Northumbria Research Link

Citation: Li, Zhijie, Wang, Junqiang, Wang, Ningning, Yan, Shengnan, Liu, Wei, Fu, Yong Qing and Wang, Zhiguo (2017) Hydrothermal synthesis of hierarchically flower-like CuO nanostructures with porous nanosheets for excellent H₂S sensing. Journal of Alloys and Compounds, 725. pp. 1136-1143. ISSN 0925-8388

Published by: Elsevier

URL: <https://doi.org/10.1016/j.jallcom.2017.07.218>
<<https://doi.org/10.1016/j.jallcom.2017.07.218>>

This version was downloaded from Northumbria Research Link:
<http://nrl.northumbria.ac.uk/id/eprint/31555/>

Northumbria University has developed Northumbria Research Link (NRL) to enable users to access the University's research output. Copyright © and moral rights for items on NRL are retained by the individual author(s) and/or other copyright owners. Single copies of full items can be reproduced, displayed or performed, and given to third parties in any format or medium for personal research or study, educational, or not-for-profit purposes without prior permission or charge, provided the authors, title and full bibliographic details are given, as well as a hyperlink and/or URL to the original metadata page. The content must not be changed in any way. Full items must not be sold commercially in any format or medium without formal permission of the copyright holder. The full policy is available online: <http://nrl.northumbria.ac.uk/policies.html>

This document may differ from the final, published version of the research and has been made available online in accordance with publisher policies. To read and/or cite from the published version of the research, please visit the publisher's website (a subscription may be required.)

Hydrothermal synthesis of hierarchically flower-like CuO nanostructures with porous nanosheets for excellent H₂S sensing

Zhijie Li¹, Junqiang Wang¹, Ningning Wang¹, Shengnan Yan¹, Wei Liu¹, Yong Qing Fu^{2*}, Zhiguo Wang^{1*}

¹ School of Physical Electronics, University of Electronic Science and Technology of China, Chengdu 610054, PR China

² Department of Maths, Physics and Electrical Engineering, Faculty of Engineering and Environment, Northumbria University, Newcastle Upon Tyne NE1 8ST, England, United Kingdom

ABSTRACT

Flower-like CuO nanostructures with porous nanosheets were synthesized on alumina tube using a hydrothermal method without using any surfactant. The flower-like CuO was comprised of interconnected nanosheets with a uniform thickness of 60 nm. These nanosheets had numerous nanoscale pores with diameters ranging from 20 nm to 160 nm. The copper complex ions of [Cu(NH₃)₄]²⁺ and NH₃ were identified to be critical for the formation of these flower-like CuO nanostructures with porous nanosheets during the hydrothermal process. Gas sensor to hydrogen sulfide (H₂S) based on these porous flower-like CuO nanostructures exhibited high sensitivity, good reproducibility and long-term sensing stability when tested at room temperature of 25 °C. The gas sensor also showed a remarkably high sensing selectivity to the H₂S gas. The gas sensing mechanism was investigated, and the formation of CuS on the surface of CuO nanostructure was identified to be critical for H₂S sensing.

Keywords: CuO; Nanoflower; Hydrothermal; Gas sensor; H₂S

---

*Corresponding author. Tel.: +86 02883200728. E-mail address: zgwang@uestc.edu.cn (Zhiguo Wang);

Richard.fu@northumbria.ac.uk (Richard YongQing Fu)

1. Introduction

CuO is one of the important p-type semiconductor metal oxides with a narrow band-gap between 1.2 and 1.5 eV, and has found wide-range applications in photovoltaics [1,2], gas sensor [3,4], magnetic storage media [5], superconductivity [6,7], photocatalysts [8,9], lithium-ion batteries [10] and electrochemical biosensors [11]. It is well-known that the physical and chemical properties of the CuO are significantly dependent on its micro-structures and morphology [4,8]. Therefore, in recent years, there are a lot of studies to develop novel CuO nanostructures with controlled morphologies and novel physical and chemical properties. Numerous CuO nanostructures including nanoparticles [12-14], nanowires [15,16], nanoflowers [17,18], nanosheets [19], nanotubes [20], nanorods [21] and nanoneedle [22] have been synthesized using various methods, such as thermal oxidation, hydrothermal synthesis and inverse micro-emulsion.

CuO has been used as sensing materials for gas sensor [23-25], and previous studies showed that performance of the CuO based gas sensors was significantly influenced by porosity, surface area and crystal size distribution of the CuO materials [24,25]. Sensors based on hierarchically porous structures generally have large surface-to-volume ratios and a reduced tendency to form agglomerates. Therefore, synthesis of porous CuO nanostructures with large surface areas and uniformly distributed crystal sizes is highly desired. However, studies on preparation of CuO with hierarchically porous structures and investigations of their sensing mechanism/performance have not been widely reported.

In this paper, flower-like CuO nanostructures with hierarchically porous nanosheets were prepared using a hydrothermal method without using any template or surfactant. The H₂S sensing performance and sensing mechanism of the CuO nanostructures based sensor have been systematically investigated.

2. Experiment procedures

2.1 Synthesis of flower-like CuO nanostructures

CuO nanostructures were synthesized on an alumina ceramic tube using

hydrothermal method. Firstly, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ of 3.0 g was dissolved in distilled water of 50 ml under a continuous stirring at room temperature of 25 °C to form a homogeneous solution of 0.3M $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$. Subsequently, under a continuous stirring, 25 ml $\text{NH}_3 \cdot \text{H}_2\text{O}$ (17 mol/L) was slowly dropped into the above solution within 10 minutes, and NaOH of 1.0 g was added into the solution and agitated for another 30 min. For the hydrothermal reaction, the obtained homogeneous solution was transferred into a Teflon-lined stainless steel autoclave with a volume of 140 ml, and an alumina ceramic tube (4 mm of length and 1.5 mm of outer diameter) was placed vertically on the bottom of the autoclave. The autoclave was kept at 180 °C for 24 hours for growth of nanostructure. After the hydrothermal process, the ceramic tube coated with resultant black precipitates was taken out and washed with distilled water. It was then dried at 80 °C for two hours to obtain the CuO nanomaterials on the ceramic tube.

2.2 Characterization of samples

Crystalline phases of the samples were characterized using X-ray diffraction (XRD, Rigaku D/max-2500) with Cu K α radiation at a wavelength of 1.5406 Å. The surface and cross-section morphologies were observed using a scanning electron microscope (SEM, Inspect F50, USA). High-resolution transmission electron microscope (HRTEM, JEM-2200FS, Japan) was used to characterize crystallographic features of the samples. X-ray photoelectron spectroscopy (XPS, Kratos Axis-Ultra DLD, Japan) with a monochromatic Al K α radiation (1486.6 eV) was used to investigate chemical binding states of the elements. UV–Vis spectroscopic analysis was performed using a UV-2101 spectrophotometer (Shimadzu, Japan).

2.3 Gas sensor based on flower-like CuO nanostructures

The flower-like CuO nanostructures based gas sensor was fabricated on the alumina tube. On the alumina tube with flower-like CuO nanostructures, there were a pair of gold electrodes, which were connected to the substrate using Pt wires. During sensing test, an appropriate working voltage ($V_s = 0.25$ V) was applied, and the response of the gas sensor was monitored through measuring resistance values as a function of the applied voltage using a Keithley 2400 source meter. The sensor was placed inside a testing chamber with a volume of two liters and the H_2S gas was injected into the

chamber using an injector. The **concentration** of the H₂S gas was controlled by injecting different **volumes** of the H₂S gas. The ratio of the resistance in detecting gas (R_g) and in air (R_a) was defined as the gas response (S) of the sensor [26,27].

3. Results and discussion

3.1 Characterization of flower-like nanostructures

Fig. 1 XRD pattern of the CuO flower-like nanostructures

Fig. 2 (a, b, c) SEM images of the CuO flower-like nanostructures at different magnifications; (d) HRTEM image showing the crystalline framework.

Fig. 1 shows the XRD pattern of the as-synthesized flower-like CuO nanostructures. The diffraction peaks can be indexed as (110), (002)/($\bar{1}11$), (111)/(200), ($\bar{2}02$), (020), (202), ($\bar{1}13$), ($\bar{3}11$), (220)/(113), (311) and (004) planes of a monoclinic CuO (JCPDS

No. 48-1548). No apparent characteristic peaks from the $\text{Cu}(\text{OH})_2$ and Cu_2O or other phases were identified, indicating that the sample was pure CuO . Figs. 2a and 2b show the SEM images of the CuO nanostructures. The SEM images clearly reveal that the obtained CuO samples have flower-like nano-structures. These flower-like nanostructures are comprised of interconnected nanosheets with a uniform thickness of 60 nm, separated by many cavities among them. From the high magnification SEM image shown in Fig. 2c, the nanosheets are actually network structures with numerous nanoscale pores with diameters ranging from 20 nm to 160 nm. This morphology is different from the previous reports of the flower-like CuO nanostructures. For example, Li et al. [28] reported that flower-like CuO hierarchical micro/nanostructures were directly fabricated on Cu foils. Gao et al. [29] synthesized flower-like CuO nanostructures with diameters ranging from 2 to 3 μm using coprecipitation method. Song et al. [30] reported that CuO nanoflower film was fabricated through the oxidation reaction of copper foil. Although those reported flower-like CuO nanostructures were composed of nanosheets, but there were no pores observed in the nano-sheets. The interspaces between the interconnected network nanosheets and inner pores within the nanosheets are favorable to accelerate gas diffusion and adsorption on the CuO surface, and enhance the sensing performance. Detailed microstructures of the CuO nanosheets obtained from the HRTEM images are shown in Fig. 2d. A well-defined crystalline structure with lattice spacings of 0.252 nm and 0.186 nm can be observed, which are attributed to the lattice constant values of the $(\bar{1}11)$ and $(\bar{2}02)$ planes of the CuO phase.

Fig. 3 (a) Cu 2p and (b) O 1s XPS spectra of the flower-like CuO nanostructures

Fig. 3 shows the high-resolution XPS spectra of Cu 2p and O 1s, respectively. The

Cu 2p core level spectrum represents four major peaks (including two main peaks and two satellite peaks). In Fig. 3a, the main peak at 933.9 eV with satellite peaks at 942.4 eV is attributed to Cu 2p_{3/2}, and the main peak 953.8 eV with satellite peaks at 962.2 eV is attributed to Cu 2p_{1/2}, respectively. These values are comparable to the previously reported values for Cu 2p levels of the CuO [31]. The width of about 19.9 eV between these two main peaks is the same as that of the standard spectrum of the Cu²⁺ [31], further confirming that the oxide in the sample is CuO. The high resolution spectrum of O1s in Fig. 3b shows a broad asymmetric curve which can be deconvoluted into three components with binding energies of 530.0, 531.7 and 532.4 eV, respectively. The **components** at the lower binding energy value of 530.0 eV is due to the oxygen in the CuO crystal lattice, corresponding to the O-Cu bond. The **components** located at the higher binding energy values of 531.7 eV and 532.4 eV are due to the chemisorbed oxygen caused by surface hydroxyl groups (the O-H bond) and the adsorbed O [32-34], respectively. From the XPS analysis, the chemical composition on the surface of flower-like CuO nanostructures is approximately 43.9 at% Cu and 56.1 at% O. The slight O rich could be due to surface adsorption of chemical species such as OH⁻ ions.

Fig. 4 (a) UV-**Vis** absorption spectrum and (b) the corresponding curve of $(\alpha h\nu)^2$ vs $h\nu$ curve of the CuO flower-like nanostructures

The UV-**Vis** absorbance spectrum (as shown in Fig. 4a) shows a broad absorption in the wavelengths ranging from 256 nm to 1000 nm with a shoulder at about 210 nm to 256 nm. Using the following standard Tauc's equation (1), the band gap energy for the direct transition of the flower-like CuO nanostructures can be obtained [35].

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (1)$$

where A is a proportionality factor, h is Planck's constant, α is the optical absorption coefficient, ν is the frequency of photon, E_g is the band gap energy. The curve of $(\alpha h\nu)^2$ versus $h\nu$ based on the direct transition is presented in Fig. 4b. The extrapolated value of E_{photon} at $\alpha=0$ gives the absorption edge energy of the flower-like CuO nanostructures, i.e., $E_g = 3.81$ eV, which is significantly larger than the reported value for the bulk CuO ($E_g = 1.85$ eV) [36]. Previous reports also showed that the **band-gap** values of the ultra-long CuO nanowires is 3.48 eV [37], and that of CuO **nano-plates** is 3.55 eV [30]. All of these results are much larger than that of the bulk CuO. The larger value in the **band-gap** of the as-prepared flower-like CuO nanostructures should be attributed to the well-known quantum size confinement effects [38]. Cheng et al. [39] **reported** a similar UV-Vis absorption spectrum of mesoporous CuO, **and** the band gap was calculated to be 3.43 eV. They **concluded** the reason of the large band gap of CuO was **that** the spatial composition fluctuation **produced an abrupt jump** in the chemical potential, which localized the free exciton states. Because the flower-like CuO **nanostructures** are **composed of** network porous nanosheets, it can **be assumed** that the spatial composition fluctuation is also one of **the reasons for the large band-gap**.

3.2 Formation Mechanism of CuO flower-like nanostructures

Based on the above experimental results, the mechanisms for the morphology evolution of surfactant free synthesis of CuO flower-like nanostructures can be explained based on a solution-phase decomposition of complex species of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ at a high reaction temperature. It was previously reported that the square-planar amino complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$ was formed due to a high concentration of precursors in the presence of ammonia molecules [40]. In this study, the mole ratio of Cu^{2+} and NH_3 was 1:22. Therefore, the concentration of aqueous NH_3 is higher than that of Cu^{2+} ions. The solution of two-dimensional square planar copper complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ions could be firstly formed when they were mixed together via the following reaction:

The square-planar structure of the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is favorable for the formation of 2D

plate-like morphology [40]. In the hydrothermal process, Cu(OH)₂ precipitates were obtained due to the reaction of [Cu(NH₃)₄]²⁺ ions with OH⁻ from NaOH and NH₃·H₂O based on the following equations:

Cu(OH)₂ is generally a layered material and easily forms 2D nanostructures with an orthorhombic phase due to coordinative self-assembly of [Cu(NH₃)₄]²⁺ ions [41]. Therefore, once the nuclei are formed on the surface of the alumina, the assembly of the Cu(OH)₂ nanosheets starts. During the nanosheet assembly, the molecular transport complex [Cu(NH₃)₄]²⁺ is critical to transport Cu²⁺ to the growing tips where the OH⁻ ligands are attached. The attachment of the [Cu(NH₃)₄]²⁺ is accompanied by the release of the NH₃ ligands. Continuous assembly in this way yields a long chain, and further assembly of many such types of long chains will finally produce the nanosheets of Cu(OH)₂. A flower-like Cu(OH)₂ structures will form by connecting of the growing network Cu(OH)₂ nanosheets. Clearly, NH₃ plays an important role for material transportation during the assembly process of the nanosheets. Entrapment of many NH₃ ligands among the Cu(OH)₂ chains will result in the formation of NH₃ gas bubbles, and finally generate the nano-pores in the CuO nanosheets [41,42]. With the increase of the hydrothermal reaction time, the flower-like Cu(OH)₂ structures are transformed into flower-like CuO structures. The entrapped NH₃ gas bubbles are finally released, and the nano-pores among the CuO nanosheets are formed accompanied by the decomposition of Cu(OH)₂ based on the following equation:

To verify the reproducibility of the hierarchically flower-like CuO nanostructures, the experiment process was repeated twice and the same hierarchically flower-like CuO nanostructures could be reproduced. Therefore, we can conclude that the synthesis method of the hierarchically flower-like CuO nanostructures have a good reproducibility.

3.3 H₂S sensing properties of the flower-like CuO nanostructure

Fig. 5 (a) Response and recovery curve and (b) the sensitivity of the CuO flower-like nanostructures based gas sensor to H₂S gas with the concentration ranging from 100 ppb to 20 ppm at room temperature; (c) reproducibility and (d) long-term stability of gas sensor by repetitively exposing to 1 ppm H₂S gas at room temperature.

Fig. 5a shows the dynamic response curves of the gas sensor based on the flower-like CuO nanostructures to different H₂S gas concentrations from 100 ppb to 20 ppm, measured at room temperature of 25 °C. Before any new measurement with the H₂S gas was started, the sensor was calibrated in the dry air in order to achieve a stable baseline. A positive sensing response (i.e., with decreased resistance values) was obtained when the H₂S gas was introduced into the chamber. After the H₂S gas was pumped away and replaced with dry air, the measured resistance could be fully recovered back to the original value. The response time and recovery time were found to be in the range from 4 to 8 minutes and from 15 to 55 minutes, respectively. Results showed that a low H₂S concentration of 100 ppb can be detected using this flower-like nanostructured gas sensor. The sensitivity of this gas sensor to the response of H₂S (in a range from 100 ppb to 20 ppm) is shown in Fig. 5b. The response sensitivity increases with the increased concentrations of the H₂S gas. A linear relationship between the increase of the sensitivity and H₂S concentration was obtained within the detection range from 1

ppm to 20 ppm. This clearly shows that the sensor presents a good linearity response characteristic to the H₂S with different concentrations above 1 ppm.

From Fig. 5b, the sensor also shows a good sensitivity to the H₂S concentration as low as 100 ppb. A linear relationship between the increase of sensitivity values and H₂S concentration was obtained at the low range H₂S concentration of sub-ppm, although the slope of this curve is dramatically different from those above 1 ppm. The difference of the linear relationship between sub-ppm and above 1 ppm of H₂S can be explained by the formation of a CuS layer. When H₂S gas is injected, the CuS layer is formed on the CuO surface, which results in a decrease of the resistance of sensor. With the increase of H₂S concentration, the CuS covered areas are increased on the CuO surface. For low H₂S concentrations of sub-ppm, the increase of CuS areas will result in a decrease of the resistance. But for the high H₂S concentrations above 1 ppm, the CuS continuous layer should form completely and quickly. With the increase of H₂S concentration, the thickness of this CuS layer will only slightly be increased. Therefore, the decrease of resistance will not be remarkable at a high H₂S concentration.

As demonstrated above, the detection limit of the gas sensor is low. The flower-like CuO nanostructures, together with the abundant pores (as shown in Fig. 2), might have large and effective diffusion surfaces, thus both gas diffusion and reactions are accelerated, resulting in a good H₂S gas sensing performance.

Reproducibility of the flower-like CuO based sensor was demonstrated by successively exposing the sensor to the H₂S gas with a fixed concentration of 1 ppm for 5 cycles at room temperature, and the results are shown in Fig. 5c. It can be seen that the response/recovery curves of the sensor are basically consistent with maximum responses between 2.10 to 2.15 for the five consecutive sensing cycles, showing a good reproducibility of the gas sensors. Fig. 5d shows the long-term stability of the gas sensor by continuously testing it with 1 ppm H₂S gas for a month. The largest fluctuation of response sensitivity value of sensor to 1 ppm H₂S is lower than 3%, indicating an excellent long-term stability for the H₂S sensing.

Fig. 6 Dynamic curve of the gas sensors to difference gases (NO_2 , H_2 , CO , $\text{C}_2\text{H}_5\text{OH}$, NH_3) at the same concentration of 100 ppm and 1 ppm H_2S at room temperature.

The good selectivity is another critical parameter to the gas sensor. Fig. 6 shows the sensing curves of the gas sensor based on the flower-like CuO nanostructure exposed to several types of gases (NO_2 , H_2 , CO , $\text{C}_2\text{H}_5\text{OH}$ and NH_3) at the same gas concentration of 100 ppm at room temperature. It can be clearly seen that, the sensor shows almost no responses to NO_2 , CO , H_2 and $\text{C}_2\text{H}_5\text{OH}$, at the concentration of 100 ppm, if compared with that to the 1 ppm of H_2S . For the 100 ppm of NH_3 , the sensor shows a response sensitivity of 1.42, but it is much lower than that to H_2S gas with the concentration of 1 ppm. The results clearly verify the high selectivity of gas sensor based on the CuO flower-like nanostructures to H_2S gas. Table 1 lists the sensing property of H_2S gas sensors listed based on different CuO nanostructures. Compared with the other reported H_2S gas sensor listed in table 1, although the hierarchically flower-like CuO based sensor might have longer recovery times, it can be operated at a low temperature of 25 °C, and it has a high sensitivity, good selectivity and low detection limit at room temperature. So, the hierarchically flower-like CuO nanostructure based sensors have a good sensing property in H_2S gas detection at room temperature.

Table 1: The sensing property of H_2S gas sensor based on different CuO nanostructures

Materials	Working temperature	Concentration	Sensitivity	Response/recovery time (s)	Selectivity	Detection limit	Ref.
CuO film	200 °C	10 ppm	1.42	75/140	High	0.1 ppm	[43]
CuO nanowires	300 °C	50 ppm	1.45	6/27	Low	10 ppm	[44]
CuO nanoparticles.	80 °C	300 ppm	1.3	180/150	Low	10 ppm	[45]
CuO nanowire	325 °C	0.01 ppm	1.3	810/1080	High	0.01 ppm	[46]
CuO-NiO core-shell microspheres	250 °C	100 ppm	48	18/29	Low	10 ppm	[47]
CuO-ZnO hollow spheres	336 °C	5 ppm	13.3	270/720	Low	5 ppm	[48]
CuO nanoparticle decorated ZnO nanorod	100 °C	100 ppm	39	126/300	Low	100 ppm	[49]
CuO/ZnO heterojunction	108 °C	50 ppm	20	--	Low	50 ppm	[50]
Hierarchically flower-like CuO	Room temperature (25 °C)	1 ppm	2.1	240/1341	High	0.1 ppm	This work

3.4 Sensing mechanism

Fig. 7 Real-time gas sensing curves of the sensor based on CuO flower-like nanostructures to 1 ppm H₂S gas at room temperature.

Fig. 7 shows a real-time gas sensing curve of the sensor based on flower-like CuO nanostructures to 1 ppm H₂S gas at room temperature. It is worth to mention that during this process, there are two-stage responses observed before reaching a plateau region.

The first stage of the response exhibited a minor decrease when the sensor was exposed to detection gas within 91 seconds, indicating that the resistance was increased. At the second stage, the response was increased significantly before reaching the final plateau region. This shows that there are two different sensing mechanisms **regarding to reactions between** flower-like CuO nanostructures **and** H₂S gas, which will be explained below.

Fig. 8 Schematic illustrations of (a) the reaction pathway of CuO with H₂S and (b) the recovery pathway of CuO under air exposure.

The behavior of the CuO based gas sensor is generally based on changes in the electrical resistance induced by adsorption/desorption of detection gas on its surface [51,52]. When the gas sensor is exposed to the air, the oxygen molecules are adsorbed on the surface of the CuO nanostructures, thus forming O₂⁻ ions. It could trap electrons and in turn increase the accumulation **of holes**, resulting in an increase in the conductivity of the gas sensor. The first stage **of increase** of resistance is attributed to the oxidation of H₂S when the oxygen species are absorbed on the CuO surface. This is the characteristic of p-type CuO which **has holes** to be served as the charge carrier when it is reacted with oxygen species. The H₂S gas acts as electron donors during the first sensing stage. The oxygen ions on the surface of the CuO interact with the H₂S gas molecules, causing the oxidization of the detection gas molecules, thus releasing electrons. On the surface of the CuO crystals, the H₂S reacts with the oxygen atoms

(O₂⁻) via the following reaction:

The generated free electrons will be transported to the CuO to combine with the positive holes, which results in a reduced layer of accumulated holes, a decrease of the charge carrier density and an increase of the resistance.

On the other hand, when a large amount of H₂S molecules reach the CuO surface, there is a rapid consumption of the adsorbed oxygen on the CuO surface. Therefore, at the second stage, the excessive amount of H₂S will directly react with nanostructured CuO, according to the following chemical reaction:

This reaction causes sequence processes of percolation of CuO to form a layer of Cu_xS (in which x>1), such as Cu₂S, and then form a layer of CuS, which covers the surfaces of CuO as shown in Fig. 8a. XPS analysis showed the formation of the CuS due to the reaction of CuO with H₂S at room temperature [53]. The CuS is a metallic-like conductor. Therefore, it can cause a decrease of the overall resistance of the gas sensor and thus an increase of the conductance. In this study, a large amount of pores in the flower-like CuO nanostructures **will** promote the adsorption of the H₂S molecules, thus facilitating the easy transformation of the CuS. In the process of H₂S sensing, the CuS formation quickly becomes dominant. It can be seen that changes of the resistance in the second stage of the CuS transformation are much more significant than those in the first stage of H₂S oxidation. It took about four minutes to reach the reaction equilibrium for the 1 ppm H₂S gas at room temperature (as see in Fig. 7). After the gas sensor is exposed to the dry air, the resistance increases immediately. As shown in Fig. 8b, the top CuS layer will be oxidized by oxygen and transform back to CuO based on the following **reactions**:

Due to **effective diffusions of O₂ at the molecular level for** the porous CuO flower-like nanostructures, this recovery process can occur at room temperature. With the removal

of H₂S gas, the CuS is transformed into Cu₂S firstly, and then Cu₂S is then transformed into CuO. In the process, it was found that the resistance of this sensor returns to the original resistance of the CuO based sensor which has not be exposed in H₂S gas. Therefore, the Cu₂S should have completely transformed into CuO after exposure to the air for a long time. The oxidation process from CuS to the original state of CuO is slow, so the recovery time of sensor is quite long, for example, the recovery time was 22.6 minutes after removing from 1 ppm of H₂S. Therefore, the sensor based on flower-like CuO nanostructures can be regenerated by exposing the sensor back to the air (as seen in Fig. 5a). The baseline resistance does not change apparently, indicating that there is no irreversible chemical reaction involved.

4. Conclusions

Using the hydrothermal method, a flower-like CuO nanostructure with a porous nanosheet was prepared on alumina tube. It was used to fabricate gas sensor to detect H₂S at room temperature. The flower-like CuO nanostructures consisted of network porous nanosheets with an average thickness of 60 nm. The diameters of these nanoscale pores were ranged from 20 nm to 160 nm. Square planar copper complex [Cu(NH₃)₄]²⁺ ions and NH₃ were identified to be critical for the formation of special network porous flower-like CuO nanostructures. The gas sensor based on flower-like CuO nanostructures showed a good performance to H₂S. It had high sensitivity, high selectivity and high reliability to detect H₂S gas at room temperature.

Acknowledgment

This work was supported by the Joint Fund of the National Natural Science Foundation

of China and the China Academy of Engineering Physics (U1330108), and UK Newton Mobility Grant (IE161019) through Royal Society and the National Natural Science Foundation of China.

References

- [1] Z. Wang, P.K. Nayak, J.A. Caraveo-Frescas, H.N. Alshareef, Recent Developments in p-Type Oxide Semiconductor Materials and Devices, *Adv. Mater.*, 28 (2016) 3831-3892.
- [2] G. Wang, R. van den Berg, C.d.M. Donega, K.P. de Jong, P.E. de Jongh, Silica-supported Cu₂O nanoparticles with tunable size for sustainable hydrogen generation, *Appl. Catal. B-Environ.*, 192 (2016) 199-207.
- [3] Y.H. Navale, S.T. Navale, M. Galluzzi, F.J. Stadler, A.K. Debnath, N.S. Ramgir, S.C. Gadkari, S.K. Gupta, D.K. Aswal, V.B. Patil, Rapid synthesis strategy of CuO nanocubes for sensitive and selective detection of NO₂, *J. Alloy Compd*, 708 (2017) 456-463.
- [4] R.-C. Wang, S.-N. Lin, J.-y. Liu, Li/Na-doped CuO nanowires and nanobelts: Enhanced electrical properties and gas detection at room temperature, *J. Alloy Compd*, 696 (2017) 79-85.
- [5] W. Gao, S. Yang, S. Yang, L. Lv, Y. Du, Synthesis and magnetic properties of Mn doped CuO nanowires, *Phys. Lett. A*, 375 (2010) 180-182.
- [6] B. Keimer, S.A. Kivelson, M.R. Norman, S. Uchida, J. Zaanen, From quantum matter to high-temperature superconductivity in copper oxides, *Nature*, 518 (2015) 179-186.
- [7] S. Sunkara, V.K. Vendra, J.H. Kim, T. Druffel, M.K. Sunkara, Scalable synthesis and photoelectrochemical properties of copper oxide nanowire arrays and films, *Catal. Today*, 199 (2013) 27-35.
- [8] X. Liu, J. Chen, P. Liu, H. Zhang, G. Li, T. An, H. Zhao, Controlled growth of CuO/Cu₂O hollow microsphere composites as efficient visible-light-active photocatalysts, *Appl. Catal. A-Gen.*, 521 (2016) 34-41.
- [9] L. Renuka, K.S. Anantharaju, Y.S. Vidya, H.P. Nagaswarupa, S.C. Prashantha, S.C.

Sharma, H. Nagabhushana, G.P. Darshan, A simple combustion method for the synthesis of multi-functional ZrO₂/CuO nanocomposites: Excellent performance as Sunlight photocatalysts and enhanced latent fingerprint detection, *Appl. Catal. B-Environ.*, 210 (2017) 97-115.

[10] Z. Bai, Y. Zhang, Y. Zhang, C. Guo, B. Tang, A large-scale, green route to synthesize of leaf-like mesoporous CuO as high-performance anode materials for lithium ion batteries, *Electrochim. Acta*, 159 (2015) 29-34.

[11] A. Uzunoglu, L.A. Stanciu, Novel CeO₂-CuO-decorated enzymatic lactate biosensors operating in low oxygen environments, *Anal. Chem. Acta*, 909 (2016) 121-128.

[12] T. Andana, M. Piumetti, S. Bensaid, L. Veyre, C. Thieuleux, N. Russo, D. Fino, E.A. Quadrelli, R. Pirone, CuO nanoparticles supported by ceria for NO_x-assisted soot oxidation: insight into catalytic activity and sintering, *Appl. Catal. B-Environ.*, 216 (2017) 41-58.

[13] X. Liu, Y. Yang, R. Liu, Z. Shi, L. Ma, M. Wei, Synthesis of porous CuO microspheres assembled from (001) facet-exposed nanocrystals with excellent glucose-sensing performance, *J. Alloy Compd*, 718 (2017) 304-310.

[14] D. Das, B.C. Nath, P. Phukon, S.K. Dolui, Synthesis and evaluation of antioxidant and antibacterial behavior of CuO nanoparticles, *Colloid Surface B.*, 101 (2013) 430-433.

[15] X. Wang, X. Wu, L. Yuan, K. Huang, S. Feng, Ultra-low reflection CuO nanowire array in-situ grown on copper sheet, *Mater. Design*, 113 (2017) 297-304.

[16] X. Liu, W. Yang, L. Chen, J. Jia, Three-Dimensional Copper Foam Supported CuO Nanowire Arrays: An Efficient Non-enzymatic Glucose Sensor, *Electrochim. Acta*, 235 (2017) 519-526.

[17] H. Peng, Y. Liu, Y. Guo, J. Zhang, L. Zhang, S. Zhou, X. Xu, W. Liu, N. Zhang, X. Wang, Treating Copper(II) Oxide Nanoflowers with Hydrogen Peroxide: A Novel and Facile Strategy To Prepare High-Performance Copper(II) Oxide Nanosheets with Exposed (110) Facets, *Chemcatchem*, 8 (2016) 3714-3719.

[18] W.-Y. Xie, F. Song, X.-L. Wang, Y.-Z. Wang, Development of Copper Phosphate

Nanoflowers on Soy Protein toward a Superhydrophobic and Self-Cleaning Film, *ACS Sustain Chem. Eng.*, 5 (2017) 869-875.

[19] P. Subalakshmi, M. Ganesan, A. Sivashanmugam, Synthesis of 3D architecture CuO micro balls and nano hexagons and its electrochemical capacitive behavior, *Mater. Design*, 119 (2017) 104-112.

[20] S.R. Chun, W.A. Sasangka, M.Z. Ng, Q. Liu, A. Du, J. Zhu, C.M. Ng, Z.Q. Liu, S.Y. Chiam, C.L. Gan, Joining Copper Oxide Nanotube Arrays Driven by the Nanoscale Kirkendall Effect, *Small*, 9 (2013) 2546-2552.

[21] R. Dang, X. Jia, X. Liu, H. Ma, H. Gao, G. Wang, Controlled synthesis of hierarchical Cu nanosheets @ CuO nanorods as high-performance anode material for lithium-ion batteries, *Nano Energy*, 33 (2017) 427-435.

[22] S. Yang, G. Li, D. Wang, Z. Qiao, L. Qu, Synthesis of nanoneedle-like copper oxide on N-doped reduced graphene oxide: A three-dimensional hybrid for nonenzymatic glucose sensor, *Sens. Actuators B Chem.*, 238 (2017) 588-595.

[23] A. Umar, J.-H. Lee, R. Kumar, O. Al-Dossary, A.A. Ibrahim, S. Baskoutas, Development of highly sensitive and selective ethanol sensor based on lance-shaped CuO nanostructures, *Mater. Design*, 105 (2016) 16-24.

[24] Z. Li, N. Wang, Z. Lin, J. Wang, W. Liu, K. Sun, Y.Q. Fu, Z. Wang, Room-Temperature High-Performance H₂S Sensor Based on Porous CuO Nanosheets Prepared by Hydrothermal Method, *ACS Appl. Mater. Inter.*, 8 (2016) 20962-20968.

[25] S. Steinhauer, E. Brunet, T. Maier, G.C. Mutinati, A. Koeck, O. Freudenberg, C. Gspan, W. Grogger, A. Neuhold, R. Resel, Gas sensing properties of novel CuO nanowire devices, *Sens. Actuators B Chem.*, 187 (2013) 50-57.

[26] Z. Li, X. Niu, Z. Lin, N. Wang, H. Shen, W. Liu, K. Sun, Y.Q. Fu, Z. Wang, Hydrothermally synthesized CeO₂ nanowires for H₂S sensing at room temperature, *J. Alloy compd.*, 682 (2016) 647-653.

[27] Z. Li, Y. Huang, S. Zhang, W. Chen, Z. Kuang, D. Ao, W. Liu, Y. Fu, A fast response & recovery H₂S gas sensor based on alpha-Fe₂O₃ nanoparticles with ppb level detection limit, *J. Hazard. Mater.*, 300 (2015) 167-174.

[28] K. Li, G. Fan, L. Yang, F. Li, Novel ultrasensitive non-enzymatic glucose sensors

based on controlled flower-like CuO hierarchical films, *Sens. Actuators B Chem*, 199 (2014) 175-182.

[29] D. Gao, G. Yang, J. Li, J. Zhang, J. Zhang, D. Xue, Room-Temperature Ferromagnetism of Flowerlike CuO Nanostructures, *J. Phys. Chem. C*, 114 (2010) 18347-18351.

[30] M.-J. Song, S.W. Hwang, D. Whang, Non-enzymatic electrochemical CuO nanoflowers sensor for hydrogen peroxide detection, *Talanta*, 80 (2010) 1648-1652.

[31] D.I. Son, C.H. You, T.W. Kim, Structural, optical, and electronic properties of colloidal CuO nanoparticles formed by using a colloid-thermal synthesis process, *Appl. Surf. Sci.*, 255 (2009) 8794-8797.

[32] Y. Huang, W. Chen, S. Zhang, Z. Kuang, D. Ao, N.R. Alkurd, W. Zhou, W. Liu, W. Shen, Z. Li, A high performance hydrogen sulfide gas sensor based on porous α -Fe₂O₃ operates at room-temperature, *Appl. Surf. Sci.*, 351 (2015) 1025-1033.

[33] M.A. Dar, Y.S. Kim, W.B. Kim, J.M. Sohn, H.S. Shin, Structural and magnetic properties of CuO nanoneedles synthesized by hydrothermal method, *Appl. Surf. Sci.*, 254 (2008) 7477-7481.

[34] Z. Li, Z. Lin, N. Wang, J. Wang, W. Liu, K. Sun, Y.Q. Fu, Z. Wang, High precision NH₃ sensing using network nano-sheet Co₃O₄ arrays based sensor at room temperature, *Sens. Actuators B Chem*, 235 (2016) 222-231.

[35] A.A. Al-Ghamdi, S. Al-Heniti, S.A. Khan, Structural, optical and electrical characterization of Ag doped lead chalcogenide (PbSe) thin films, *J. Lumin.*, 135 (2013) 295-300.

[36] K. Santra, C.K. Sarkar, M.K. Mukherjee, B. Ghosh, Copper-oxide thinfilms grown by plasma evaporation method, *Thin Solid Films*, 213 (1992) 226-229.

[37] W. Wang, L. Wang, H. Shi, Y. Liang, A room temperature chemical route for large scale synthesis of sub-15 nm ultralong CuO nanowires with strong size effect and enhanced photocatalytic activity, *Crystengcomm*, 14 (2012) 5914-5922.

[38] P. Chand, A. Gaur, A. Kumar, U.K. Gaur, Effect of NaOH molar concentration on morphology, optical and ferroelectric properties of hydrothermally grown CuO nanoplates, *Mat. Sci. Semicon. Proc.*, 38 (2015) 72-80.

- [39] L. Cheng, M. Shao, D. Chen, Y. Zhang, Preparation, characterization, and electrochemical application of mesoporous copper oxide, *Mater. Res. Bull.*, 45 (2010) 235-239.
- [40] Y. Ni, H. Li, L. Jin, J. Hong, Synthesis of 1D Cu(OH)₂ Nanowires and Transition to 3D CuO Microstructures under Ultrasonic Irradiation, and Their Electrochemical Property, *Cryst. Growth. Des.*, 9 (2009) 3868-3873.
- [41] X.G. Wen, W.X. Zhang, S.H. Yang, Solution phase synthesis of Cu(OH)₂ nanoribbons by coordination self-assembly using Cu₂S nanowires as precursors, *Nano Lett.*, 2 (2002) 1397-1401.
- [42] S. Yang, C. Wang, L. Chen, S. Chen, Facile dicyandiamide-mediated fabrication of well-defined CuO hollow microspheres and their catalytic application, *Mater. Chem. Phys.*, 120 (2010) 296-301.
- [43] S. Sonia, P. Suresh Kumar, N.D. Jayram, Y. Masuda, D. Mangalaraj, C. Lee, Superhydrophobic and H₂S gas sensing properties of CuO nanostructured thin films through a successive ionic layered adsorption reaction process, *RSC Adv.*, 6 (2016) 24290-24298.
- [44] D. Lee, C. Jin, Y. Noh, S. Park, S.-W. Choi, Morphology and gas sensing characteristics of density-controlled CuO nanostructures obtained by varying the oxygen partial pressure during growth, *J. Korean. Phys. Soc.*, 69 (2016) 45-51.
- [45] A.I. Ayesh, A.F.S. Abu-Hani, S.T. Mahmoud, Y. Haik, Selective H₂S sensor based on CuO nanoparticles embedded in organic membranes, *Sens. Actuators B Chem*, 231 (2016) 593-600.
- [46] S. Steinhauer, E. Brunet, T. Maier, G.C. Mutinati, A. Köck, Suspended CuO nanowires for ppb level H₂S sensing in dry and humid atmosphere, *Sens. Actuators B Chem*, 186 (2013) 550-556.
- [47] Y. Wang, F. Qu, J. Liu, Y. Wang, J. Zhou, S. Ruan, Enhanced H₂S sensing characteristics of CuO-NiO core-shell microspheres sensors, *Sens. Actuators B Chem*, 209 (2015) 515-523.
- [48] S.-J. Kim, C.W. Na, I.-S. Hwang, J.-H. Lee, One-pot hydrothermal synthesis of CuO-ZnO composite hollow spheres for selective H₂S detection, *Sens. Actuators B*

Chem, 168 (2012) 83-89.

[49] L. Wang, Y. Kang, Y. Wang, B. Zhu, S. Zhang, W. Huang, S. Wang, CuO nanoparticle decorated ZnO nanorod sensor for low-temperature H₂S detection, *Mat. Sci. Eng. C-Mater.*, 32 (2012) 2079-2085.

[50] Y. Hu, X. Zhou, Q. Han, Q. Cao, Y. Huang, Sensing properties of CuO–ZnO heterojunction gas sensors, *Mat. Sci. Eng. B-Adv.*, 99 (2003) 41-43.

[51] N. Barsan, C. Simion, T. Heine, S. Pokhrel, U. Weimar, Modeling of sensing and transduction for p-type semiconducting metal oxide based gas sensors, *J. Electroceram.*, 25 (2010) 11-19.

[52] D.P. Volanti, A.A. Felix, M.O. Orlandi, G. Whitfield, D.-J. Yang, E. Longo, H.L. Tuller, J.A. Varela, The Role of Hierarchical Morphologies in the Superior Gas Sensing Performance of CuO-Based Chemiresistors, *Adv. Funct. Mater.*, 23 (2013) 1759-1766.

[53] J. Hennemann, C.-D. Kohl, B.M. Smarsly, H. Metelmann, M. Rohnke, J. Janek, D. Reppin, B.K. Meyer, S. Russ, T. Wagner, Copper oxide based H₂S dosimeters - Modeling of percolation and diffusion processes, *Sens. Actuators B Chem*, 217 (2015) 41-50.