Hydrothermal Synthesis of CuO Nanoplates For Gas Sensor

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Received: August 21, 2019; Accepted: June 22, 2020

Abstract

Metal oxide nanomaterials have been widely utilized in gas sensors due to their excellent performance. Comparing to n-type metal oxides, p-type ones have been less studied for gas sensing applications. In this work, CuO nanoplates were synthesized at different temperatures by a facile hydrothermal route at different temperatures without using any surfactant to study the effect on the gas sensing properties. The morphologies and crystal structures of the synthesized materials were characterized by filed-emission scanning electron microcopy (FE-SEM) and X-ray diffraction (XRD). Gas sensing characteristics were measured at various concentrations of H_2 in the range of 50-1000 ppm at working temperatures from 250 to 400^{o}C. The results demonstrated that the synthesized CuO nanoplates exhibited p-type semiconducting behavior when the sensor resistance increased upon exposure to H_2. The sensing mechanism for the gas sensing behavior of CuO nanoplates was also mentioned.

Keywords: CuO nanoplates, hydrothermal, H_2 sensing.

1. Introduction

Semiconductor metal oxides have been extensively used for development of high performance gas sensors in the past few years [1]. Different metal oxides such as tin oxide (SnO_2) [2] tungsten oxide (WO_3) [3], zinc oxide (ZnO) [4] and indium oxide (In_2O_3) [5] have been used as gas sensing materials [6]. The mentioned oxides are n-type semiconductors. However, compared with n-type metal oxides, p-type semiconductor nanomaterials have been relatively less studied despite their low cost and facile synthesis, non-toxicity, thermal and mechanical stabilities, excellent electrical and electronic properties. In recent years, p-type semiconducting metal oxide nanomaterials such as NiO [7], CuO [8], Cr_2O_3 [9] and Co_2O_3 [10] have attracted the attention of many researchers throughout the world [11]. Among these oxides, copper oxide (CuO) is an important p-type metal oxide semiconductor with narrow band gap (1.2 eV) [12], it possesses unique physical properties and great potential for many applications, including of gas sensors [13-15].

In this article, we report the synthesis of CuO nanostructures by a simple and convenient surfactant-free hydrothermal method. The formation mechanism of CuO nanostructure and its fundamental properties were proposed and discussed through investigating the influence of hydrothermal temperature on the growth of crystals. Then, fabrication of sensors and survey with H_2 gas with different concentrations at various temperatures ranging from 250^{o}C to 400^{o}C were presented.

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2. Experiments

2.1. Hydrothermal synthesis of CuO nanoplates at different temperatures

Copper (II) chloride ($CuCl_2$, ≥99.995%) and potassium hydroxide (KOH, ≥85%) were purchased from Sigma-Aldrich and used as received without any further purification. All the chemicals are analytical grade.

CuO nanoplates were synthesized by a facile hydrothermal method without using any surfactant. Fig.1 shows the hydrothermal processes for the fabrication of CuO nanoplates using $CuCl_2$ and KOH as precursors.

In a typical synthesis, 1.2 g CuCl2 and 1.7 g of KOH were dissolved in 80 mL of deionized water using a magnetic stirring for 15 min at room temperature [16]. The blue solution was transferred into a Teflon-lined autoclave (100 mL in volume) for hydrothermal treatment at different temperatures (140, 160, 200 and 220^{o}C) for 23 h. The precipitated products consisting of nanoplates were collected and washed several times using deionized water and subsequently ethanol solution by centrifugation at 4000 rpm. Finally, the collected products were air dried at 60^{o}C for 20h before sending for morphological and structural characterization by scanning electron microscopy (SEM) and x-ray diffraction (XRD) analysis.

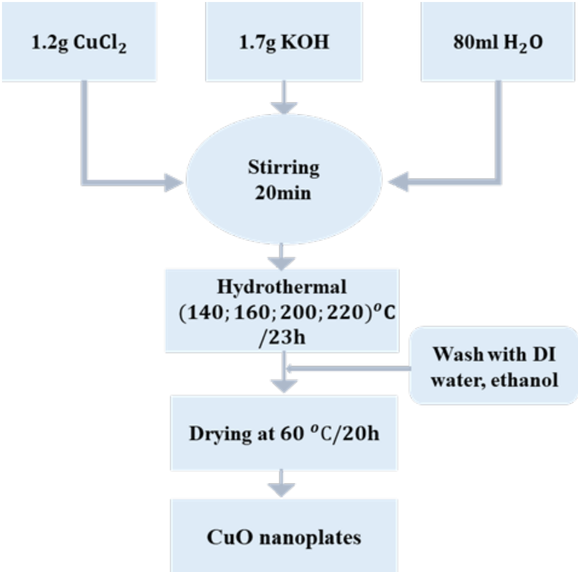

Fig. 1. Process of the hydrothermal synthesis of CuO nanoplates.

2.2. Material characterization

The morphologies of the synthesized materials were investigated by field-emission scanning electron microscopy (FESEM, JEOL 7600F) and the crystal structures of the materials were studied by powder X-ray diffraction (XRD; Advance D8, Bruker) using CuKα X-radiation with a wavelength of 1.54178 Å in the range of 30 – 70°.

Table 1. Experimental conditions and sample symbols

Substances participating in the reaction	Hydrothermal temperature	Sample notation
1.2g $CuCl_2$+ 1.7g KOH	140°C	CuO140
	160°C	CuO160
	200°C	CuO200
	220°C	CuO220

2.3. Gas sensor fabrication and characterization

For sensor fabrication, 15 mg of the synthesized materials were dispersed in ethanol solution by ultrasonic vibration for 5 minutes. Thereafter, the obtained suspension was dropped onto a thermally oxidized Si substrate equipped with a pair of comb-type Pt electrodes. The sensors were dried at room temperature for 2 h, and then heat treated at 500°C for 2h with a heating rate of 5°C per minute to stabilize the sensor's resistance and increase the contact between the sensing materials and the comb-type Pt electrodes.

The gas-sensing properties were measured at temperatures ranging from 250°C to 400°C in atmospheric pressure with dry air as carrier. The H_2 concentrations were controlled between 50 to 1000ppm. The gas sensors were measured by a flow-through technique with a standard flow rate of 400sccm for both dry air and tested gas using a homemade sensing system. The sensor resistance was continuously measured during sensing measurement by using a Keithley 2700, which was interfaced with a computer. The sensor response was defined as (*Rgas*- *Rair*)/*Rair*, where *Rgas* and *Rair* are the sensor resistance in the presence of H_2 and dry air gases, respectively.

3. Results and discussion

3.1 Materials characterization

The morphologies of the CuO nanostructures fabricated with different hydrothermal temperatures were characterized by FE-SEM images, and the results are shown in Fig. 2A-D, respectively.

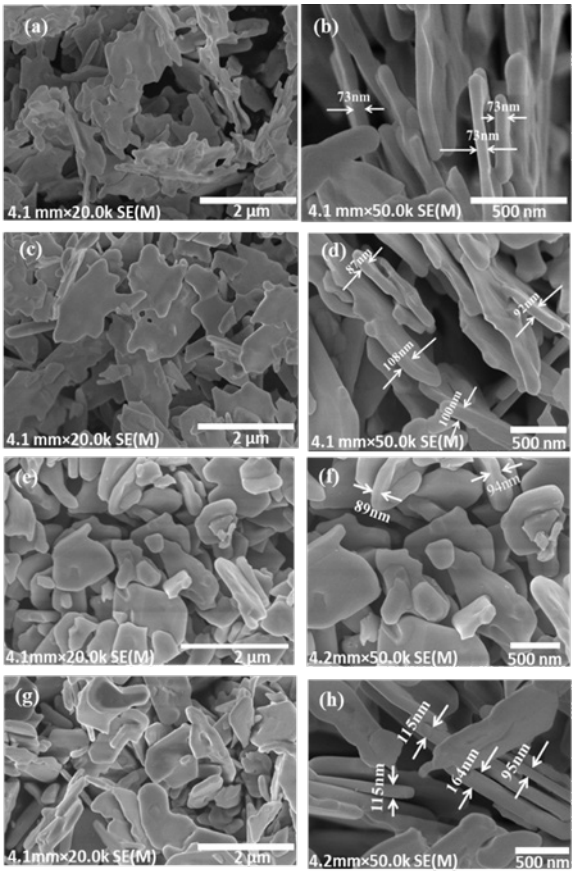

Fig. 2. FE-SEM images of CuO nanoplates with different hydrothermal temperatures: (a, b) at 140°C; (c, d) at 160°C; (e, f) at 200°C; (g, h) at 220°C.

As can be seen, with the increasing of hydrothermal temperature, the size of CuO nanostructures slightly changed. The length and the width of the nanoplates become larger with the increasing hydrothermal temperature, as shown in

Fig.2a-h. We can see that when the hydrothermal temperature increases up to 220ºC, the width of the CuO nanoplates increases from 70 nm to more than 165 nm.

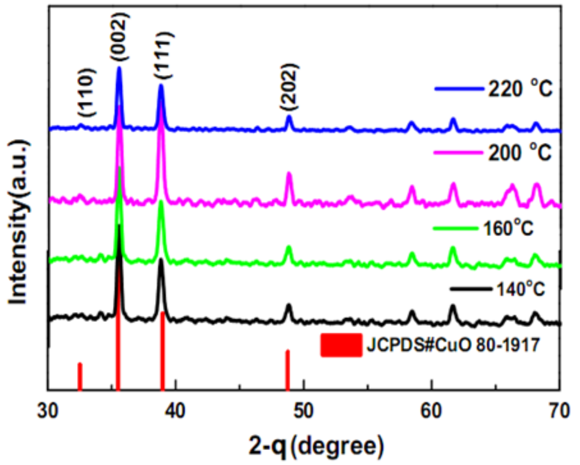

Fig.3. X-ray diffraction pattern of CuO nanoplates obtained by hydrothermal synthesis at different temperatures.

Fig. 3 presents the XRD patterns of the fabricated CuO nanoplates. All typical diffraction peaks can be readily indexed to the monoclinic structure of CuO (JCPDS PDF card No. 5-661), as previously reported [8, 16]. The major peaks located at $2\theta = 35.5^{\circ}$ and 38.7° are indexed as (002) and (111) crystal planes, respectively. No other impurity peaks were observed in the pattern, which verified that the synthesized nanostructures were pure CuO.

3.2 Gas-sensing properties

The fabricated CuO sensor was measured at different concentrations of H_2 at different temperatures. As can be seen in Fig.4, the transient resistance versus time of the CuO140 sensor upon exposure to different concentrations of H_2 gas (50 to 1000 ppm), in the range of working temperature from 250 to 400ºC exhibits good sensing characteristics. The resistances of CuO140 sensor increases with the presence of H_2 gas molecules. Therefore this confirms that the obtained CuO140 is a p-type semiconductor metal oxide [18].

The results show that sensor responses increase with the increasing of H_2 gas concentration. At a working temperature of 250ºC the sensor shows the highest response.

The increase of sensor resistance upon exposure to H_2 gas can be explained by the modulation of the accommodation layer. At a relatively high operation temperature, the oxygen adsorbs on the surface of CuO in the forms of O_2-, O- and O_2-. These oxygen ions take electrons from the nanoplates, increasing the conductivity of the metal oxide [18]. When H_2 was introduced to the sensor, its molecules react to oxygen ions, releasing electrons back to the sensor. This makes the hole concentration lower or the sensor resistance higher.

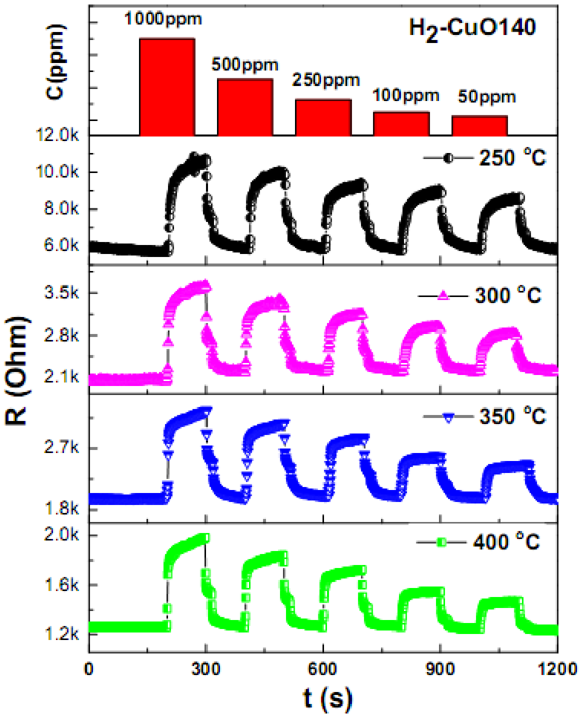

Fig.4. H_2 sensing properties of the CuO140: transient resistance vs. time upon exposure to various concentrations of H_2 at different working temperatures.

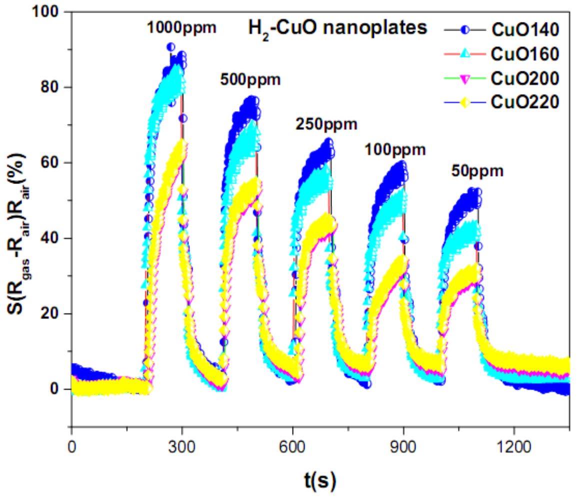

Fig.5. Comparative response result of the CuO nanoplates prepared at various hydrothermal temperatures to different H_2 gas concentrations at the working temperature of 250ºC.

Fig.5 shows the response to hydrogen of the CuO140, CuO160, CuO200, CuO220 sensors measured at 250ºC. The response of the sensor CuO140 at working temperature 250ºC to 25, 50, 100, 250, 500 ppm H2 was respectively 52, 59, 66, 77, 88.5%. The response of the CuO220 sensor to 50, 100, 250, 500, 1000 ppm H_2 at working temperature of 250ºC was 32, 34, 46, 55, 65%, respectively. Therefore, with the decrease of hydrothermal temperature, the sensor response increases. The response of the CuO140 sensor is the highest. This can be explained by the thickness of the plates changing due to hydrothermal temperature. When hydrothermal temperature decreases, the thickness of CuO nanoplates becomes thinner leading the sensor response increases. Comparing to other previous publications [19,20], the response of the sample CuO140 is quite comparable. The response of 88.5% of the sensor CuO140 to 1000 ppm H2 at operating temperature of 250ºC is very comparable to that of 140% to 10000 ppm H_2 in [19] and that of 5% to 100000 ppm H_2 in [20] at the same operating temperature.

4. Conclusion

In this work, we have introduced an effective facile hydrothermal method to control the morphologies of CuO nanoplates for gas sensing application. The effect of hydrothermal conditions on the morphologies and gas sensing properties of CuO was studied and discussed in detail. The length and the width of the nanoplates become larger with the increasing hydrothermal temperature. The CuO nanoplates is suitable for development of highly sensitive H2 gas sensor for environmental pollution monitoring applications.

Acknowledgment

This research is funded by the Hanoi University of Science and Technology (HUST) under the project number T2018-PC-074.

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