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A New Approach towards Gas Sensing through A.C. Conductivity of Tin Oxide-Copper Oxide Composite

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Abstract

Tin oxide- Copper oxide composites were synthesized by a hydrothermal method using tin chloride dihydrate and copper nitrate trihydrate as precursors in different molar ratios. The obtained powders were characterized by X-ray diffraction and dielectric analysis. The average crystallite sizes were determined. The analysis exhibited a tetragonal phase for tin oxide and cubic phase for copper oxide. The microstructure of the composites were examined by the scanning electron microscopy. Optical properties were investigated by a UV-Vis absorption spectrophotometer. Good electrical response of the composites to cigarette smoke was observed in dielectric analysis, holding substantial promise for SnO2-CuO as a challenging material for novel sensing applications.

Keywords: Cigarette smoke; A.C.Conductivity; hydrothermal; composite; morphology.

Introduction

Cigarette smoke has proven to be a major health concern over the past years and it is a complex and reactive mixture containing chemicals that are both toxic and carcinogenic. The literature reveals that cigarette smoke contains more than 5000 chemicals including 90 ingredients that are hazardous [1]. Passive smoking is equally dangerous; non-smokers who breathe in this second hand smoke containing nicotine and other harmful substances on regular basis are susceptible to toxic effects that are absorbed into the body [2].

Metal oxide semiconductors such as tin oxide [SnO_2] are attractive materials for sensing applications from both the scientific and technological viewpoint [3]. The n-type wide band gap (3.4-4.6eV) semiconductor is known for its high chemical stability, low operating temperature and low resistivity [4, 5]. In addition, this oxide holds the key to understanding the viewpoint of the surface properties because of the dual valency of Sn. In fact, the gas response is stimulated not due to the chemisorbed oxygen causing an increase or decrease in conductivity [6].

Composite materials have novel and distinct properties and more effort has been taken to explore their high performance. Much pioneering research has been done in tin oxide with copper oxide as a catalyst [7].Cupric oxide is an important p-type semiconductor metal oxide with band gap of 1.2eV [8] with a potential prospective for gas sensors. It is a promising candidate because of its long stability, low power consumption [7], high specific surface area and good electrochemical activity [9, 10].

Gas Sensing technology is of immense importance and has received significant attention over the past decade. From literature we see that considerable research is going into these sensors, in order to enhance its functioning by improving the features like sensitivity, response and recovery time and stability [11-15]. SnO_2 has been widely studied with respect to sensing and it is known to sense a wide variety of gases [14, 16-18]. Tailoring this oxide with other metal oxides like CuO and ZnO and studying the sensitivity has been reported [19-22]. There has been to a great extent reported work on the SnO_2-CuO composite and its sensitivity to various gases [19,20,23,24].The general procedure is to measure the sensitivity of the sample to the respective gas through the change in resistance[11,24]; we have taken up an innovative method of studying the a.c.conductivity response of the composite to cigarette smoke.

In the present work, the tin oxide-copper oxide composites were prepared by the hydrothermal method and characterized by XRD, SEM, UV and Dielectric analysis. The crystal structure and crystallite size of the composites have been reported and their morphology have been observed. The optical band gap has been determined. In addition, the electrical response of the composites to cigarette smoke was investigated which is a decisive factor for sensitive sensor fabrication.

Experimental

The composites were prepared by adding $Cu(NO_3).2H_2O$ [A] and $SnCl_2.2H_2O$ [B] in the molar ratio 0.5:0.5 M to 150ml of deionized water under magnetic stirring.0.2M of urea was added to the above solution under continuous stirring for an hour. Next the mixed solution was transferred into a Teflon lined autoclave and treated at 180ºC for 3 hours. Finally, the product obtained was washed with distilled water and acetone to remove unexpected ions and dried at 200ºC in air. Other samples were prepared by the similar procedure by just changing the molar ratios of the precursors A and B as [0.75:0.25] and [0.25:0.75] respectively.

Microstructure analysis were performed using X-ray diffraction (XRD) and Scanning electron microscopy (SEM). For the XRD, the Seifert 3003T/T X-ray diffractometer with CuKα radiation in the 2θ range 20 to 70º was used. Surface morphologies of the samples were observed using a FEI Quanta FEG 200 Scanning electron microscope equipped with an EDAX detector. The electrical properties of the sample with respect to the cigarette smoke was measured by the Hitachi 3532-50 LCR Hitester.
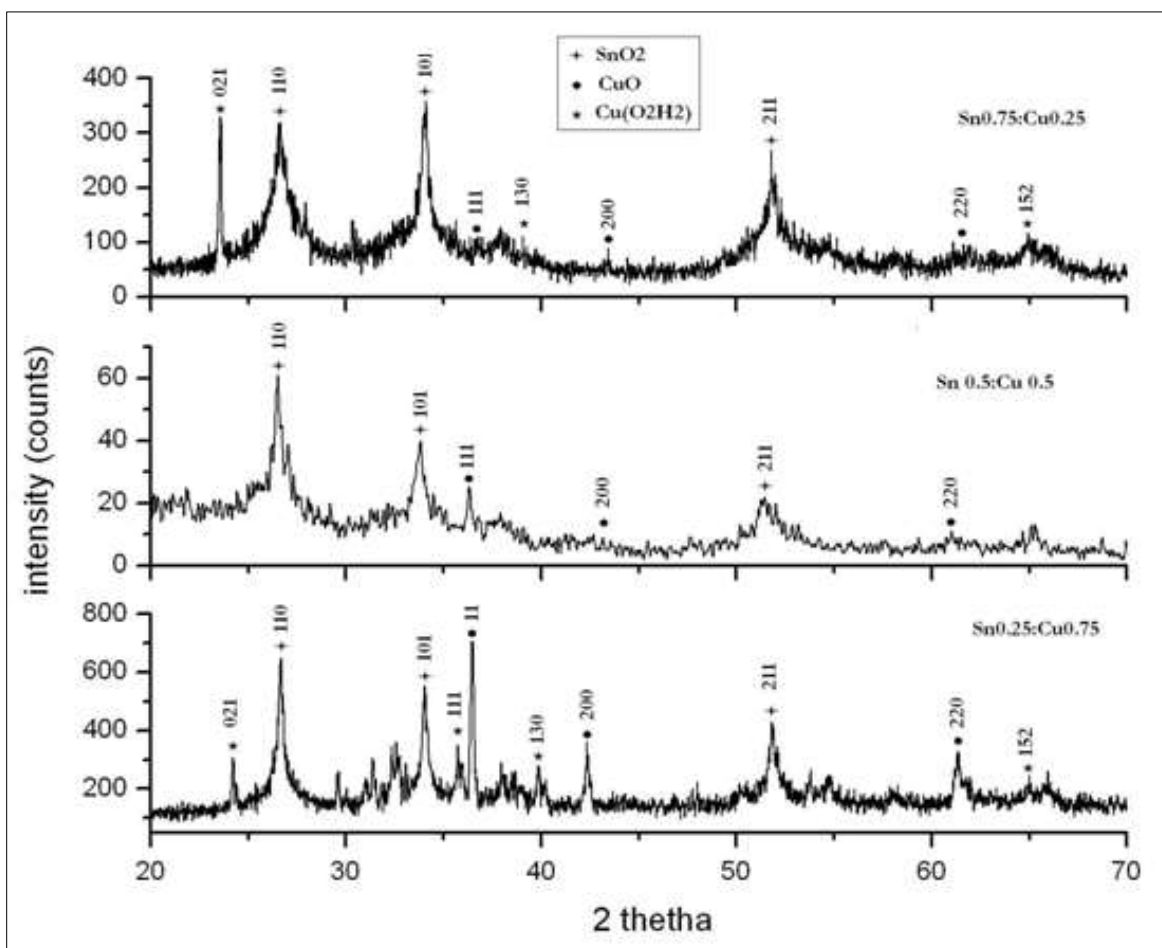
Results and discussion

Figure 1:XRD patterns of the as-prepared SnO₂ – CuO composite particles annealed at 200•C that were initially synthesized using 3 different molar ratios

Figure 1 shows the XRD patterns of the as-prepared composites of SnO_2-CuO. All of the tin oxide peaks match well with the standard SnO_2 XRD pattern [JCPDS card file no: 88-0287] and are attributed to the tetragonal phase.The lattice constants thereby calculated are tabulated (Table 1). The average crystallite size is related tothe peak broadening. The average crystallite size of the tin dioxide particles was estimated by the Scherrer equation.

$$d = \frac{k\lambda}{\beta cos\theta}$$

k is the shape factor equal to 0.89, λ is the X-ray wave length for Cu Kα radiation (1.5418 Å), θ is the Bragg diffraction angle and β is the full width at half maximum (FWHM) of the observed peak. It is also observed that the tin oxide peaks are more pronounced than the peaks of the cubic phase of the copper oxide [JCPDS card file no: 77-0199]. A few additional peaks of copper hydroxide can be accounted to be present due to the low annealing temperature. We see that tin oxide begins crystallising earlier than copper oxide which requires higher annealing temperatures to completely oxidize [25].Ming-you et al. also reports that CuO may have entered the crystal lattice thereby resulting in no distinct peaks. However, its presence in the composite can be confirmed by the EDAX analysis. From the tabulation (table 2) no other element is detected other than Sn and Cu for all three molar ratios.

SnO$_2$ [88-0287]	SnO$_2$[0.25]:CuO[0.75]	SnO$_2$[0.5]:CuO[0.5]	SnO$_2$[0.75]:CuO[0.25]
a = b= 4.737[Å]	4.747 ± 0.089	4.772 ± 0.058	4.723 ±0.045
c = 3.186[Å]	3.141 ± 0.080	3.186 ± 0.100	3.178 ±0.083
V = 71.49[Å^3]	70.77	72.54	70.88
Crystallite size	38.31nm	13.76 nm	16.01nm

Table 1: Lattice constants calculated for the distinct SnO$_2$ peaks for the 3 molar ratios.

| SnO$_2$: CuO	Atomic%		
	0.25:0.75	0.5:0.5	0.75:0.25
Sn	10.18	23.85	19.82
Cu	22.17	8.32	03.64
O	64.38	67.84	56.45

Table 2: Comparison of the Atomic % of the elements present in the 3 synthesized composites obtained by the EDX analysis

Figure 2 (a), (b) and (c) shows the topographical images of the as-grown products of the Tin oxide-Copper oxide composites synthesized by the hydrothermal method. The surface morphology is observed to have flake –like appearance in all three cases though the overall morphology varies in each case.
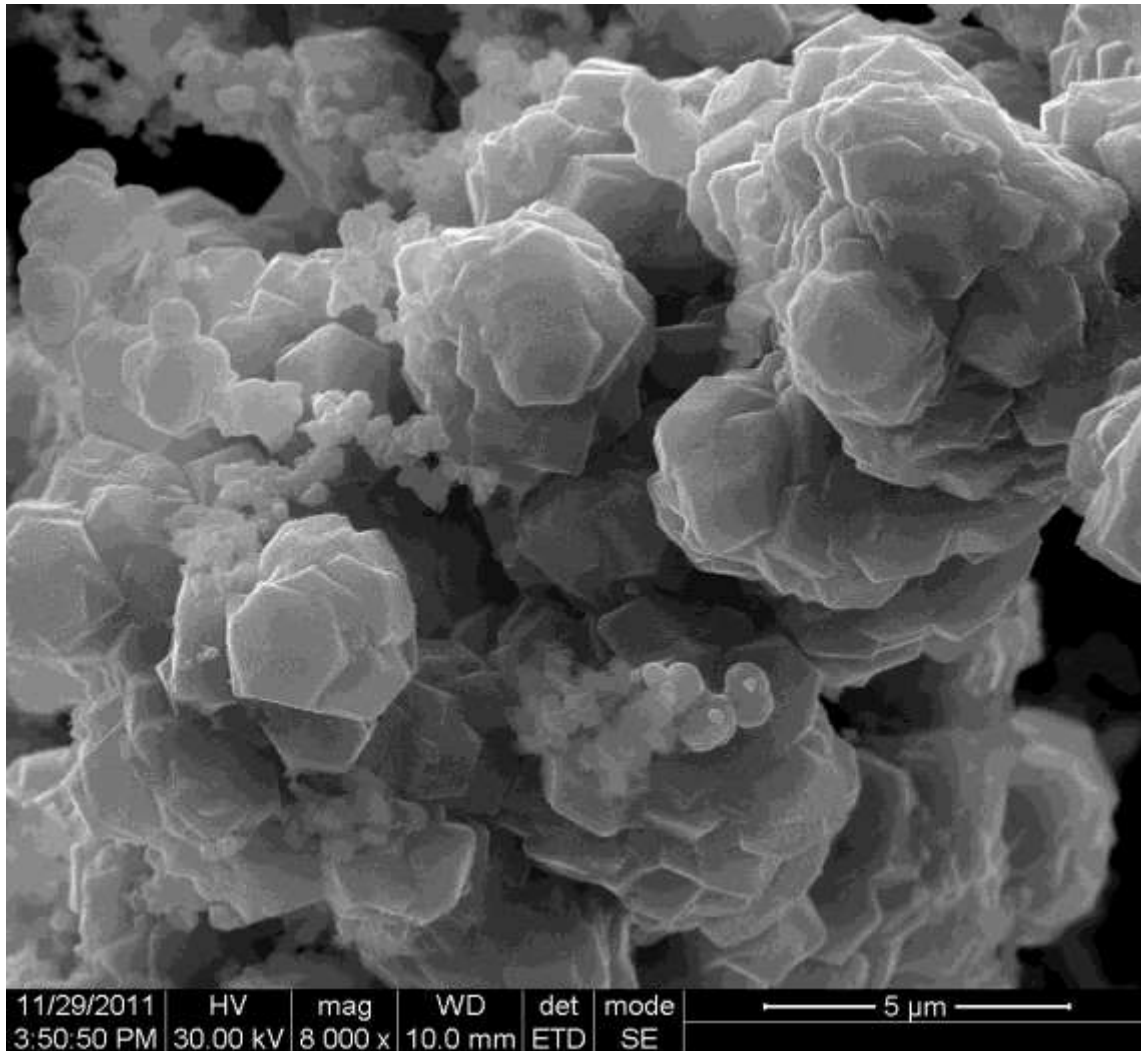
Figure 2a: HRSEM morphology for the SnO₂-CuO composite with molar ratio 0.25:0.75
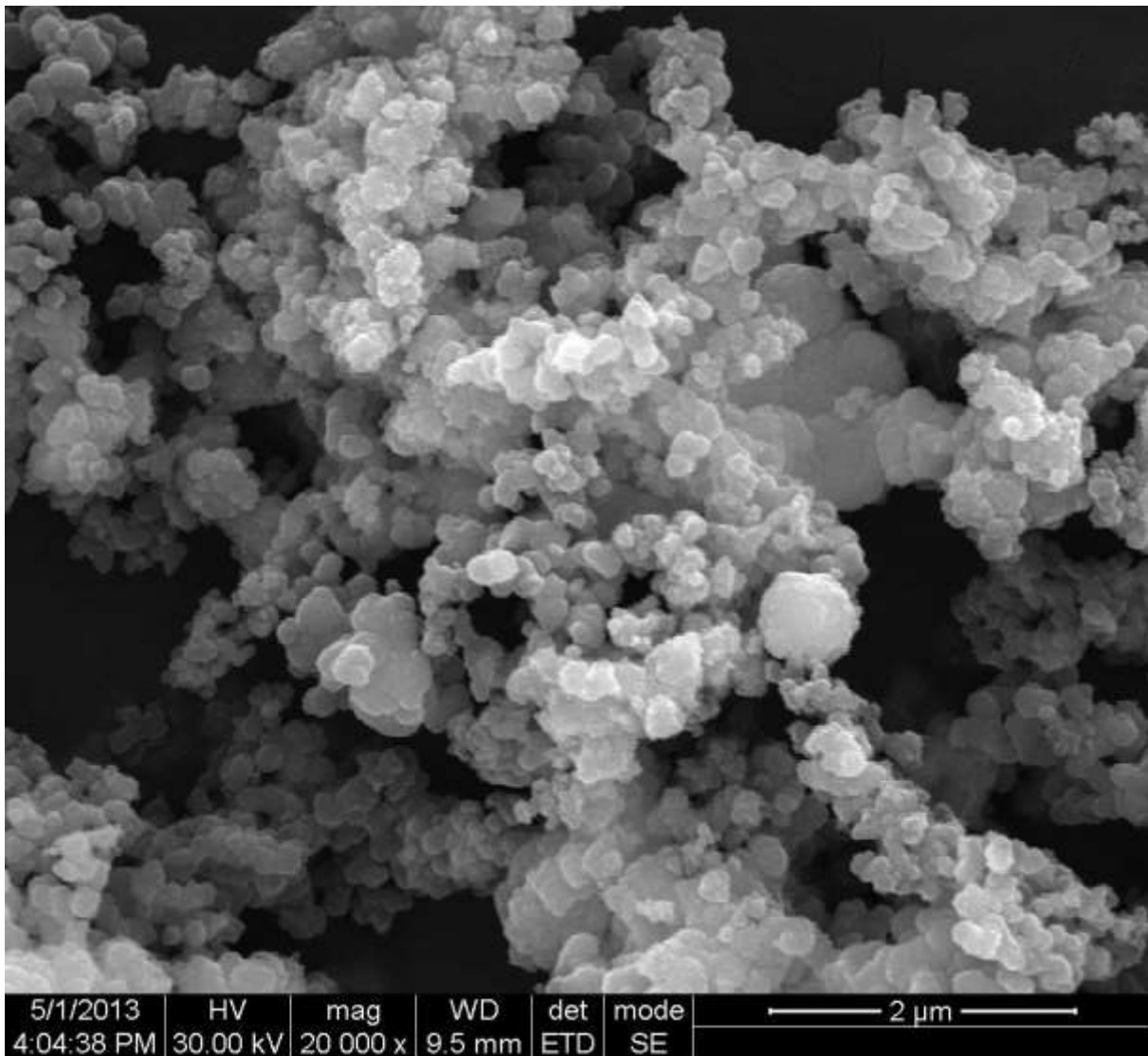
Figure 2b: HRSEM morphology for the SnO₂-CuO composite with molar ratio 0.5:0.5
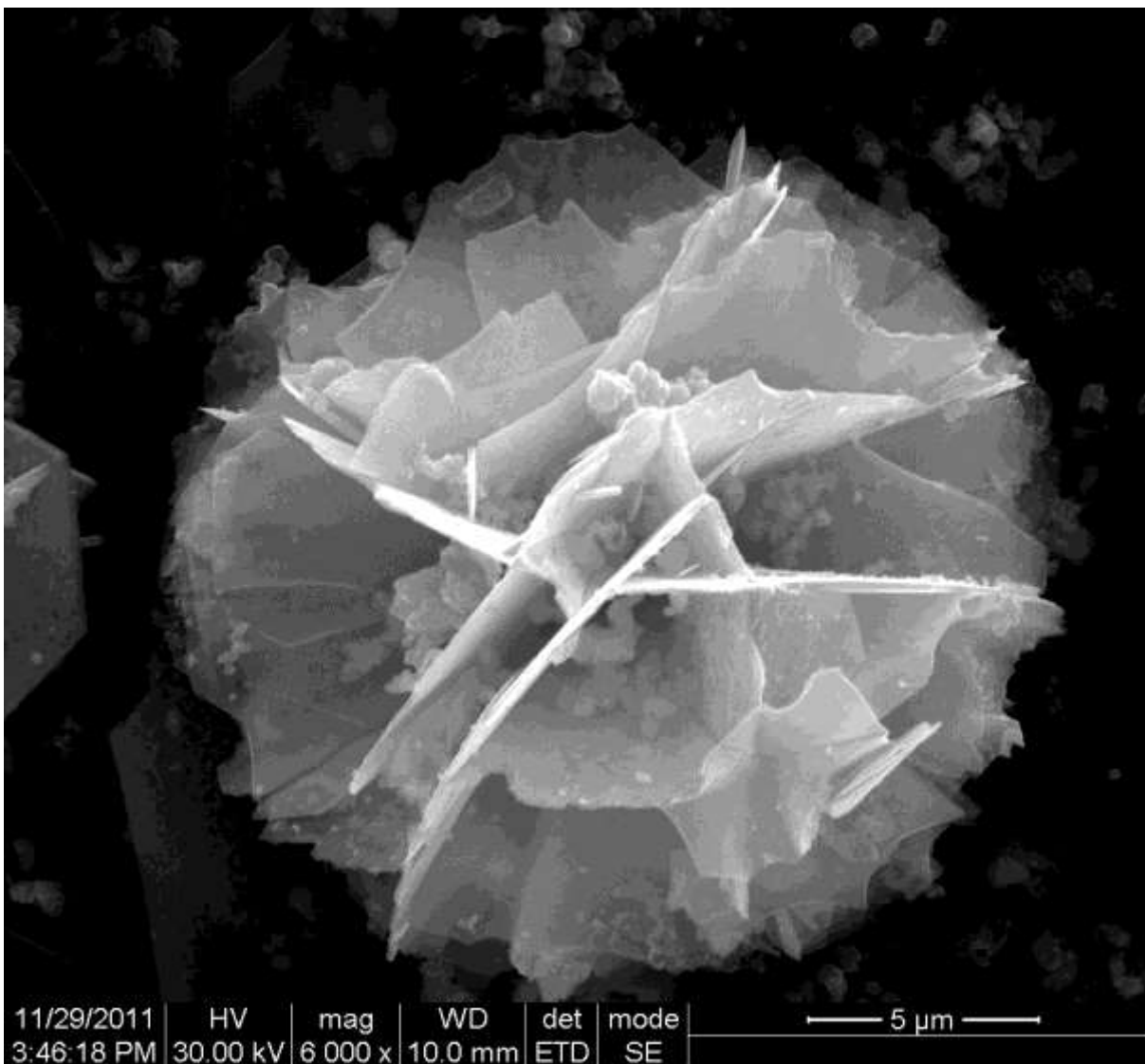
Figure 2c: HRSEM morphology for the SnO₂-CuO composite with molar ratio 0.75:0.25

The UV–Vis absorption spectra data of the composites are tabulated in table 3. The excited wavelength was obtained from the absorption spectra (λ_{ex}). The band gap was thereby calculated using the formula $E_g = \frac{hc}{\lambda}$. The difference between band gap thereby calculated and the bulk band gap of the material was reported. A blue shift of the band gap is observed compared to the bulk materials in all three cases. As reported by Zhu et al. the blue shift indicates the onset of the absorptions that can be assigned to the direct transition of the electron in the sample [26].

Sample		Std BG (eV)	Cal λ (nm)	BG (eV)	BG Difference (eV)
	0.25		308.08	4.04	0.44
SnO₂	0.5	3.6	300.79	4.1	0.5
	0.75		334.09	3.7	0.1
	0.75		1002.84	1.24	0.04
CuO	0.5	1.2	979.04	1.27	0.07
	0.25		919.13	1.35	0.15

Table 3: Tabulation of the observed excitation wavelengths and the comparison between the bulk and calculated band gaps of SnO₂ and CuO for the different molar ratios.

Tobacco smoke is a varied, dynamic and reactive combination containing an estimated 5000 chemicals [27-29] .The main ingredients being nicotine, tar and carbon monoxide. Nicotine is a tertiary amine composed of a pyridine and a pyrrolidine ring, this along with carbon monoxide and tar are known to have independent effects on the human body .This toxic and carcinogenic blend is probably the most major source of toxic chemical exposure and chemically mediated disease in humans [30,31]. Literature has revealed that highly exposed non-smokers and active smokers share the same level of hair nicotine [32,33]. Thus there is an urgent need to monitor cigarette smoking in free living conditions.

The responses of the composite materials are investigated by studying the change in the dielectric constant of the samples in ambient and cigarette smoke environment using a dielectric analyser. The as-prepared composites were pelletized under a pressure of 10 tonnes. The pelletized sample was loaded between two electrodes and then subjected to an alternating voltage. The responses of the composites were studied in a sealed chamber. The electrical parameters at different frequencies in the presence of air are first noted, then a known volume (100ml) of cigarette smoke is injected into the chamber using a syringe and the parameters are noted again.

The A.C. conductivity is calculated using the formula $\sigma_{ac} = 2\pi f \varepsilon_o \varepsilon_r tan\delta$,

where ε_o=8.854 x 10^{-12} F/m, ε_r is the dielectric constant and $tan\delta$ is the dielectric loss. The figures 3(a),(b) and (c) graphically represent the A.C.conductivity of the composites at room temperature. It is observed that the A.C. conductivity σ_{ac} increases with increase in the frequency of the applied voltage. It is also observed that there is an increase in the A.C. conductivity of all the three composites when the smoke is introduced and the difference (at 5MHz) is tabulated below (Table 4). Comparing the readings of the composites with the pure samples, we note that there is an increase in the a.c.conductivity for the composites.

SnO₂:CuO	[0.25:0.75]	[0.5:0.5]	[0.75:.25]	Pure SnO₂	Pure CuO
Difference in σ_{ac} in cigarette smoke and ambience (S/m)	1.106 x 10^{-5}	1.480 x 10^{-5}	0.892 x 10^{-5}	0.847 x 10^{-5}	0.61 x 10^{-5}

Table 4: Difference in A.C. conductivity value of the composites

The a.c.conductivity response to cigarette smoke was recorded for continuously for 10 trials and the graphs were plotted as shown in figure 4(a), (b) and (c). It is observed that the conductivity remains a constant.

The elementary sensing mechanism involved in metal oxide based gas sensors depends on the change in electrical conductivity as a result of the interaction process between the surface complexes such as O⁻, O²⁻, H⁺ and OH⁻ reactive chemical species and the molecules of the gas that is to be sensed. Oxygen ions are adsorbed on the materials surface removing electrons from the bulk and thereby constructing a potential barrier that curbs the electron movement and conductivity. So when the material interacts with an oxidising or reducing gas, the concentration of the adsorbed oxygen changes causing a variation in the conductivity. Therefore we attribute this change in
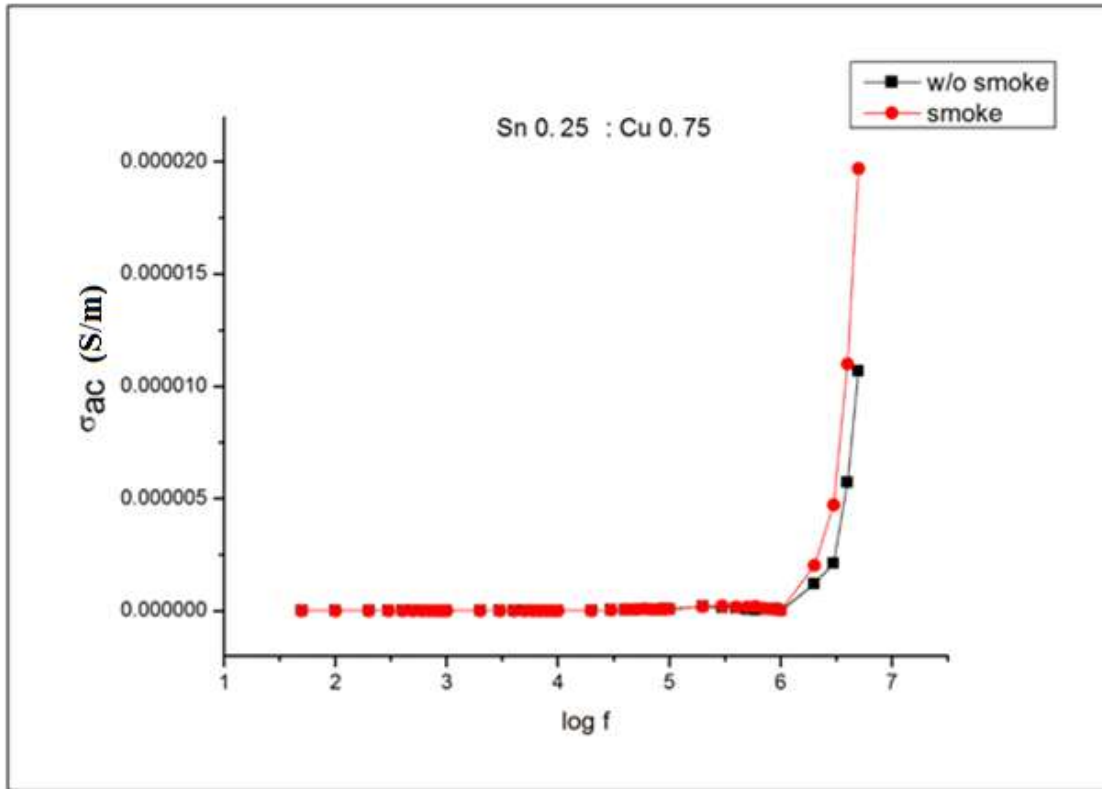
conductivity as a measure of the gas concentration.
[34].

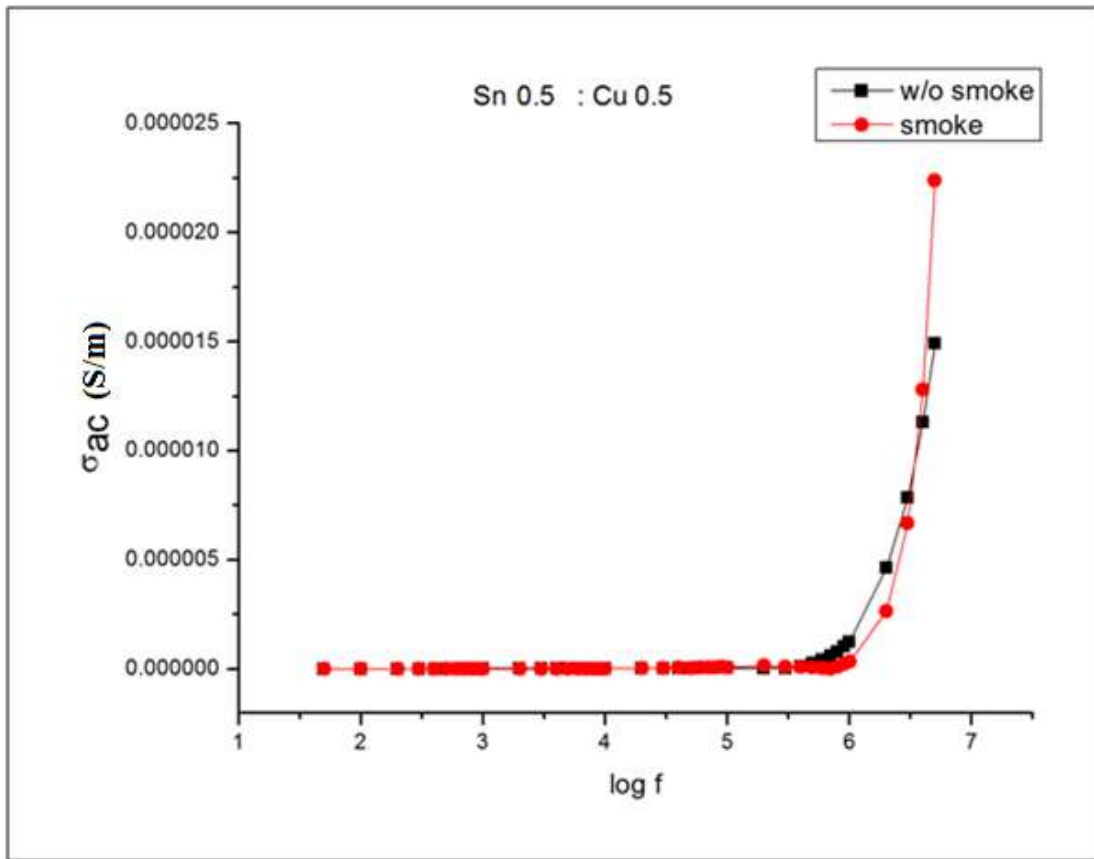*Figure 3a: Plot of A.C. conductivity for the 0.25:0.75 ratio of the SnO₂-CuO composite*

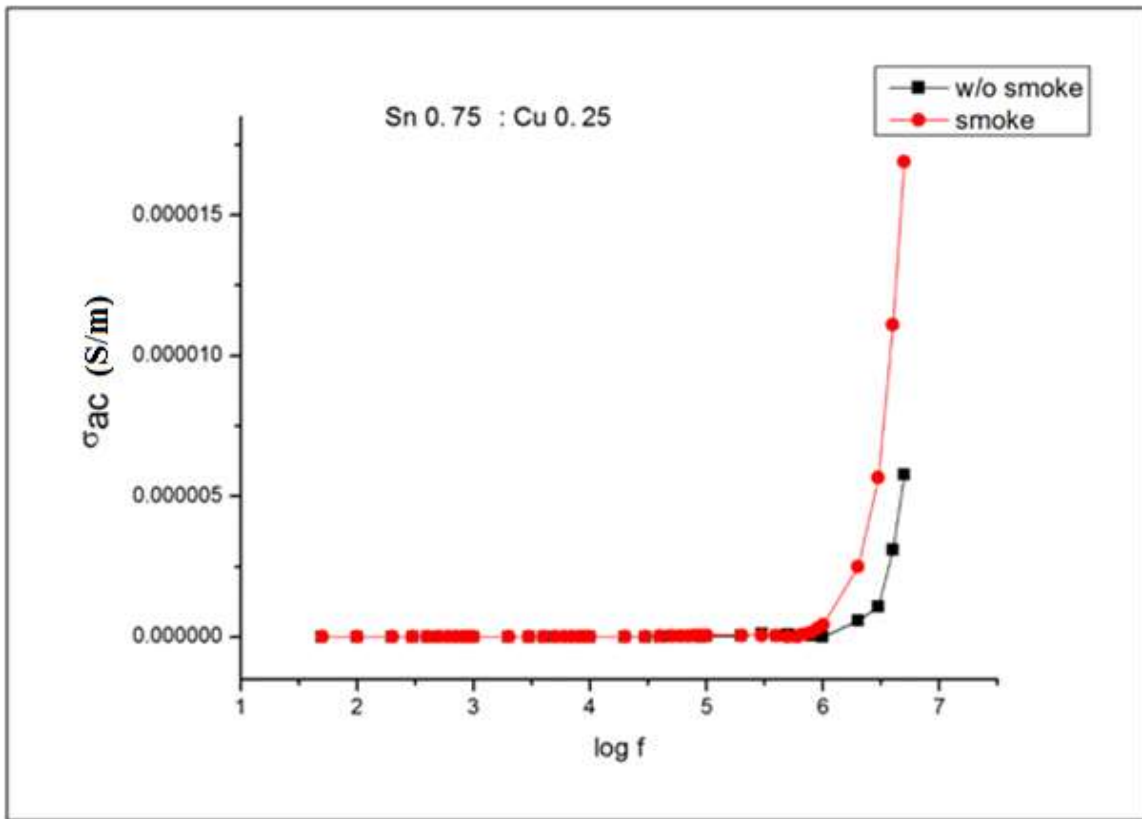*Figure 3b: Plot of A.C. conductivity for the 0.5:0.5 ratio of the SnO$_2$-CuO composite*

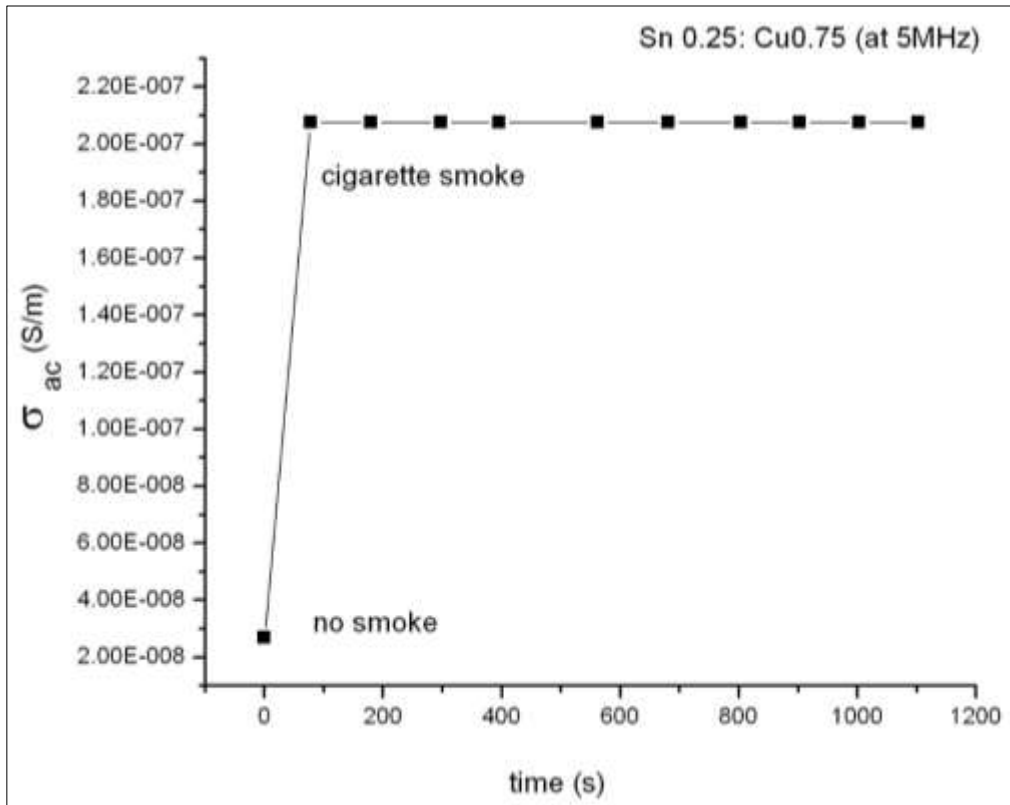***Figure 3c: Plot of A.C. conductivity for the 0.75:0.25 ratio of the SnO$_2$-CuO composite***

Figure 4a: The a.c. conductivity vs time (s) at freq 5MHz for the 0.25:0.75 ratio of the SnO₂-CuO composite
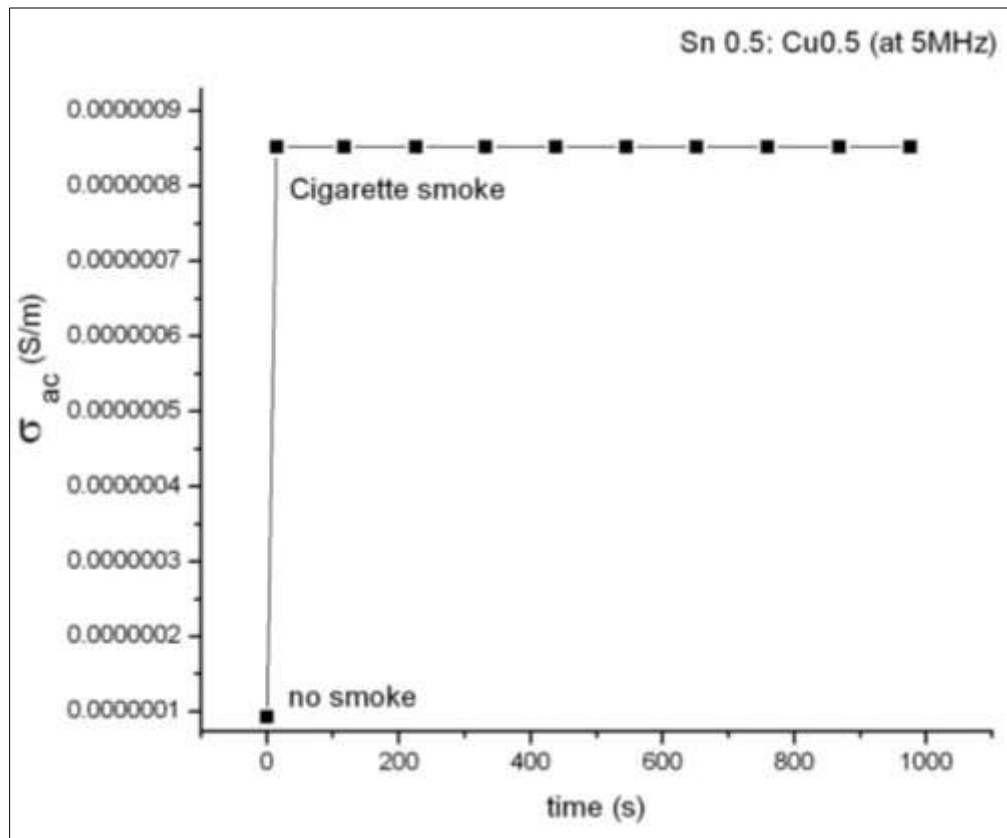
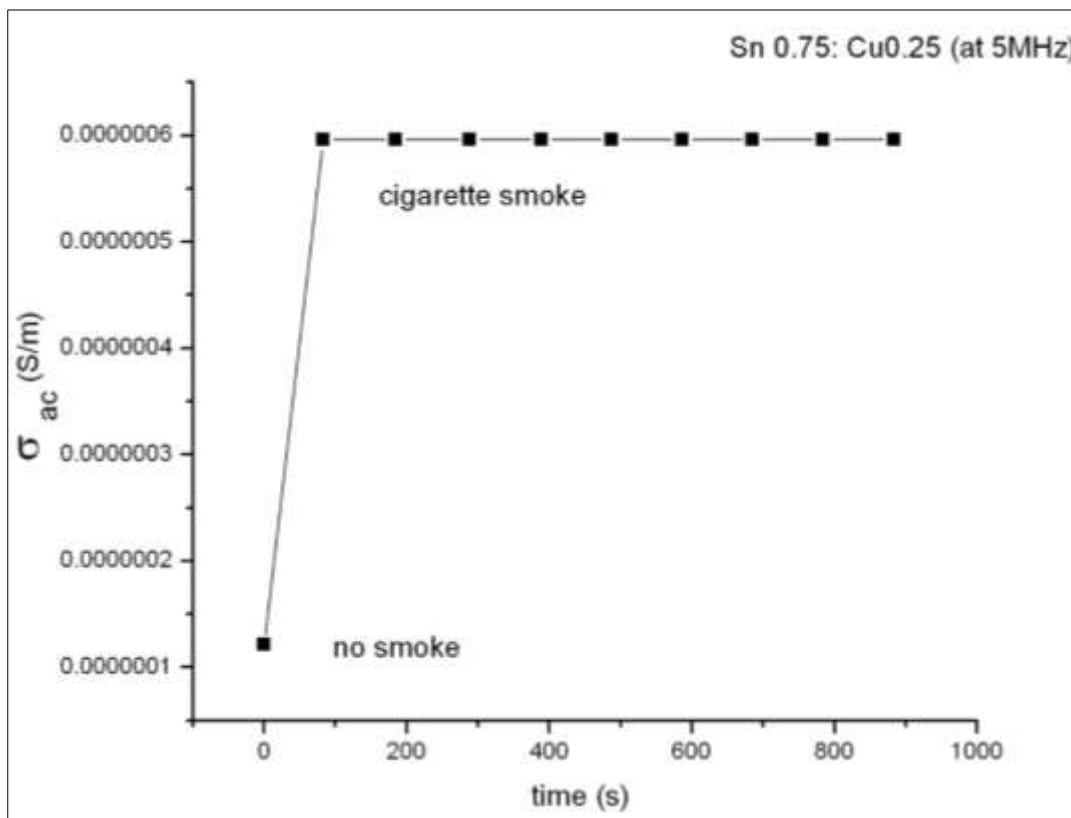*Figure 4b: The a.c. conductivity vs time (s) at freq 5MHz for the 0.5:0.5 ratio of the SnO₂-CuO composite*

Fig 4c: The a.c. conductivity vs time (s) at freq 5MHz for the 0.75:0.25 ratio of the SnO₂-CuO composite

Conclusion

In summary, a facile hydrothermal method was used to synthesize flake-like tin oxide-copper oxide composites at different molar ratios. The XRD pattern demonstrates that the samples have peaks of both tin oxide with a tetragonal rutile structure and copper oxide in the cubic phase.

Furthermore from the electrical analysis, a noticeable change in the A.C. conductivity of the samples were observed in response to cigarette smoke. This technique of studying the dielectric parameters could open up novel ways of investigating gas sensing through device fabrication.

Reference

1. Reinskje Talhout, Thomas Schulz, Ewa Florek, Janvan Benthem, Piet Wester, Antoon Opperhuizen , Hazardous Compounds in Tobacco Smoke, Int J Environ Res Public Health, (2011); 8(2): 613–628.
2. Dangers of Second-Hand Smoke (Online) Available fromhttp://my.clevelandclinic.org/healthy_living /smoking/hic_dangers_of_secondhand_smoke.as px [Accessed on 1st Sept 2013]
3. H. Salehi, M. Aryadoust, M. Farbod, Electronic and Structural Properties of Tin Dioxide in Cubic Phase, Iranian Journal of Science & Technology, Trans. A, Volume 34, Number A2 (2010)
4. B. Thangaraju, Structural and electrical studies on highly conducting spray depositedfluorine and antimony doped SnO thin films from SnCl precursor, Thin Solid Films 402 (2002) 71–78.
5. Zhu, J.; Tay, B. Y.; Ma, *Synthesis* of *mesoporous tin oxide* on *neutral surfactant templates,* J. Mater. Lett. 2006, 60, 1003.
6. Matthias Batzill, Ulrike Diebold, The surface and materials science of tin oxide, Progress in Surface Science 79 (2005) 47–154

7. Le DuyDuc, Dang ThiThanh Len , Nguyen Van Duy, Nguyen Duc Hoa, Nguyen Van Hieu, Single crystal cupric oxide nanowires: Length- and density-controlled growth and gas-sensing characteristics, Physica E 58 (2014) 16–23

8. Xue Wang, Chenguo Hu, Hong Liu, Guojun Du, Xiaoshan He,Yi Xi, Synthesis of CuO nanostructures and their application for nonenzymatic glucose sensing, Sensors and Actuators B,144 (2010) 220–225

9. C. Batchelor-McAuley, Y. Du, G.G. Wildgoose, R.G. Compton, The use of cop-per(II) oxide nanorod bundles for the non-enzymatic voltammetric sensing of carbohydrates and hydrogen peroxide, Sens. Actuators B: Chem. 135 (2008)230–235.

10. Z.J. Zhuang, X.D. Su, H.Y. Yuan, Q. Sun, D. Xiao, M.M.F. Choi, An improved sensitivity non-enzymatic glucose sensor based on a CuO nanowire modified Cu electrode, Analyst 133 (2008) 126–132

11. Patil Shriram B., More Mahendra A., Patil Arun V, Nanocrystalline Cobalt-doped SnO2 Thin Film:A Sensitive Cigarette Smoke Sensor, Sensors & Transducers Journal, Vol. 134, Issue 11, November 2011, pp. 163-169

12. Hassan Karami, Investigation of sol-gel Synthesized CdO-ZnO Nanocomposite for CO Gas Sensing, Int. J. Electrochem. Sci., 5 (2010) 720 – 730

13. Kong, J.; Franklin, N.; Zhou, C.; Chapline, M.; Peng, S.; Cho, K.; Dai, H. Nanotube molecular wires as chemical sensors. Science 2000, 287, 622-625.

14. Gopel, W.; Schierbaum, K. SnO2 sensors current status and future prospects. Sensor Actuator B-Chem 1995, 26, 1-12.

15. Yamada, Y.; Seno, Y.; Masuoka, Y.; Yamashita, K. Nitrogen oxides sensing characteristics of Zn2SnO4 thin film. Sensor Actuator B-Chem 1998, 49, 248-252.

16. Divya Haridas, K. Sreenivas, Vinay Gupta, Improved response characteristics of SnO2 thin film loaded with nanoscale catalysts for LPG detection, Sensors and Actuators B 133 (2008) 270–275

17. A. Chaturvedi, V.N. Mishra, R. Dwivedi, S.K. Srivastava, Response of oxygen plasma-treated thick film tin oxide sensor array for LPG, CCl4 , CO and C3H7OH, Microelectronics Journal 30 (1999) 259–264

18. Nguyen Van Hieu , Nguyen Anh Phuc Duc , Tran Trung ,Mai Anh Tuan , Nguyen Duc Chien, Gas-sensing properties of tin oxide doped with metal oxides and carbon nanotubes: A competitive sensor for ethanol and liquid petroleum gas, Sensors and Actuators B 144 (2010) 450–456

19. Jinhuai Liu , Xingjiu Huang , Gang Ye , Wei Liu , Zheng Jiao , Wanglian Chao , Zhongbai Zhou ,Zengliang Yu, H2S Detection Sensing Characteristic of CuO/SnO2 Sensor, Sensors 2003, 3, 110-118

20. Xinyu Xue , Lili Xing, Yujin Chen, Songlin Shi, Yanguo Wang, Taihong Wang, Synthesis and H2S Sensing Properties of CuO-SnO2 Core/Shell PN-Junction Nanorods, J. Phys. Chem. C 2008, 112, 12157–12160

21. Dang Thi Thanh Le,Do Dang Trung,Nguyen Duc Chinh, Bui Thi Thanh Binh, Hoang Si Hong,Nguyen Van Duy,Nguyen Duc Hoa,Nguyen Van Hieu, Facile synthesis of SnO2– ZnO core–shell nanowires for enhanced ethanol sensing performance,Current Applied Physics, Volume 13, Issue 8, October 2013, Pages 1637– 1642

22. *Sun-Woo Choi, Jae Young Park and Sang Sub Kim,Synthesis of SnO2–ZnO core–shell nanofibers via a novel two-step process and their gas sensing properties,Nanotechnology Vol. 20 46 (2009) 5603*

23. B.C.Yadav,Preeti Sharma, P.K.Khanna, Morphological and humidity sensing characteristics of SnO2–CuO, SnO2–Fe2O3 and SnO2–SbO2 nanocooxides,Bull. Mater. Sci., Vol. 34, No. 4, July 2011, pp. 689–698.

24. Satyendra Singh, Nidhi Verma, Archana Singh, B.C.Yadav, Synthesis and characterization of CuO–SnO2 nanocomposite and its application as liquefied petroleum gas sensor,Materials Science in Semiconductor ProcessingVolume 18, February 2014, Pages 88–96

25. M. A. Ming-you, H. E. Ze-qiang, X. Z. Bing,. H. Ke-long, X. Li-zhi, W. Xiang-ming, Synthesis and electrochemical properties of SnO2-CuO nanocomposite powders, Trans. Nonferrous Met. Soc China. 16 (2006) 791-794.

26. Z. Zhu, G. Ouyang, and G. Yang, Bandgap shift in SnO2 nanostructures induced by lattice strain and coordination imperfection ,J. Appl. Phys. 108 (2010) 083511

27. Hoffmann D.; Hoffmann I. Letters to the editor, tobacco smoke components. Beitr. Tabaksforsch. Int. 1998, 18, 49-52.

28. Thielen A.; Klus H.; Muller, L. Tobacco smoke: unraveling a controversial subject. Exp. Toxicol. Pathol. 2008, 60, 141-156.

29. Borgerding M.; Klus H. Analysis of complex mixtures—cigarette smoke. Exp. Toxicol. Pathol. 2005, 57, 43-73.
30. Fowles J.; Dybing E. Application of toxicological risk assessment principles to the chemical constituents of cigarette smoke. Tob. Control 2003, 12, 424-430.
31. Ezzati M.; Lopez A.D. Estimates of global mortality attributable to smoking in 2000. Lancet 2003, 362, 847-852
32. Al-Delaimy W, Fraser T, Woodward A., Nicotine in hair of bar and restaurant workers,N Z Med J. (2001) 114(1127):80-3.
33. Dimich-Ward H., Gee H., Brauer M., Leung V., Analysis of nicotine and cotinine in the hair of hospitality workers exposed to environmental tobacco smoke, JOccup Environ Med. (1997) 39(10):946-8.
34. A. K. Singh, Microwave Assisted Growth of ZnO Nanorods and Nanopolypods Nanostructure Thin Films for Gas and Explosives Sensing, Journal of Nanoparticles,Volume 2013 (2013)