CuO$_x$/SnO$_2$ nanostructures by microwave-assisted thermal oxidation for ethanol sensing

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Abstract. In this work, CuO$_x$/SnO$_2$ nanostructures were synthesized by a microwave-assisted thermal oxidation. Mixture of Sn and Cu$_2$O was loaded into a cylindrical quartz tube and further radiated in a microwave oven under atmospheric ambient for two minute. Ratio of the mixture was varied. The as-synthesized products were characterized by transmission electron microscope and x-ray diffractometer. The results showed that CuO$_x$/SnO$_2$ nanoparticles were obtained. Brown content of the products was increased as amount of Cu$_2$O in the mixture increasing. Most of the products were in nanoparticle form with the diameter ranging from 20 − 150 nm. The SnO$_2$ nanoparticles were in the cassiterite rutile structure phase. Both CuO and Cu$_4$O$_3$ phase were observed in the products and confirmed to be monoclinic and tetragonal phase, respectively. In addition, the CuO$_x$/SnO$_2$ nanoparticles were applied as ethanol sensor. The results showed that the CuO$_x$/SnO$_2$ nanoparticles exhibited extra high sensitivity to ethanol vapor.

1. Introduction

SnO$_2$ is one of the promising materials for technological development. It can be seen that SnO$_2$ nanostructures have been investigated intensively to use in various applications, such as solar cells[1], gas sensors[2], and transparent conductive devices[3] due to their high specific surface area and activity, good thermal and chemical stability, low resistivity and high transmittance. In gas sensing application, the SnO$_2$ nanostructures can further improve their sensing performance by loading noble metal on their surface as catalyst or coupling with another metal oxides to form heterostructures of n-p junctions. Bai et al. [4] have prepared SnO$_2$-CuO heterostructures of nanofibers via electrospinning technique. The 30 wt% CuO in the composites exhibited highest sensitivity of 95 to 10 ppm of CO at 235°C, greater than 2.5 times to that of pure SnO$_2$ nanofibers. The assistance of microwave radiation to many techniques have been shown to provide a better product quality, saver time and lower power consumption. For example, Zhu et al. [5] have synthesized SnO$_2$ quantum dots by using microwave assisted hydrothermal route within 0.5 min at 160°C. However, in hydrothermal route, the organics contaminated in the product needed to be remove at above 400°C for a few hours. Whereas, nanostructures of ZnO and SnO$_2$ have been prepared via microwave-assisted thermal oxidation in a few minutes at atmospheric ambient without further treatment [6,7].

In this work, SnO$_2$, 3.6 eV n-type semiconductor, were coupled with CuO, 1.4 eV p-type semiconductor[8], to form n-p heterostructures by a simple thermal oxidation technique in

atmospheric ambient with microwave radiation assistance and mixture of Cu_2O and Sn powder was used as precursor. The synthesized CuO_x/SnO_2 nanostructures were characterized for morphology, crystal structure, and ethanol sensing performance.

2. Experimental

CuO_x/SnO_2 nanostructures were synthesized by microwave-assisted thermal oxidation (MWTO) technique which its details can be found elsewhere[7]. Cu_2O was used as a source of CuO due to its instability. Firstly, mixtures of Sn and Cu_2O powder were milled in mortar and employed as precursor. $Sn:Cu_2O$ ratio was varied as 1g:0g, 1g:0.1g, 1g:0.2g, 1g:0.3g, and 1g:0.4g. Each mixture was loaded into the middle of a 10 cm long cylindrical quartz tube with diameter of 2.8 cm. Then the quartz tube was placed into a household microwave oven (SHARP). Note that both ends of the quartz tube were opened. The mixture was then heated by microwave power of 800 W at a frequency of 2.45 GHz under atmospheric ambient for 2 min. After the system was cooled down naturally, the quartz tube was taken out from the microwave oven. Finally, the products were collected to characterize by transmission electron microscope (TEM) and x-ray diffractometer (XRD) and to fabricate ethanol sensors.

3. Results and discusion

3.1 Morphology and crystallinity

Figure 1a shows the result of x-ray diffractometry analysis of the thick films. It exposes that the white thick film was the tetragonal rutile SnO_2 with lattice parameter of $a = 4.738$ Å and $c = 3.187$ Å (JCPDF No. 41−1445). In addition, the brown thick films composed of the tetragonal rutile SnO_2, the monoclinic CuO with lattice parameter of $a = 4.689$ Å, $b = 3.426$ Å, $c = 5.132$ Å, $\alpha = \gamma = 90°$, and $\beta = 99.65°$ (JCPDF No. 80−1917) and the tetragonal Cu_4O_3 with lattice parameter of $a = 5.837$ Å and $c = 9.932$ Å (JCPDF No. 83−1665). Moreover, it can be seen that the x-ray spectra intensity of the (002) plane of CuO and the (202) plane of Cu_4O_3 increased as the Cu_2O content in the mixture increasing and occurred obviously in the products corresponding to the mixtures of $1gSn+0.3gCu_2O$ and $1gSn+0.4gCu_2O$.
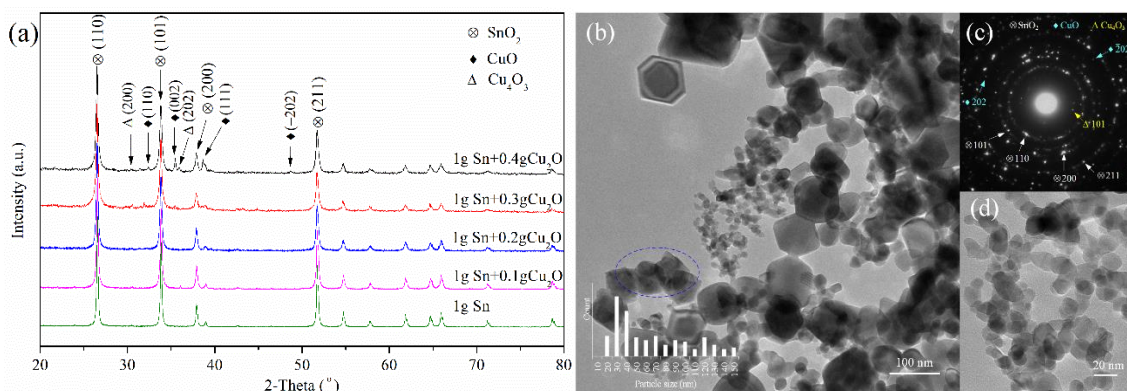

Figure 1. (a) X-ray spectrum of the CuO_x/SnO_2 nanoparticles, (b) representative TEM bright field image of the CuO_x/SnO_2 nanoparticles corresponding to the mixture of $1gSn+0.3gCu_2O$, (c) SAED pattern of the CuO_x/SnO_2 nanoparticles, and (d) higher magnificent TEM image zoomed into smaller particles in (a)

The brown thick films were further characterized using TEM for evaluating particle size, confirming crystal structure, and formation of CuO_x/SnO_2 in atomic scale. Figure 1b−1d show a representative TEM bright field image of the CuO_x/SnO_2 nanoparticles corresponding to the mixture of $1gSn+0.3gCu_2O$. Figure 1b and 1d reveal the nanoparticles with the diameter of 20-150 nm. The inset in figure 1b shows the size distribution of the nanoparticles. Figure 1c shows the SAED of the CuO_x/SnO_2 nanoparticles corresponding to figure 1b. It reveals that the brown thick film composed of the cassiterite SnO_2, CuO, and Cu_4O_3, consistent with the XRD analysis. In addition, the unclear

surface particles in the dash-line circle highlight in figure 1b would be assigned as CuO or Cu_4O_3 because EDS analysis indicated that Cu atomic percent higher than other area.

The formation of the SnO_2 nanostructures have been explained in our previous work [7] by using the nucleation probability which depends on the supersaturation ratio (α) between the actual vapor pressure and the equilibrium vapor pressure corresponding to the absolute temperature T. The high α leads to the growth of nanowires. In vice versa, the low α leads to the formation of nanoparticles. The temperature difference between vapour source and growth area also plays an important role to shape of crystal. In MWTO, the vapor of tin oxide and copper oxides was generated by thermal oxidation and thermal evaporation, respectively, where the heat was given by the microwave power. In this work, SnO_2 nanowires were also observed mostly at the ends of the quartz tube. Whereas, the CuO_x/SnO_2 nanoparticles were found mostly at the middle of the quartz tube. This can be explained that the end of the tube possessed the greater temperature difference, leading to faster condensation of crystal in preferential direction. The middle of the tube possessed the lower temperature difference therefore the vapour of SnO_2 or copper oxides gradually condensed into liquid phase. The vapor surrounding the liquid was possibly trapped into the liquid to form a larger liquid drop which further developed to be nanoparticle. Note that Cu_2O can be decomposed to CuO or Cu_4O_3 due to its instability.

3.2 Ethanol sensing performance
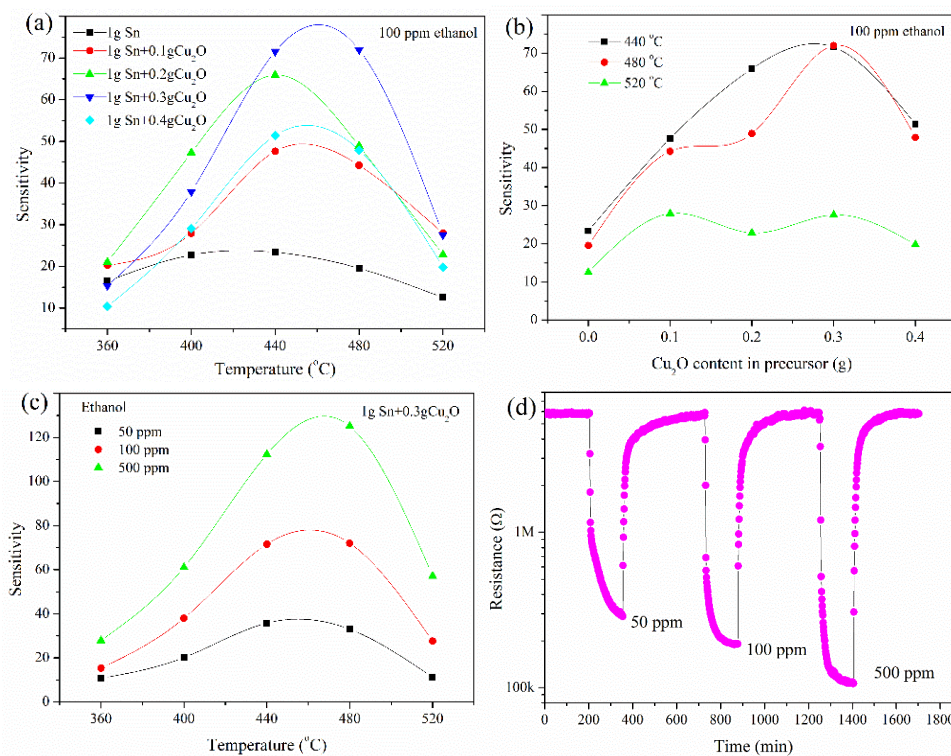
Figure 2. The plot of sensitivity against (a) operating temperature for all mixture ratios, (b) Cu_2O content in precursor at 440°C, 480°C and 520°C for 100 ppm ethanol, and (c) operating temperature for 50 ppm, 100 ppm, and 500 ppm and corresponding to the mixture of $1gSn+0.3gCu_2O$. (d) The resistance against time in explosion of different ethanol concentration at 400°C corresponding to the mixture of $1gSn+0.3gCu_2O$.

The sensitivity of the CuO_x/SnO_2 nanoparticles was shown in figure 2. Figure 2a shows the sensitivity to 100 ppm ethanol concentration for all mixture ratios against operating temperature. It can be seen

that the sensitivity was optimal at the operating temperature 440°C-480°C. The highest sensitivity of 72 was obtained from the CuO_x/SnO_2 nanoparticles of the mixture of $1gSn:0.3gCu_2O$. Figure 2b shows the sensitivity to 100 ppm ethanol concentration against the Cu_2O content in precursor. At 440°C and 480°C, the sensitivity increased as the Cu_2O content increasing up to 0.3 g in 1 g of Sn and then dropped down. This suggests that the optimal sensitivity could be obtained from the CuO_x/SnO_2 nanoparticles in which the Cu_2O content range in 0.2 g - 0.4 g to 1 g of Sn. The sensor corresponding to the mixture of $1gSn:0.3gCu_2O$ was further examined to 50 ppm and 500 ppm ethanol concentration at various operating temperature, which its sensitivity is shown in figure 2c. The highest sensitivity to 50, 100, and 500 ppm ethanol is 35, 72, and 125, respectively. Figure 2d shows the change of the sensor resistance against time at 400°C in different alcohol concentration, taken from the mixture of $1gSn+0.3gCu_2O$, which shows the stability of the sensors.

The higher sensitivity of the CuO_x/SnO_2 nanoparticles over that of the SnO_2 nanoparticles could be explained in the term of the depletion width due to p-n heterojunction at the interface between p-Cu_4O_3 or p-CuO[8] and n-SnO_2 nanoparticles[9]. Therefore, $CuO-SnO_2$ or $Cu_4O_3-SnO_2$ contact could create the larger depletion width over SnO_2-SnO_2 contact. This resulted in higher ethanol sensitivity of the CuO/SnO_2 nanoparticles compared to that of SnO_2 nanoparticles in this work and in previous reported [5,10,11]. In addition, the p-n heterojunction CuO_x/SnO_2 nanoparticles led to much higher sensitivity to carbon monoxide over that of pure SnO_2 nanoparticles and pure CuO nanoparticles[4].

4. Conclusion
The CuO_x/SnO_2 nanoparticles were simply synthesized in a few minutes using microwave-assisted thermal oxidation technique. The analysis indicated that the products were not only consisted of the cassiterite SnO_2 and monoclinic CuO but also the tetragonal Cu_4O_3. The diameter of the CuO_x/SnO_2 nanoparticles was 20-150 nm. The characterization of ethanol gas sensing showed that the sensor made of the CuO_x/SnO_2 nanoparticles was enhanced from 23 to 72 corresponding to 100 ppm ethanol concentration, regarding to that of the pure SnO_2 nanoparticles.

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