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

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**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](javascript:void(0);) 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 oC. 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

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**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, Cu(CH3COO)2·H2O of 3.0 g was dissolved in distilled water of 50 ml under a continuous stirring at room temperature of 25 oC to form a homogeneous solution of 0.3M Cu(CH3COO)2·H2O. Subsequently, under a continuous stirring, 25 ml NH3·H2O (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 oC 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 oC 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 Kα 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 Kα 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 (Vs = 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 H2S 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 (Rg) and in air (Ra) was defined as the gas response (S) of the sensor [26,27].

**3. Results and discussion**

**3.1** **Characterization of flower-like nanostructures**

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

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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)/(11), (111)/(200), (), (020), (202), (), (11), (220)/(113), (311) and (004) planes of a monoclinic CuO (JCPDS No. 48-1548). No apparent characteristic peaks from the Cu(OH)2 and Cu2O 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](javascript:void(0);) 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 (11) and () planes of the CuO phase.

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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 2p3/2, and the main peak 953.8 eV with satellite peaks at 962.2 eV is attributed to Cu 2p1/2, 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.

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Fig. 4 (a) UV–Vis absorption spectrum and (b) the corresponding curve of (αhν)2 vs hv 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].

(αhν)2 = A(hν − Eg ) (1)

where A is a proportionality factor, h is Planck's constant, α is the optical absorption coefficient, ν is the frequency of photon, Eg is the band gap energy. The curve of (αhν)2 versus hν based on the direct transition is presented in Fig. 4b. The extrapolated value of Ephoton at α=0 gives the absorption edge energy of the flower-like CuO nanostructures, i.e., Eg = 3.81 eV, which is significantly larger than the reported value for the bulk CuO (Eg = 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 [Cu(NH3)4]2+ at a high reaction temperature. It was previously reported that the square-planar amino complex [Cu(NH3)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 Cu2+ and NH3 was 1:22. Therefore, the concentration of aqueous NH3 is higher than that of Cu2+ ions. The solution of two-dimensional square planar copper complex [Cu(NH3)4]2+ ions could be firstly formed when they were mixed together via the following reaction:

Cu2++4NH3→[Cu(NH3)4]2+ (2)

The square-planar structure of the [Cu(NH3)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:

NH3+H2O↔(aq)+(aq) (3)

[Cu(NH3)4]2++→Cu(OH)2↓+4NH3 (4)

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:

Cu(OH)2→CuO+H2O (5)

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**

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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 oC. 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.

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Fig. 6 Dynamic curve of the gas sensors to difference gases (NO2, H2, CO, C2H5OH, NH3) at the same concentration of 100 ppm and 1 ppm H2S 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 (NO2, H2, CO, C2H5OH and NH3) at the same gas concentration of 100 ppm at room temperature. It can be clearly seen that, the sensor shows almost no responses to NO2, CO, H2 and C2H5OH, at the concentration of 100 ppm, if compared with that to the 1 ppm of H2S. For the 100 ppm of NH3, the sensor shows a response sensitivity of 1.42, but it is much lower than that to H2S 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 H2S gas. Table 1 lists the sensing property of H2S gas sensors listed based on different CuO nanostructures. Compared with the other reported H2S 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 oC, 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 H2S gas detection at room temperature.

Table 1: The sensing property of H2S gas sensor based on different CuO nanostructures

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

**3.4 Sensing mechanism**

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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.

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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:

2H2S(g) +3O2−(ads) → 2H2O(g) +2SO2(g) +3e−  (6)

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:

H2S(g) +CuO(s) → CuS(s) +H2O(g) (7)

This reaction causes sequence processes of percolation of CuO to form a layer of CuxS (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:

2CuS(s) + O2(g) → Cu2S(s) + SO2(g)  (8)

2CuS(s) + 3O2(g) → 2CuO(s) + 2SO2(g)  (9)

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.

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