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ETHANOL VAPOR SENSING PROPERTIES OF ZnO/CuO NANOCOMPOSITES

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ABSTRACT

CuO leaf-like with thickness of 20 nm, and ZnO plates with thickness of 40 nm have been successfully prepared through a wet chemical method. The two materials were mixed with different weight ratios (CuO/ZnO) to produce nanocomposite materials. Ethanol vapor sensing properties of films derived from obtained materials on SiO_2/Si substrates attached with Pt interdigitated electrodes were investigated at operating temperatures in the range of 250 °C – 400 °C and ethanol vapor concentration in the range of 125 - 1500 ppm. The results showed that the composite of 30 wt% CuO/70 wt% ZnO exhibited the highest response to ethanol vapor at an optimum temperature of 375 ^{o}C.

Keywords: ZnO nanoplates, leaf-like CuO, nanocomposites, sensor.

1. INTRODUCTION

ZnO is a traditional n-type semiconductor due to the existence of oxygen vacancies. ZnO nanostructures with wide, direct bandgap (3.37 eV, at 300 K) and a large free exciton binding energy (60 meV) have attracted intense research interest due to their morphologies and potential optical and electrical applications, such as field emitter [1], ultraviolet laser [2], biosensor [3], gas sensor [4 - 13] and UV devices [14 – 19]. In contrast, CuO is a p-type transition-metal oxide semiconductor with a narrow bandgap (1.2 eV). Their nanostructures have been extensively studied in recent years and have been considered as promising materials in many fields such as gas sensors [20], lithium ion electrode materials [21] and field emission emitters [22]. Composite nanostructures of ZnO and CuO may form a p-n junction in low dimensional scale. It is expected that the nanocomposites of ZnO and CuO materials exhibit novel or improved properties in different fields such as gas sensors and emitters.

In this paper, we report the fabrication of single crystalline ZnO nanoplates and CuO leaf-like to produce CuO/ZnO nanocomposite materials by wet chemical method. Uses of catalyst for the materials were not needed in our technique. The structures and ethanol sensing properties of the composites nanostructures also were studied.

2. EXPERIMENT

ZnO nanoplates were prepared through a wet chemical method according to the Ref. [23]. CuO leaf-like have been prepared by using $Cu(NO_3)_2.2H_2O$ (99 %) and NH_4OH. Firstly, 5 ml of solution of NH_4OH 1M were dropped to 250 ml solution $Cu(NO_3)_2$ 0,02M under stirring at room temperature for 20 minutes. The obtained blue-white precipitation was collected, washed and filtered. Afterwards the precipitation was added to 80 ml of de-ionized (DI) water and transferred into teflon lined sealed stainless steel autoclaves and maintained at 120 ^oC for 2 h under autogenous pressure. The last product was washed, filtered several times with ethanol and DI water, then dried in air in the laboratory oven at 80^oC for 24 h. CuO/ZnO nanocomposite materials have been prepared through a simple mixing of ZnO nanoplates and CuO leaf-like with different weight ratios. These materials are presented in Table 1.

Crystal structure identification of ZnO nanoplates and CuO leaf-like were obtained using Siemens D5005 X-ray diffratometer with a CuK_α radiation (λ = 1.54065 Å) at a scanning rate of 0.03^o/2s in the 2θ range from 10^o to 70^o. The morphology of ZnO and CuO nanopowders were identified by a scanning electron microscope SEM (JEOL-JSM7600F) using an electron beam energy of 10 kV. The morphology of the composite of 30 wt% CuO/70 wt% ZnO (M3) was identified by a scanning electron microscope SEM (HITACHI S4800).

Table 1. Prepared nanocomposite materials.

ZnO (wt%)	CuO(wt%)	Symbol
0	100	M1
50	50	M2
70	30	M3
30	70	M4
80	20	M5
20	80	M6
100	0	M7

These as-prepared products were coated onto Pt-interdigitated electrodes with gap between the fingers of about 20 μm by spin-coating method, then dried in air at 80 ^oC for 24 h and heated at 600 ^oC for 2 h to evaporate the organic species and to stabilize the materials structure. These sensor samples were placed in a hot plate inside a glass chamber. The working temperature of the films was determined by a thermocouple attached near the sensor sample. The response of these samples to ethanol (C_2H_5OH) vapor was tested in static gas sensing system at temperature in the range of 250 ^oC – 400 ^oC. The principle for gas sensing applications using metal oxide semiconductor bases on the change in resistance of the sensitive layer in the presence of gases. The sensor response was defined as a ratio: $S = \frac{R_{air}}{R_{gas}}$, where R_{air} is the resistance in air and R_{gas} is the resistance in presence of C_2H_5OH gas.

3. RESULTS AND DISCUSSION

Typical SEM image and XRD pattern of the pure ZnO nanoplates are shown in Figure 1. The Figure 1(a) indicates that plate-like ZnO has average thickness of about 40 nm and clean surface with average size of 200 × 400 nm. As indicated in Figure 1(b), most of the diffraction peaks can be indexed to the hexagonal wurtzite structure of ZnO with lattice constant of $a = b$ = 0.3249 nm and c = 0.5206 nm (JCPDS 36-1451). The strong and narrow diffraction peaks indicate that the material has a good crystallinity and size. No other minority phase peaks were detected.

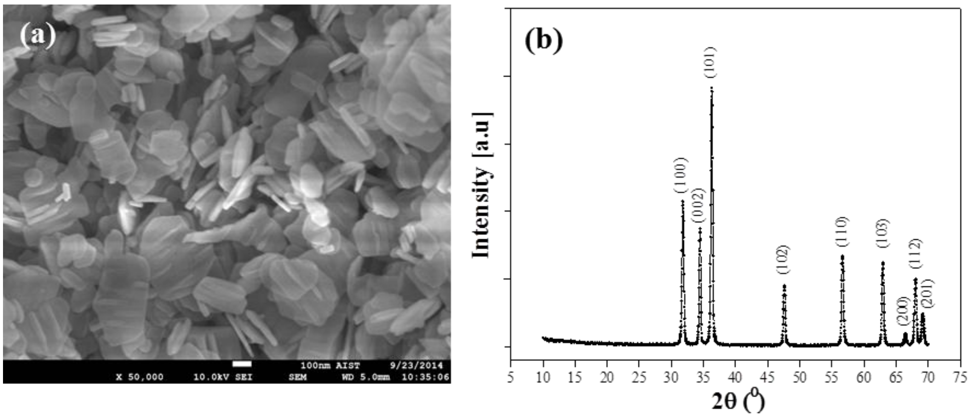

Figure 1. SEM image (a) and XRD pattern (b) of ZnO nanoplates after annealing at 500 ^{0}C for 2 h.

Figure 2 shows typical SEM image (a) and XRD pattern (b) of CuO leaf-like which has average thickness of about 20 nm and width of about 100 nm. We observed that CuO leaf-likes have different lengths and smooth surface. As indicated in figure 2(b), all peaks are indexed to the monoclinic phase of CuO (JCPDS 80-1917).

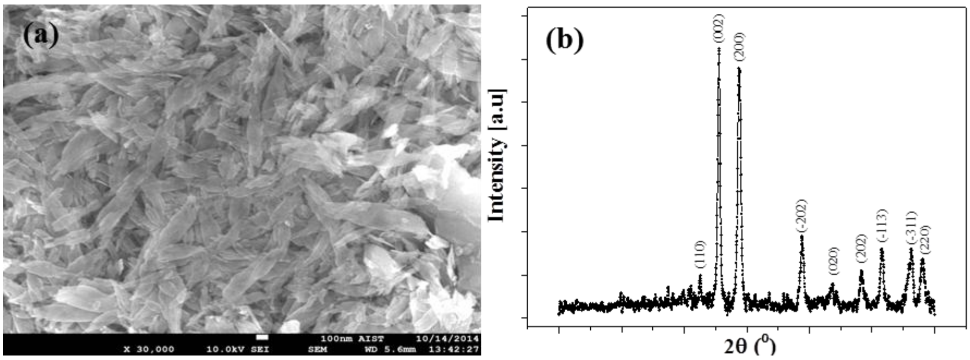

Figure 2. SEM image (a) and XRD pattern (b) of CuO leaf-like after drying at 80 ^{o}C for 24 h.

The mechanism of ZnO nanoplate formation was depicted in the Ref. [23]. A proposed route of the synthesis of CuO leaf-like is as follows: Cu^{2+} ions reacted with $NH_3.H_2O$, forming a amino complexes easily. When amino complexes were heated, they decomposed to CuO. The following reactions should take places in aqueous solutions [24]:

$$Cu^{2+} + NH_3.H_2O \leftrightarrow [Cu(NH_3)_4]^{2+} + OH^- \leftrightarrow CuO + NH_3 + H_2O \qquad (1)$$

Figure 3(a) shows SEM image of nanocomposite of 30 wt% CuO/70 wt% ZnO (M3). It is apparent that the existence of the secondary oxide (CuO) did not affect the size and morphology of ZnO nanoplates. The energy dispersive x-ray spectroscopy analysis (EDX) of M3 sample is shown in Figure 3(b), which demonstrates that both ZnO and CuO have been presented in the material. There is no impurity element.

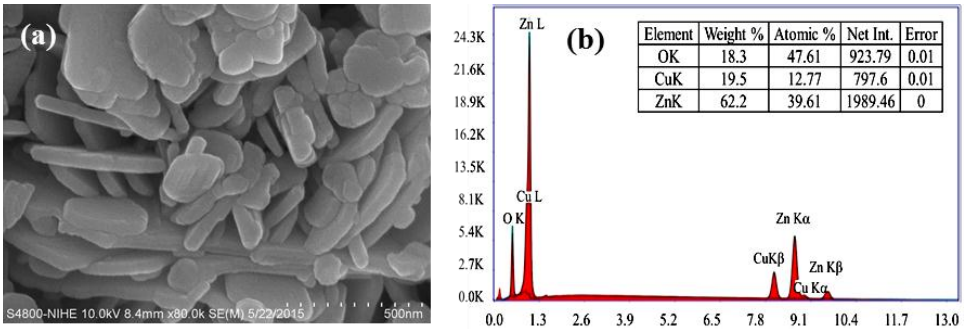

Figure 3. SEM image (a) and EDX spectrum (b) of nanocomposite 30 wt% CuO/70 wt% ZnO (M3).

ZnO is a traditional sensing material for the detection of toxic and flammable gases. However, compared to other gases such as H_2 and NH_3, ZnO is less sensitive for the detection of ethanol vapor because the detection of gases is mainly based on the catalytic oxidation of gas molecules on n-type semiconductor surfaces, where H_2 can be oxidized more easily than C_2H_5OH.

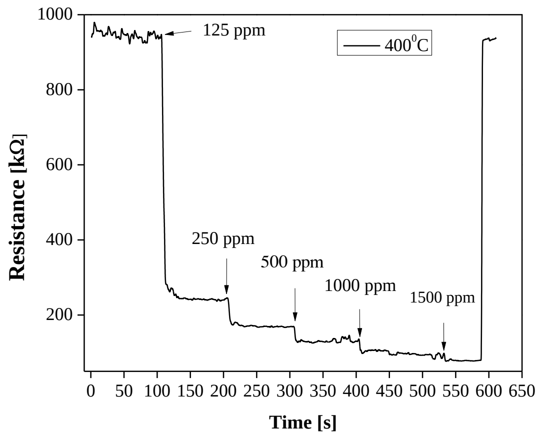

Figure 4. Transient response of nanocomposite material M3 to various C_2H_5OH vapor concentration at 400 ^{0}C.

The bulk heterocontact CuO/ZnO composite materials have been demonstrated to improve the sensitivity as well as the reproducibility of the C_2H_5OH vapor sensor since the introduction of the p-type CuO forms a heterocontact interface with the ZnO [25 - 27]. Yanagida *et al* suggested that the adsorbed reductive molecules form interface states that can change the potential barrier height and consequently the current across the junction [28]. In our case, the composite consisting of CuO and ZnO phases form the heterocontact interface on the nanoscale. The C_2H_5OH vapor sensing properties of the CuO/ZnO composite are expected to be improved. Therefore, gas sensor samples based on the composite nanostructure film were fabricated.

Typical response transient of nanocomposite materials is shown in Figure 4. We noted that a slight resistance ripple occurred, which may be due to the inhomogeneous morphologies of the CuO/ZnO composite nanostructures. In addition, it can be seen that in ethanol concentration of 1500 ppm, the resistance change is least which indicates the saturation of sensor sample.

Since these sensor samples presented different responses at various testing temperatures and concentrations of the testing gas, we investigated the effect of these two factors. Figure 5 shows the sensitivity of the nanocomposite material M3 as a function of temperature. As can be seen from Figure 5, the response of the M3 sensor sample reaches the maximum at 375 ^oC in the temperature range from 250 ^oC to 400 ^oC. Therefore, 375 ^oC was chosen as the testing temperature to investigate a dependence of the response on C_2H_5OH vapor concentration of the CuO/ZnO sensor samples. Figure 6 shows the sensing responses of the corresponding CuO/ZnO nanocomposite materials, pure ZnO and pure CuO gas sensor samples when exposed to C_2H_5OH vapor to different concentrations in the range of 150 to 1500 ppm at 375 ^oC.

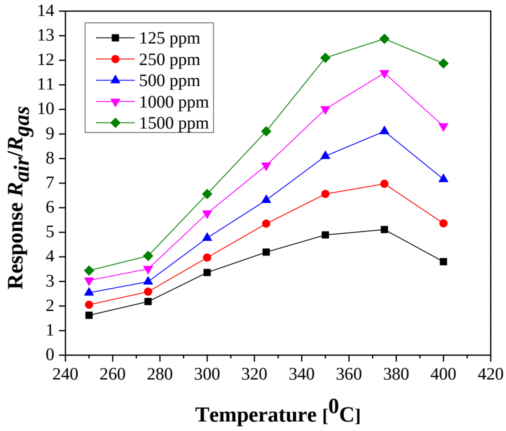

Figure 5. The dependence of sensitivity of nanocomposite material M3 to various C_2H_5OH vapor concentration on temperature.

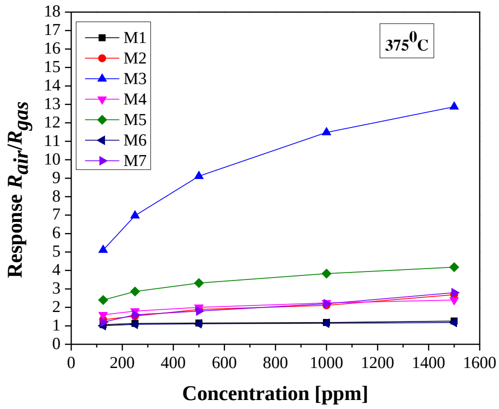

Figure 6. The dependence of sensitivity of nanocomposite materials different weight ratios on C_2H_5OH vapor concentration.

At this temperature, as can be seen in Figure 6 the M3 sensor sample shows the highest response of all concentrations of C_2H_5OH vapor in comparing with other nanocomposite materials, pure ZnO and CuO. Its response to the C_2H_5OH vapor is about 13 for concentration of 1500 ppm. It indicated the improved sensitivity of the CuO/ZnO composite to the C_2H_5OH vapor. These results indicate that the best performance can be achieved with a composite of 30 wt% CuO/70 wt% ZnO sensor sample compared to a single-phase plate ZnO or leaf-like CuO sensor samples.

We propose the mechanism of ethanol vapor sensing properties of nanocomposite materials as follows: In these materials, large number of p-n heterojunctions are formed between the CuO leaf-like and ZnO nanoplates, and an electron depletion layer will be generated. The existence of numerous p–n heterojunctions causes a remarkable increase in the resistance of CuO/ZnO hybrid compared with pure ZnO, CuO. However, the electrons mainly transfer between ZnO nanoplates. Therefore, the leaf-like CuO/ZnO nanoplate materials with numerous p–n heterojunctions behave as an n-type semiconductor. These p–n heterojunctions play a key role in detecting ethanol vapor. The charges existed on the CuO/ZnO surface of the p–n heterojunction, resulting in the ability of CuO/ZnO nanostructures to attract reductive ethanol vapor more easily. Consequently, the surface adsorption reaction occurring between adsorbed C_2H_5OH molecules and adsorbed oxygen species on the ZnO surface releases the electrons back to the semiconductor. The CuO leaf-like provide more active sites for ethanol molecule adsorption. Then, the reductive ethanol molecule combines with the holes in CuO and produces the intermediates which will react with absorbed oxygen on the n-type ZnO. Possible reactions are as follows:

$$C_2H_5OH + 6O^- \rightarrow 2CO_2 + 3H_2O + 6e^- \quad (2)$$

$$C_2H_5OH + 2h^+ + e^- + O^- \;\; O_2^-/O^{2-} \;\rightarrow CH_3CHO + H_2O \quad (3)$$

$$CH_3CHO + 5h^+ + 5O^- \;\; O_2^-/O^{2-} \;\rightarrow 2CO_2 + H_2O + 6e^- \quad (4)$$

Overall, the addition of p-type CuO enhanced the ethanol adsorption kinetics. The CuO/ZnO heterojunction active sites convert C_2H_5OH with O^- to CH_3CHO and H_2O, thereby increasing the sensitivity of the heterocontact sensor.

4. CONCLUSION

In summary, we have presented a hydrothermal method for the synthesis of pure ZnO nanoplates, leaf-like CuO and their composites. The nanocomposite material of 30 wt% CuO/70 wt% ZnO showed remarkably improved sensing properties for C_2H_5OH vapor compared to the single-phase ZnO nanoplates, or CuO leaf-like and other composites. Its response to the C_2H_5OH vapor achieves about 13 in concentration of 1500 ppm. These results also show that the composite of 30 wt% CuO/70 wt% ZnO may be a promising material to fabricate ethanol sensor.

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TÓM TẮT

ĐẶC TÍNH NHẠY HƠI CỒN CỦA VẬT LIỆU TỔ HỢP ZnO/CuO KÍCH THƯỚC NANO

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Lá CuO với bề dày khoảng 20 nm, tấm ZnO với chiều dày khoảng 40 nm được chế tạo thành công bằng phương pháp hóa ướt. Hai vật liệu này được trộn với nhau theo các tỉ lệ phần trăm khác nhau về khối lượng (CuO/ZnO) để tạo ra các vật liệu tổ hợp có cấu trúc nano. Đặc tính nhạy hơi cồn của các vật liệu tổ hợp được khảo sát bằng cách tạo màng trên đế SiO_2/Si có gắn sẵn hệ điện cực răng lược Pt trong dải nhiệt độ làm việc 250 ^oC – 400 ^oC và dải nồng độ 125 - 1500 ppm. Kết quả thu được cho thấy độ đáp ứng của vật liệu tổ hợp có tỉ lệ 30/70 là cao nhất so với các tổ hợp khác tại nhiệt độ làm việc tối ưu 375 ^oC.

Từ khóa: tấm nano ZnO, lá CuO, tổ hợp cấu trúc nano, cảm biến.