

# Synthesis and characterization of MWCNTs reinforced cuprous oxide nanocomposite

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The polyol process was used for the synthesis of cuprous oxide-multi walled carbon nanotubes (MWCNTs) reinforced nanocomposite. During synthesis process the pristine MWCNTs were purified and functionalized using HNO<sub>3</sub>. In this process copper acetate mono hydrate was used as Cu precursor. Limited supply of oxygen resulted in copper oxidation and cuprous oxide was formed. The copper oxide matrix was reinforced with different weight percentages of MWCNTs, varying from 1% to 3%. FTIR analysis of activated MWCNTs showed the attachment of functional groups. Variation in the morphology and size of cuprous oxide was noted with different content of MWCNTs. A change in resistance of nanocomposites was also reported here with varying percentage of MWCNTs.

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**Keywords:** Cuprous oxide, MWCNT, Polyol Process, Nanocomposite

## 1. Introduction

Due to their outstanding electronic, thermal, chemical, mechanical and optical properties and exceptional atomic structure and high aspect ratio, carbon nanotubes (CNTs) have attracted great attention in the field of nanoscience and nanotechnology [1, 2]. To extend the range of potential application of CNTs, the attachment of appropriate nanostructure is necessary [3]. Recently many studies have focused on the formation of CNTs-metal or CNTs-metal oxide composites because the composite combines their individual properties and shows some new outstanding properties [4-11].

Cuprous oxide is p-type semiconductor material with a direct band gap of 2 eV [12-14]. It has great potential application in the hydrogen production, solar energy conversion, negative electrode material for lithium ion batteries and catalysis [15-19]. Due to the redox chemistry, excellent thermal, electrical, sensing and catalytic properties increase attention has been given to cuprous oxide nanoparticles among different metal oxide nanoparticles [3, 20]. However when such a narrow band gap semiconductor is used as a photocatalyst, there is a drawback that the visible light generated charge carriers can not be effectively transferred and are lost due to recombination. This drawback of the charge carriers recombination of cuprous oxide can be removed and its photocatalytic activity can be enhanced by CNTs-Cu<sub>2</sub>O composition. It is due to the properties of excellent electron transfer and high surface area of CNTs [21, 22].

In this paper polyol method was used for the synthesis of MWCNTs reinforced cuprous oxide nanocomposite using copper acetate monohydrate as the Cu source. The effect of different MWCNTs wt% in nanocomposites was investigated on the morphology and size of cuprous oxide

particles. The resistance vs MWCNTs wt% measurement was also studied.

## 2. Experimental

### 2.1. Purification and oxidation of MWCNTs

MWCNTs with purity more than 95%, length 10-30  $\mu\text{m}$  and diameter less than 7 nm, were selected for this study. 2.5 g of MWCNTs were sonicated in 200 ml of 65% concentrated nitric acid (HNO<sub>3</sub>) for 30 min and then refluxed for 5 h at boiling temperature. This acid treatment of MWCNTs purified them as well as attaches functional groups like OH and COOH on their surfaces. The MWCNTs were then filtered and washed with deionized water until its pH become neutral and then dried at 100 °C.

### 2.2. Synthesis of MWCNTs/Cu<sub>2</sub>O nanocomposites

The MWCNTs/Cu<sub>2</sub>O nanocomposites were prepared by polyol method. Three samples were prepared with different wt% of MWCNTs. For the preparation of every sample, 1.4 g of Cu(CH<sub>3</sub>COO)<sub>2</sub> · H<sub>2</sub>O precursor together with different wt% of MWCNTs was sonicated in 130 ml of ethanol for 30 min, filtered and then dried at 80 °C. The obtained mixture were dissolved in 170 ml of glycerol and then heated at 200 °C for 2 and 1/2 h in 500 ml closed beaker under magnetic stirring in the presence of nitrogen atmosphere. Subsequently the obtained composites were filtered, washed several times with ethanol to remove the remaining glycerol and dried for 7 h in vacuum oven at a temperature of 60 °C.

### 3. Results and discussion

The surface morphology of pristine and functionalized MWCNTs specimens are shown in Fig. 1 (a) and (b) respectively. The image of pristine MWCNTs show that they are highly agglomerated and there are some black dots as impurities like nanometal particles and amorphous carbon on the surface and in between these MWCNTs. The acid treated MWCNTs appear granulated to some extent, well dispersed and having low impurities.

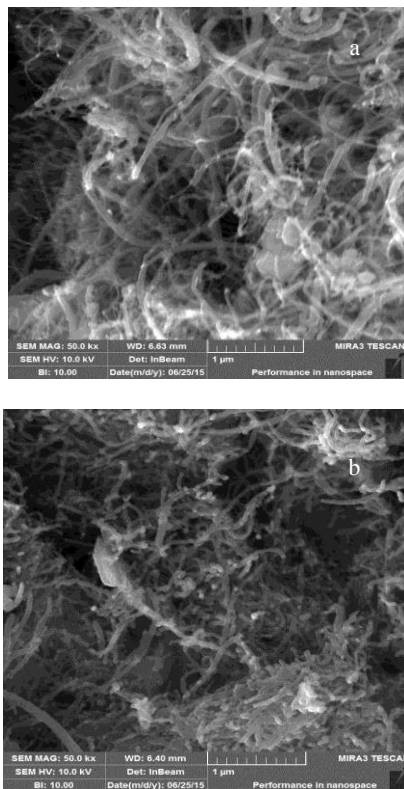


Fig. 1. SEM images of pristine (a) and functionalized (b) MWCNTs

FTIR spectra comparison in the range 450 to 4000  $\text{cm}^{-1}$  for pristine and functionalized MWCNTs is given in Fig. 2. It is clear from the figure that some new peaks appear in the FTIR curve of functionalized MWCNTs.

Peaks at 3430  $\text{cm}^{-1}$  and 1453  $\text{cm}^{-1}$  can assigned to OH stretching vibration and in-plane OH bending of carboxylic acid group. The peak appear at 1748  $\text{cm}^{-1}$  can assigned to C=O stretching of carboxylic acid. The peak at 1630  $\text{cm}^{-1}$  can attributed to the stretching vibration of C=C and C=O of quinone which is created at the surface of MWCNTs after acid treatment. The peaks at 2920  $\text{cm}^{-1}$  and 2852  $\text{cm}^{-1}$  is due to the attachment of methylene group [23, 24].

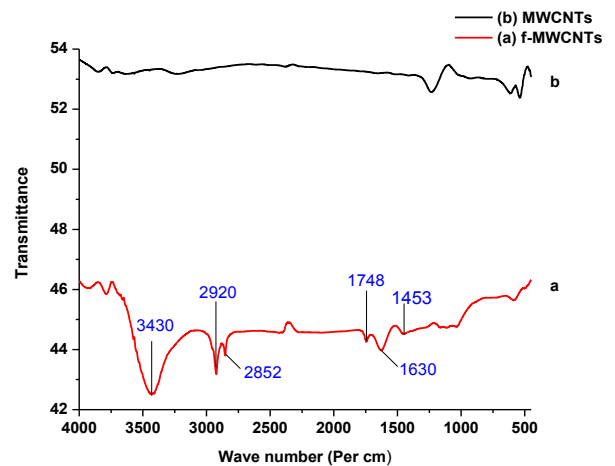


Fig. 2. Comparison of FTIR Spectrum of pristine and acid treated MWCNTs

Fig. 3 shows the SEM images of synthesized nanocomposites. It is clear from the figure that the size of cuprous oxide in the nanocomposites decreases as the quantity of MWCNTs (wt%) is increases. This decrease in size may be attributed to the higher surface energy associated with carbon nanotubes. Carbon nanotube exhibits high surface area and thereby high surface energy. The high surface energy will tend to decrease by depositing cuprous oxide molecules on MWCNTs. This may be the same as in the case of Ostwald's ripening. Carbon nanotube may act as heterogeneous nucleation sites in the growth of nanocomposite particles.

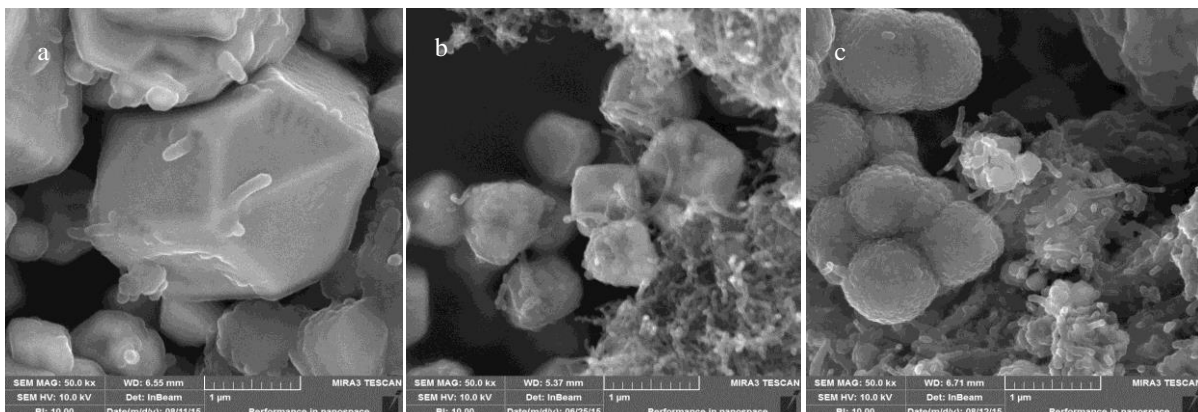


Fig. 3. SEM images comparison of nanocomposites with (a) 1% CNTs (b) 2% CNTs and (c) 3% CNTs

Fig. 4 shows the comparison graph of XRD analysis for cuprous oxide doped with MWCNTs and undoped cuprous oxide. In curve (a) the (111), (200), (220), and (311) planes of cuprous oxide are observed at  $2\theta = 36.6^\circ$ ,  $42.4^\circ$ ,  $61.6^\circ$  and  $73.6^\circ$  respectively. The curve (b) of doped cuprous oxide shows an additional small peak at  $26.6^\circ$  corresponding to (002) reflection of graphitic structure of MWCNTs. While the diffraction peaks at  $36.4^\circ$ ,  $42.35^\circ$ ,  $61.4^\circ$  and  $74.1^\circ$  are attributed to (111), (200), (220) and (311) crystal planes of cuprous oxide respectively. But due to doping of MWCNTs the peaks of cuprous oxide in curve (b) are slightly shifted towards left.

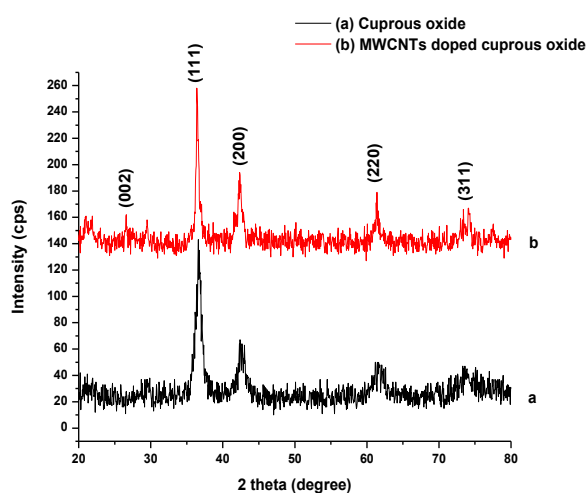


Fig. 4. XRD pattern of (a) cuprous oxide and (b) MWCNTs doped cuprous oxide

The effect of the content of MWCNTs on the electrical properties such as resistance of nanocomposite is revealed in Fig. 5. This can be seen that with increase the content of MWCNTs (wt %) in the nanocomposites, its resistance decreases. This decrease in resistance may be attributed to the better percolation of MWCNTs inside the cuprous oxide matrix because of its high surface area [25, 26]. This better percolation of

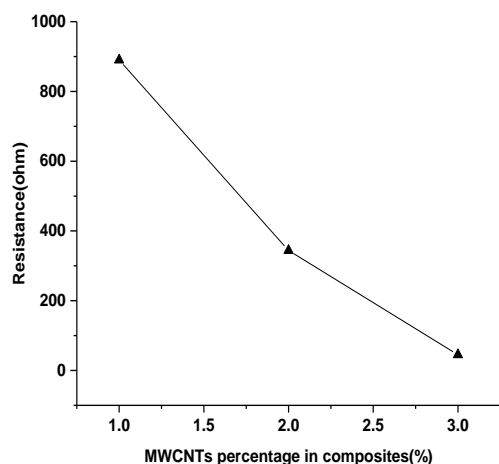


Fig. 5. MWCNTs wt % vs Resistance of nanocomposites

MWCNTs enhances the charge carriers mobility and inhibits their recombination in the narrow bandgap cuprous oxide.

Ying Yu et al. [27] also used polyol process for cuprous oxide deposition on MWCNTs, but due to difference in deposition parameters, the morphology of the cuprous oxide particles made here were different from that synthesized by Ying Yu et al. This difference in morphology and cuprous oxide MWCNTs distribution result in different properties of the composites.

#### 4. Conclusion

MWCNTs reinforced cuprous oxide nanocomposite was synthesized by using polyol process. Glycerol was used as a solvent and reducing agent. FTIR was used for the analysis of functional groups on the surface of MWCNTs. The existence of  $\text{Cu}_2\text{O}$  and MWCNTs in the nanocomposites was confirmed through SEM and XRD. The relationship between wt% of MWCNTs in nanocomposites and their resistance was also investigated through digital multi-meter.

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#### References

- [1] C. S. Chen, X. H. Chen, B. Yi, T. G. Liu, W. H. Li, L. S. Xu, Z. Yang, H. Zhang, Y. G. Wang, *Acta Mater.* **54**, 5401 (2006).
- [2] A. Martı́nez-Ruiz, G. Alonso-Nun̄ez, *Mater. Res. Bull.* **43**, 1492 (2008).
- [3] Kakarla Raghava Reddy, ByungCheol Sin, Chi Ho Yoo, Wonjung Park, Kwang Sun Ryu, Jae-Shin Lee, Daewon Sohn, Youngil Lee, *Scr. Mater.* **58**, 1010 (2008).
- [4] Rui Yang, Lian Gao, *Solid State Commun.* **134**, 729 (2005).
- [5] S. J. Wang, S. F. Yin, L. Li, B. Q. Xu, C. F. Ng, C. T. *Appl. Catal., B* **52**, 287 (2004).
- [6] Shuhui Sun, Dequan Yang, Gaixia Zhang, Edward Sacher, Jean-Pol Dodelet, *Chem. Mater.* **19**, 6376 (2007).
- [7] Cailu Xu, Gongwei Wu, Zheng Liu, Dehai Wu, Thomas T. Meek, Qingyou Han, *Mater. Res. Bull.* **39**, 1499 (2004).
- [8] Y. Zhang, Nathan W. Franklin, Robert J. Chen, Hongjie Dai, *Chem. Phys. Lett.* **331**, 35 (2000).
- [9] Keishin Ota, Akio Kawabata, Hirohiko Murakami, Eiji Kita, *Mater. Trans.* **42**(8), 1684 (2001).

- [10] Yanhui Li, Jan Ding, Junfeng Chen, Cailu Xu, Bingqing Wei, Ji Liang, Dehai Wu, *Mater. Res. Bull.* **37**, 313 (2002).
- [11] Cailu Xu, Junfeng Chen, Yan Cui, Qingyou Han, Hahn Choo, Peter K. Liaw, Dehai Wu, *Adv. Eng. Mater.* **8**(1-2), 73 (2006).
- [12] Abdul Mateen, *J Pak Mater Soc* **2**(1), 40 (2008).
- [13] Ming Yang, Jun-Jie Zhu, *J. Cryst. Growth* **256**, 134 (2003).
- [14] Ling-I Hung, Chia-KuangTsung, Wenyu Huang, Peidong Yang, *Adv. Mater.* **22**, 1910 (2010).
- [15] Ying Yu, Fei-Peng Du, Jimmy C. Yu, Yuan-Yi Zhuang, Po-Keung Wong, *J. Solid State Chem.* **177**, 4640 (2004).
- [16] Wenzhong Wang, Guanghou Wang, Xiaoshu Wang, Yongjie Zhan, Yingkai Liu, Changlin Zheng, *Adv. Mater.* **14**(1), 67 (2002).
- [17] Linfeng Gou, Catherine J. Murphy, *Nano Lett.* **3**, 231 (2003).
- [18] Jianbo Wang, Luying Li, DongxiaXiong, Renhui Wang, Dongshan Zhao, Changping Min, Ying Yu, Lili Ma, *Nanotechnology* **18**, 1 (2007).
- [19] Xiuying Wang, Feng Zhang, Baiying Xia, Xingfu Zhu, Jiesheng Chen, ShilunQiu, Ping Zhang, Jixue Li, *Solid State Sciences* **11**, 655 (2009).
- [20] Praveen Martis, Antonio Fonseca, Zineb Mekhalif, Joseph Delhalle, *J. Nanopart. Res.* **12**, 439 (2010).
- [21] Lisha Zhang, Jialin Li, Zhigang Chen, Yiwen Tang, Ying Yu, *Appl. Catal., A* **299**, 292 (2006).
- [22] Ying Yu, Li-Li Ma, Wen-Ya Huang, Jia-Lin Li, Po-Keung Wong, Jimmy C. Yu, *J. Solid State Chem.* **178**, 1488 (2005).
- [23] F. Avilés, J. V. Cauich-Rodríguez, J.A. Rodríguez-González, A. May-Pat, *Polym. Lett.* **5**, 766 (2011).
- [24] Saeed S. Ba Hashwan, M. F. Fatin, A. RahimRuslinda M. K. Md Arshad, UdaHashim, R. M. Ayub, *Applied Mechanics and Materials* **754-755**, 1156 (2015).
- [25] Kh. S. Karimov, F. A. Khalid, M. Tariq Saeed Chani, A. Mateen, M. Asif Hussain, A. Maqbool, *Optoelectron. Adv. Mat.* **6**, 194 (2012).
- [26] Kh. S. Karimov, Muhammad Tariq Saeed Chani, Fazal Ahmad Khalid, Adam Khan, Rahim Khan, *Chin. Phys. B* **21**(1), 016102 (2012).
- [27] Y. Yu, L. L. Ma, W.Y. Huang, F. P. Du, J. C. Yu, Jia-Guo Yu, Jian-Bo Wang, Po-Keung Wong, *Carbon*, **43**(3), 670 (2005).

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