孔隙结构可调的Cu₂O球状纳米结构及其NO₂气体传感性质

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摘要: 报道在聚乙烯吡咯烷酮(PVP)的协助作用下, 通过简单调节OH⁻离子的浓度及Cu²⁺的释放速度, 将Cu₂O调节为具有不同空腔特征(介孔、空心及实心)结构的纳米球. 研究表明, OH⁻根离子的扩散动力学是决定产物结构的关键因素. 当[OH⁻] > 0.05 mol·L⁻¹时, 高的化学势使其迅速扩散到PVP胶团内部, 与吸附在PVP链上的Cu²⁺反应形成Cu(OH)₂, 在抗坏血酸(Vc)的还原作用下经过重结晶得到Cu₂O实心球纳米结构; 当[OH⁻] < 0.025 mol·L⁻¹时, 其扩散速度下降, 首先与吸附在PVP胶团外部的Cu²⁺反应形成Cu(OH)₂, Cu(OH)₂的形成阻碍了OH⁻离子的向内扩散, 形成具有较大空腔(~220 nm)的空心球; 当0.025 mol·L⁻¹ < [OH⁻] < 0.05 mol·L⁻¹时, 形成较小空腔(30–60 nm)的空心球. 以NH₃水为OH⁻缓释源时, 虽然OH⁻浓度较低, 但同时Cu²⁺的浓度也低, 胶团外部形成的Cu(OH)₂不足以阻碍OH⁻离子的向内扩散, 反应过程中NH₃的释放及较低的OH⁻浓度阻碍了重结晶的发生, 从而形成Cu₂O介孔纳米球. 对三种典型结构特征的产物进行了NO₂气体传感性质研究, 结果表明, Cu₂O介孔纳米球相比空心结构和实心结构具有更为优异的响应性. 结合比表面积数据, 我们认为介孔纳米球疏松的结构有利于NO₂气体的扩散和O₂的吸附, 从而表现出了更灵敏的气体传感性.

关键词: Cu₂O; 纳米球; 孔隙可调; 气敏性能; 扩散控制

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Cavity-Tunable Cu₂O Spherical Nanostructures and Their NO₂ Gas Sensing PropertiesZHANG Dong-Feng ZHANG Yan ZHANG Hua QI Juan-Juan
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Abstract: We report the preparation of cavity-controlled Cu₂O nanospheres, having various mesoporous, hollow, and solid structures, by simply adjusting the OH⁻ concentration and the release rate of Cu²⁺ with the assistance of polyvinyl pyrrolidone (PVP). It indicates that the OH⁻ diffusion kinetics is the key factor that determines the morphology of the products. For [OH⁻] > 0.05 mol·L⁻¹, the high chemical potential made them rapidly diffuse into the PVP micelle interiors. Adsorbed Cu²⁺ on the PVP produced Cu(OH)₂, which was subsequently reduced to Cu₂O. After re-crystallization, Cu₂O solid spheres formed. For [OH⁻] < 0.025 mol·L⁻¹, the OH⁻ diffusion rate was reduced, and the Cu(OH)₂ layer on the PVP micelles blocked diffusion into the interior. After re-crystallization, Cu₂O hollow spheres had large cavities (~220 nm). For 0.025 mol·L⁻¹ < [OH⁻] < 0.05 mol·L⁻¹, hollow spheres with smaller cavities (30–60 nm) formed. When an aqueous NH₃ solution was the OH⁻ source, although the concentration of OH⁻ is low, the small amount of Cu(OH)₂ formed with the limited Cu²⁺ was not enough to block OH⁻ diffusion into the micelles. The free NH₃ and the low OH⁻ concentration did not promote re-crystallization; thus, mesoporous Cu₂O spheres were formed.

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We characterized NO₂ gas sensing of the three structures. The porous structures exhibited more sensitivity than did the hollow or solid structures. Together with the specific surface area data, the improved gas sensitivity suggests that the open structure of the mesoporous spheres facilitates NO₂ diffusion and O₂ adsorption.

Key Words: Cu₂O; Nanosphere; Cavity-tunable; Gas sensitivity; Diffusion-controlled

1 Introduction

With the increasing environment pollution, monitoring air quality has become a critical issue. NO₂ is an important component of air contaminants, which is extremely toxic and can be generated by various means both in daily life and in industry production process such as automotive emission, combustion or natural gas manufacturing. The permissible exposure limit of NO₂ is 5×10^{-6} (volume fraction, φ) ceiling concentration. The human body would be posed into danger when the concentration of NO₂ is higher than 20×10^{-6} (φ). It is crucial to develop reliable NO₂ sensors with high sensitivity and low cost from the perspective of both industrial safety and the human health.

Metal oxide semiconductors have been studied extensively for solid gas detecting devices owing to their high sensitivity, low cost, and easy production.^{1,2} As a *p*-type semiconductor with a narrow band (2.2 eV), cuprous oxide (Cu₂O) exhibits great potential in gas sensing³⁻⁶ and other areas, such as the solar energy conversion,^{7,8} catalyst,⁹⁻¹¹ and lithium-ion batteries.^{12,13} Stimulated by the unique properties, great efforts have been devoted to the fabrication of Cu₂O with various morphologies, including polyhedrons,¹⁴⁻¹⁶ nanocages,^{17,18} nanorods,^{19,20} and hierarchical nanostructures.^{6,21,22} Among various structures, porous materials hold great promise for gas sensing because of their efficient interaction with the gases. Although there are a few successful examples on the preparation of Cu₂O porous materials,²³⁻²⁶ little attention has been concentrated on their application as NO₂ gas sensors. On the other hand, construction of Cu₂O porous structure with tunable cavities, an important factor influencing the gas sensing property, is still a challenge.

In this paper, we report the fine tuning of the cavities of Cu₂O spherical structures by simply controlling the reaction kinetic. NaOH and NH₃·H₂O with different concentrations were used as the sources of OH⁻ ions to adjust the concentration of OH⁻ and the releasing rate of Cu²⁺. We also investigate the gas sensing properties of different structured Cu₂O towards NO₂.

2 Experimental

2.1 Synthesis

All the chemical reagents were of analytical grade and used without further purification. A typical synthesis process was as follows.

First, 0.06 g CuAc₂·H₂O and 1.11 g PVP (MW 30000) were dissolved in 30 mL of distilled water by intensive stirring for 2 h and a homogenous transparent solution was obtained. Then,

the given amount of NaOH or NH₃·H₂O was added dropwise into the above solution. After stirring for 1 h, the ascorbic acid (Vc) solution (5.0 mL, 0.25 mol·L⁻¹) was added dropwise into the blue solution. A turbid yellow or red liquid gradually formed. The mixture was heated in water bath at 55 °C for 30 min. All the procedure was carried out under constant stirring. The resulted precipitate was collected by centrifugation and decanting, followed by washing with distilled water for 3 times and absolute ethanol for twice to remove the residual polymer, and finally dried in vacuum at 50 °C for 5 h for further characterizations.

2.2 Gas sensitivity measurement

The different structured Cu₂O spheres were used for sensing measurements. The synthesized samples were dispersed in the ethanol and the paste was laid uniformly on the ceramic tubes on which a pair of gold electrode was previously printed. The gas sensors were dried at 60 °C for 24 h. The heating resistance coil was inserted into the tube to control the temperature during detection. The sensors were connected to the outside electronics to monitor their resistance change during the sensor test. Resistances were determined using a WS-30A test system (Hanwei Co., China). The sensors were operated at the working temperature of 146 °C.

2.3 Instruments

X-ray powder diffraction (XRD) pattern was recorded on a powder sample with Rigaku, D/max-2200 diffractometer employing Cu K_{α1} radiation ($\lambda = 0.154056$ nm) ranging from 30° to 80°. Scanning electron microscopy (SEM) observations were carried out with Hitachi-S4300 operated at an acceleration voltage of 20 kV. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) characterizations were performed with JEOL JEM-2100F operated at 200 kV.

3 Results and discussion

Using Vc to deoxidize Cu (NH₃)₄²⁺ precursor in the presence of PVP, mesoporous Cu₂O spheres with average size of 150 nm were obtained as shown in Fig.1a. High-magnified scanning electron microscopy (SEM, Fig.1b) and transmission electron microscopy (TEM, Fig.1c) observations clearly show that the porous Cu₂O spheres are assembled by small nanoparticles of about 5 nm in diameter. The bright dots in Fig.1c demonstrate the nanoparticles are organized in a loose manner. Selected area electron diffraction (SAED) pattern recorded on an individual Cu₂O porous sphere (inset in Fig.1c) reveals its polycrystalline character. All the diffractions can be indexed to the cuprite

Fig.1 Morphology and structure of the Cu₂O mesoporous spheres obtained in the presence of NH₃·H₂O (0.025 mol·L⁻¹)

(a, b) SEM images, (c) TEM image, (d) HRTEM images. The inset in Fig.1c is the SAED pattern of an individual sphere.

Cu₂O with JCPDS No. 77-0199. A typical high-resolution TEM (HRTEM) image taken from the edge of an aggregated particle is shown in Fig.1d. Evidently, the Cu₂O porous spheres are polycrystalline, and there is no specific orientation relationship among the grains. The observed interplanar spacing is about 0.24 nm (inset in Fig.1d), matching well with the distance between (111) planes of cuprite Cu₂O.

NH₃·H₂O is found crucial for the formation of the porous

structures. When NH₃·H₂O was substituted by the same amount of NaOH (0.025 mol·L⁻¹) while other conditions kept identical, nanospheres of about 250 nm dominated the products as shown in Fig.2a. The opening in the SEM images (inset in Fig.2a) and the obvious contrast between the edge and the center of the spheres in TEM observation (Fig.2b) indicate the hollow feature of the nanospheres. Although the surfaces of the spheres were quite smooth compared with the porous ones, it can be clearly observed that they were also composed by small particles. A typical SAED pattern taken from an individual hollow sphere (Fig.2c) shows discrete bright-elongated dots, which indicates the improved crystallinity and the oriented assembly of the primary nanoparticles in the hollow spheres.²⁷

When the concentration of NaOH was increased, the hollow spheres evolved into solid ones. Fig.2d shows the SEM image of the products achieved with the concentration of NaOH as 0.05 mol·L⁻¹. The surface of the spheres became much smooth and no small particles could be identified. TEM images provide the vivid evidence for their solid structure. SAED pattern demonstrates that the solid spheres are of single crystallinity.

Fig.3 shows the XRD patterns of the spheres with porous, hollow, and solid structure features, respectively. All the diffractions can be well indexed to the cuprite Cu₂O with JCPDS No. 77-0199 (Fig.3a). Obviously, the diffraction peaks experienced a sharpened process from porous to hollow and solid structures, which are believed to originate from the improved crystallinity and the enlarged crystal sizes as discussed above.

According to the experimental procedure, the reaction for the formation of Cu₂O involves the hydroxylation of Cu²⁺ into

Fig.2 Morphology and structure of the Cu₂O hollow and solid spheres obtained at the NaOH concentration of 0.025 and 0.5 mol·L⁻¹

(a, d) SEM images, (b, e) TEM images, (c, f) SAED patterns

Fig.3 XRD patterns of different structured Cu_2O

(a) standard XRD pattern of the bulk Cu_2O (JCPDS No. 77-0199),
(b) mesoporous spheres, (c) hollow spheres, (d) solid spheres

$\text{Cu}(\text{OH})_2$ and the subsequent reduction by Vc into Cu_2O following the equations (1) and (2):

The formation rate of $\text{Cu}(\text{OH})_2$, determined by the concentration of either Cu^{2+} or OH^- ions, would impact on the nucleation and growth process of Cu_2O , and eventually influence their morphologies and sizes.

Reports have demonstrated that PVP intends to coil into pseudo-spherical structures in solution,²⁴ which provide adsorption sites for Cu^{2+} ions driven by the elastic interaction between Cu^{2+} and carbonyl group. When NaOH was introduced, $\text{Cu}(\text{OH})_2$ rapidly precipitated. Since the OH^- contacted primarily with Cu^{2+} ions adsorbed on the surface of PVP, the precipitate preferred to form on the outsides of the PVP coils. The $\text{Cu}(\text{OH})_2$ cover prevented OH^- from further diffusing into the interior and thus hollow structures were preferred to form. The increasing concentration of NaOH and the high chemical potential would accelerate the diffusion of OH^- and thus reduce the hollow voids of the spherical structures.

Since the reduction from $\text{Cu}(\text{OH})_2$ to Cu_2O is fast, it is expected that *in situ* conversion would happen. As described earlier, when the concentration of NaOH was increased from 0.025 to 0.05 $\text{mol} \cdot \text{L}^{-1}$, the as-prepared Cu_2O transformed from hollow to solid spheres. To further verify the proposal, we conducted the experiments with the NaOH of 0.035 $\text{mol} \cdot \text{L}^{-1}$. As shown in Fig.S1 (Supporting Information), the diameters of the hollow interior are in the range of 30 to 60 nm, much smaller than those with NaOH concentration as 0.025 $\text{mol} \cdot \text{L}^{-1}$ (Fig.2a).

It is well known that in Cu^{2+} -containing aqueous solution, $\text{NH}_3 \cdot \text{H}_2\text{O}$ serves as both the complexing agents (Eq.(3)) and the OH^- producer by hydrolyzation (Eq.(4)),

Although in comparison with NaOH, the concentration of

OH^- is lower with $\text{NH}_3 \cdot \text{H}_2\text{O}$ as alkali source. The controlled release of Cu^{2+} by complexation would slow the formation rate of $\text{Cu}(\text{OH})_2$ and thus benefit the deep infiltration of OH^- ions. Therefore, hollow structures cannot be observed by using $\text{Cu}(\text{NH}_3)_4^{2+}$ as precursor.

Driven by the minimum surface energy, the freshly-formed adjacent Cu_2O nanoparticles intended to attach and fuse into each other. In fact, aggregation-based phenomena have been observed by many groups during their studies for nanocrystals^{28,29} since oriented-attachment was first proposed by Benfield *et al.*^{30,31} We believe that recrystallization competed and coworked with the attachment during the growth process. The main function of the crystallization was to remedy the defects resulted by the nanoparticle mergence. The higher OH^- concentration might accelerate the recrystallization process. As revealed by SEM observation (Fig.2), the surface of the nanospheres became more smooth and the crystallinity was gradually improved with the increase of the NaOH concentration. When the NaOH concentration was further increased to 0.4 $\text{mol} \cdot \text{L}^{-1}$, Cu_2O octahedrons were the exclusive products as shown in Fig.S2 (Supporting Information). The regular shapes indicate the highly crystallinity, which provide additional evidence for the OH^- promoted recrystallization process.

In the case of $\text{NH}_3 \cdot \text{H}_2\text{O}$ -involved system, the reaction follows the equations (5)–(7):

On the one hand, the release of NH_3 during the reaction might block the attachment of the nanoparticles. On the other hand, the lower OH^- concentration and the slowed releasing rate of Cu^{2+} greatly lowered the recrystallization process. Thus, the products exhibited as porous spheres assembled by tiny particles. The whole growth process is illustrated in Scheme 1.

Stimulated by the morphology-dependent properties, the Cu_2O nanocrystals with porous, hollow, and solid structures

Scheme 1 Illustration of the growth mechanism of the cavity-controlled Cu_2O shperes

Fig.4 (a) Response and recovery of the porous, hollow, and solid structures sensors upon exposure to 30×10^{-6} , 50×10^{-6} , 100×10^{-6} , 300×10^{-6} , 500×10^{-6} (ϕ) at the working temperature of 146 °C; (b) response upon different concentrations of NO₂ gas

were selected to evaluate the sensitive activities. Fig.4a shows the typical response-recovery curves of the three kinds of Cu₂O nanocrystal sensors towards NO₂ at a working temperature of 146 °C. The response is defined as the R_{air}/R_{NO_2} ratio, where R_{air} and R_{NO_2} are the resistance of the sensor in air and in NO₂, respectively. Obviously, the response of the porous spheres is much higher than those of the hollow and solid ones. For example, at the NO₂ concentration of 30×10^{-6} (ϕ), the porous spheres have a response of 6.8, while the responses are 2.7 and 1.4 for hollow and solid spheres, respectively. The responses of the sensors upon different concentrations of NO₂ gas are shown in Fig.4b. Along with the increase of the NO₂ concentrations, the response of the porous spheres significantly increases. It reaches about 23 with NO₂ as 500×10^{-6} (ϕ). It is noted that the prepared sensors have lower working temperature of 146 °C and possess high sensitivity compared with previous report.³²

It is well recognized that the sensing behavior of a gas sensor is extremely sensitive to grain size and surface conditions. The smaller grain size and higher surface area usually lead to better sensing properties. The sensing mechanism of metal oxide semiconductors involves an adsorption-desorption process in which the chemisorbed oxygen ions, such as O₂⁻, O⁻, and O²⁻, play a crucial role. Because the electrons of sensing materials are trapped by adsorbed oxygen species, a space charge region form on the surface of the metal oxides. When the *p*-type semiconductor oxide sensor is exposed to the oxidizing gas (NO₂), the adsorption of NO₂ on the sensing materials leads to dissociation to NO and O⁻ following the reaction $NO_2 + e^- \rightarrow NO + O^-$. The resultant O⁻ add up to the pre-adsorbed O⁻ that already existed at the surface, which will decrease the sensor resistance as a result of the enhanced hole concentration introduced by the surface reaction.

To get insight of the gas sensing mechanism, we measured the specific surface areas using the Brunauer-Emmett-Teller (BET) method. The measured surface areas of the mesoporous, hollow, and solid spheres are 46.85, 39.33, and 14.13 cm²·g⁻¹, respectively. It indicated that the surface area of the mesoporous spheres is just slightly larger than that of the hollow ones. We believe that the porous and loose structures of the mesopor-

ous spheres made the diffusion of NO₂ gas for detection and the oxygen for adsorption to both the inner and surface regions much easier, which will enhance the available active surface area and provide a great number of active sites. Thus, the higher response can be obtained. In comparison with the porous spheres, the dense surface of the hollow spheres would make the gas sensing reaction occur only near the surface region, while the inner part of the hollow spheres became inactive. The conductivity change near the surface region resulted in the lower gas response. The thickness of the hollow spheres is much thinner than the solid ones, the bulk interaction dominate the response of the solid spheres sensor rather than surface interaction. The modulation in the carrier concentration caused by the surface reaction has no obvious influence on the conductivity change of the sensors. This is why the solid spheres possess the lowest response towards NO₂.

To test the stability, we cycled the Cu₂O mesoporous sensor between air and NO₂ in N₂ ($I_{NO_2} : I_{N_2} = 1 : 10^{-4}$) for five times. As shown in Fig.S3a (Supporting Information), the on and off responses were stable with only a slight sensitivity deviation (< 1%). The response time, at which the sensitivity attains 90% of the stabilized value, is less than 80 s and the recovery time after the NO₂ was shut off is within 27 s, which is kept constant in the five cycles. It shows the good stability and reversibility of the Cu₂O sensor towards NO₂ gas.

Selectivity is another important parameter determining the gas sensing property. We also measured the response of the Cu₂O mesoporous spheres towards other common gas contaminants such as NH₃, methanol, ether, acetone, etc. with the gas concentration kept as $I_{NO_2} : I_{N_2} = 1 : 10^{-4}$. No stable signal was detected under the conduction temperature of 146 °C. Then, we elevated the temperature to 200 °C. As shown in Fig.S3b (Supporting Information) the response is all smaller than 2.4, about 6.5 times lower than that towards NO₂. It indicates that the products possess excellent gas sensing selectivity.

4 Conclusions

Cu₂O nanocrystals were successfully controlled as porous, hollow, and solid spheres by simply adjusting the concentra-

tion of OH^- and the releasing rate of Cu^{2+} . The formation of Cu_2O nanostructures is believed experienced three stages: (1) the formation of $\text{Cu}(\text{OH})_2$ by the reaction of OH^- with Cu^{2+} ions adsorbed on the PVP coils; (2) the *in situ* reducing of $\text{Cu}(\text{OH})_2$ into Cu_2O nanostructures; (3) the attachment and recrystallization of Cu_2O nanoparticles. The diffusion kinetic of OH^- played crucial roles for the construction of different structures. In the growth process, the higher OH^- concentration facilitated the recrystallization process. The gas sensing experiments exhibited that the porous Cu_2O spheres offered much higher sensitivity than the hollow and solid counterparts at low working temperature. It demonstrated that the Cu_2O mesoporous spheres have promising applications in the low working temperature gas sensors.

Supporting Information: available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

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孔隙结构可调的 Cu₂O 球状纳米结构及其 NO₂ 气体传感性质

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Cavity-Tunable Cu₂O Spherical Nanostructures and Their NO₂ Gas Sensing Properties

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Fig.S1 TEM image of the products obtained with the concentration of NaOH as $0.035 \text{ mol}\cdot\text{L}^{-1}$

Fig.S2 TEM image of the products obtained with the concentration of NaOH as $0.4 \text{ mol}\cdot\text{L}^{-1}$

Fig.S3 (a) Five cycles by modulating the mesoporous Cu_2O nanospheres between air and NO_2 in N_2 ($V_{\text{NO}_2}:V_{\text{N}_2} = 1 : 10^{-4}$), (b) sensitivity of the mesoporous Cu_2O nanospheres towards different gases with concentration as 10^{-4} (V/V)