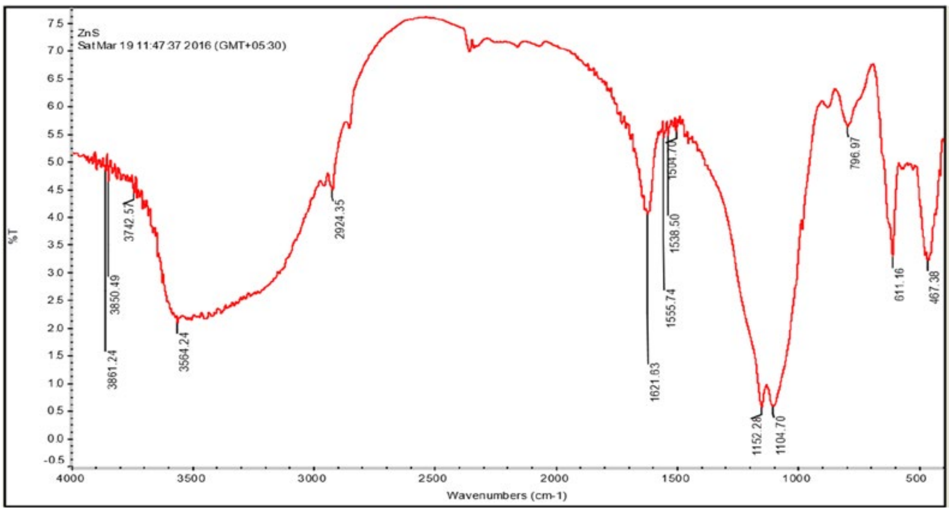

Fig. 7. FTIR Image of ZnO -SiO_2 nanocomposite

FTIR Characterization

FTIR (Fourier transform infrared spectroscopy) was recorded with JASCO FTIR spectrophotometer. FTIR is used to find the type of bonds present in the sample. Figs. 7 and 8 show the FTIR spectrum for ZnO - SiO_2 and Bi_2O_3– CuO.

Tables 1 and 2 give the characteristic peaks and functional groups present in both nanocomposites. The peaks obtained at 460 cm^{-1} indicates Zn-O bonding [5] and 796 cm^{-1} indicates O-Si-O bonding .The peak at 1150 cm^{-1} also indicate intense Si-O bonding. The peak at 587 cm^{-1} is assigned to Bi-O bonding, and 511 cm^{-1} is indicative of CuO. The broad peak at 3400 cm^{-1} in both samples indicates that O-H bond exists in both samples, and water molecules have been absorbed by both nanocomposites.

PL Spectra

Fig 9. shows PL spectra of the prepared nanocomposites. ZnO – SiO_2 nanocomposite shows high intensity absorption for all wavelengths in comparison to Bi_2O_3– CuO nanocomposite. ZnO – SiO_2 nanocomposite has a strong peak at 465 cm^{-1} with peak energy 2.65 eV. The same results have been predicted by Fan and co-workers [16]. Secondary peaks are observed at 365 nm and 420 nm that may be due to defects of oxygen vacancies in the sample.

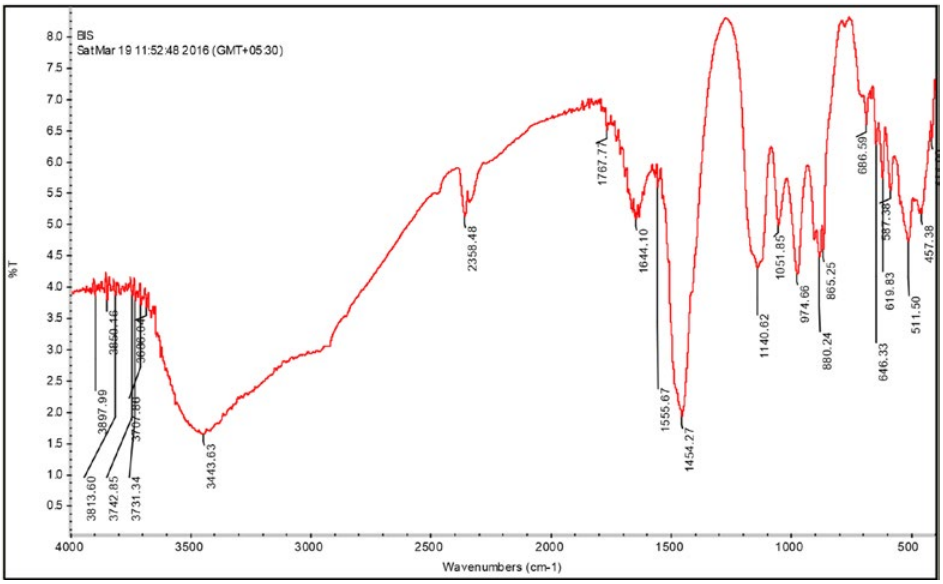

Fig. 8. FTIR Image of Bi_2O_3– CuO nanocomposite

Table1. List of peaks and functional groups in ZnO-SiO_2 nanocomposite

Wavenumber(cm^{-1})	Group identified
3564.24	O-H
1621.63	O-Zn Indicating presence of Zinc oxide
1152.28	Intense Si-O
796.97	O-Si-O Indicating presence Of SiO_2

Table2. List of peaks and functional groups in Bi_2O_3– CuO nanocomposite

Wavenumber(cm^{-1})	Group identified
3850.16	O-H
1644.10	O-Cu-O Showing presence of copper oxide
587.38	O-Bi-O Showing Bismuth oxide
457.38	O-H

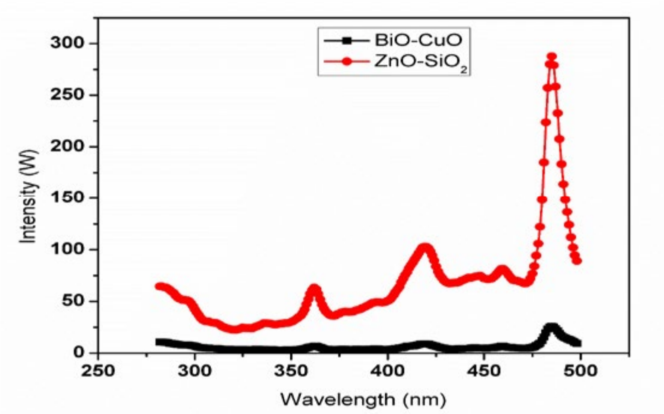

Fig. 9. PL spectra of the prepared nanocomposites

CONCLUSION

$ZnO-SiO_2$ and Bi_2O_3-CuO nanocomposites were prepared by sol gel with alternate precursors existing in the literature, and characterised by XRD, SEM, UV, FTIR and PL. Both nanocomposites have a crystallize of 80 nm, and have compressive microstrain in the sample. The band gap of $ZnO-SiO_2$ and Bi_2O_3– CuO obtained from Taucs plot is 4.1 eV and 2.85 eV, respectively. Based on the results, we suggest Bi_2O_3– CuO for efficient optical coatings with thermal management and good cathode material for solid oxide fuel cells. $ZnO-SiO_2$ nanoocmposite is recommended as a better catalyst for photo degradation in comparison to Bi_2O_3-CuO. The PL spectra show high intensity absorption for $ZnO-SiO_2$ in comparison to Bi_2O_3-CuO.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper.

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