Temperature-Controlled Synthesis of Porous CuO Particles with Different Morphologies for Highly Sensitive Detection of Triethylamine

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Supporting Information

ABSTRACT: Because porous metal oxides with controllable morphologies have been attracting much attention for their potential applications in the fields of adsorption/separation, sensing, energy storage, and conversion, it is highly desirable to prepare new morphology of metal oxides and investigate their performance. In this work, CuO particles with different shapes such as octahedron, sponge-like octahedron, and sphere have been synthesized through thermal decomposition of crystalline Cu(II)−organic frameworks (HKUST-1). The structure and morphology of as-prepared CuO particles have been fully characterized by the usage of XRD, XPS, SEM, and TEM. The gas-sensing behaviors of these CuO samples have been investigated and our results show that CuO-400 with spherical shape displays unprecedented high response (maximum value, 102) for triethylamine (TEA) at 100 ppm with a low detection limit of 5 ppm, a lower working temperature (230 °C), excellent reproducibility, and long-term stability. The highly sensing behavior of CuO-400 sphere might be due to its special structural factor with many open active sites for oxygen adsorption, which could react with TEA molecules more efficiently. Our results clearly suggest that porous CuO particles should be promising candidates for future practical application to detect TEA vapor at relatively low temperature.

INTRODUCTION

Triethylamine (TEA) not only has been considered as an important raw material for industrial organic synthesis but also has been widely used as preservatives, catalysts, synthetic dyes, and energy fuels.1,2 Besides these, TEA can also generate from microbial degradation of triethylamine N-oxide during the deteriorating of dead fish and marine organisms. As such, TEA has been widely employed as one of effective indicators to assess the freshness of fish and seafood. Furthermore, TEA has also been known for a long time to irritate the eyes and skins, which further result in acute diseases such as pulmonary edema or even death.3–5 Due to its potential hazards to human body, the threshold limit of TEA concentration is 10 ppm on volumetric basis decided by National Institute for Occupational Safety and Health (NIOSH).6 It is well-known that many metal oxide semiconductors sensors such as SnO2, TiO2, and their composites show response to TEA (Table S1). However, relatively high working temperature and lower sensitivity are required to be improved. Generally, the microstructures and morphologies of metal oxides are crucial factors for gas sensing selectivity, sensitivity, and working temperature. Typically, CuO is a p-type semiconducting material (bandgap 1.2 eV) and has many potential applications including magnetic storage media, solar cells, catalyst, gas sensor, and supercapacitors.7–9 Many excellent methods have been established for the fabrication of CuO nanostructures with various morphologies including nanosheet, nanofibers, nanospheres, nanoflowers, nanoslices, and nanowires.7–10 Prior works have already reported that CuO nanostructures with different morphologies display efficient sensing behaviors to detect different types of toxic or combustible gases, including hydrogen sulfide, acetone, carbon...
monoxide, ethanol, ammonia, and so on (Table 1). However, no exploration has been reported on pure CuO nanomaterials for the detection of TEA, although only one case\(^1\) mentioned that CuO/ZnO hybrid nanorods could show a good response to TEA at 50 ppm level under 40 °C.

Recently, MOFs (metal—organic frameworks) have been widely employed as important precursors to fabricate many different types of porous carbon/metal/metal oxide nanostructures (M/MONs) via thermal decomposition under controlled atmospheres\(^1\) because these as-obtained materials have several important factors including different compositions, morphologies, and diverse structures, which make them desirable for potential applications in lithium-ion batteries, gas sensor, solar cells, hydrogen production, supercapacitors, and super adsorbent material.\(^1\) For example, Li et al.\(^1\) fabricated high purity porous Co\(_3\)O\(_4\) concave nanocubes for the detection of ethanol through calcining ZIF-67 at a certain temperature. Li et al.\(^1\) obtained a unique hierarchical ZnO nanocage for the detection of acetone by direct temperature-programmed decomposition of MOF-5. However, diverse CuO/CuO\(_2\) nanoparticles derived from Cu—MOFs have been observed,\(^1\) and the as-prepared materials displayed some promising properties such as CO oxidation, lithium-ion batteries, and sensing properties. Unfortunately, until now, a systematic study on the morphology control of these materials under calcination conditions is lacking. Such gap strongly motivates us to systematically investigate this type of material.

Here by controlling calcination conditions, octahedral, sponge-like, or spherical CuO materials were readily obtained through thermal decomposition of octahedra Cu-MOF (HKUST-1). Remarkably, the as-synthesized CuO-400 sphere nanomaterial exhibits high sensitivity to TEA with a very low detection limit, a lower working temperature, high reproducibility, and steady stability. To the best of our knowledge, this is first CuO sensor derived from MOFs template, which shows high sensitivity to TEA.

### RESULTS AND DISCUSSION

#### TGA Measurements

The TGA was conducted to investigate the thermal stabilities and determine the calcination temperature for HKUST-1 materials. As shown in Figure 1b, a weight loss of 70% was observed before 370 °C suggesting that large amounts of CO\(_2\) or H\(_2\)O were released during the thermal decomposition process of MOFs. Three stages of mass loss can be seen in Figure 1b: one occurs at temperature below 320 °C, which is attributed to the loss of physically absorbed H\(_2\)O and DMF molecules. Selecting 300 °C as calcining temperature for 5 h, CuO-300 sample with octahedron shape can be obtained in this stage. The next stage for mass loss (about 40% weight loss) appears from 320 to 370 °C. Employing 350 °C as calcining temperature for 5 h, the sponge-like CuO-350 sample can be ready obtained. Since the weight loss in last stage (starting at 370 °C) is not obvious, we tried different calcining temperatures such as 400, 450, and 500 °C to complete the decomposition of HKUST-1 precursors. As shown in Figure 1a, if system temperature reaches or overpasses the decomposition temperature of HKUST-1, the guest molecules or organic ligands in HKUST-1 are released or burned away in air to generate CO\(_2\), H\(_2\)O, or NO\(_x\), while Cu(II) ions will be converted into CuO with different morphology through reacting with O\(_2\).

#### Formation Mechanism of CuO Products

The morphologies of the as-obtained materials at various calcination temperatures are shown in Figure 1a, which are confirmed by SEM images (Figure 2 and Figure S1). According to TGA results, below 320 °C, different types of solvents in the pores almost have no effect on the decomposition temperature, and the as-synthesized HKUST-1 crystalline sample could maintain its framework at this stage,\(^2\) which can explain why the octahedron CuO-300 has similar morphology to that of the precursor HKUST-1. During heating stage at 300 °C in air, some carbon formed to protect frameworks from the further contraction. Note that these carbons can be removed through oxidation to generate porous CuO materials during the annealing step. Such precise control of the shape, size, and chemical composition of nanocrystal structure not only allows to study their unique properties but also is helpful to finely tune
their physical and chemical properties.\textsuperscript{23} When the calcination temperature increased, the frameworks of HKUST-1 collapse to form sponge-like CuO materials (Figure 2d and Figure S1). Such formation might be owing to the existence of different facets and pore sizes of HKUST-1 as well as the faster releasing rates of decomposed gas composing stage I. Interestingly, when the calcination temperature reaches $\sim 400$ °C, the morphology of CuO products evolved from sponge to sphere. Further gradually increasing temperature leads to the collapse of sphere CuO structure and forms an irregular morphology. The SEM images of CuO-450 and CuO-500 are shown in Figure S1g–i.

The general reaction process can be described through the following equation:

$$\text{[C}_{18}\text{H}_6\text{Cu}_3\text{O}_{12}]_n + \text{O}_2 \rightarrow \text{CuO} + \text{CO}_2 \uparrow + \text{H}_2\text{O} \uparrow$$

**Morphological and Structural Characteristics.** Figure 2 shows the typical morphologies and microstructures of CuO particles derived from HKUST-1 precursors. The uniform HKUST-1 octahedron particles were synthesized at room temperature according to the reported procedure.\textsuperscript{24} A subsequent thermal transformation process was introduced to convert Cu-MOFs into CuO particles with different shapes. Generally, the size of CuO-300 (4 $\mu$m) is smaller than that of CuO-350 (12 $\mu$m). The size of sphere CuO-400 is only 1 $\mu$m as shown in Figure 2h.

High-resolution TEM suggests that the lattice interplane distances of CuO-300 sample are 0.267, 0.31, 0.255, and 0.215 nm, which can be assigned to the (202), (202), (112), and (111) interplane spacing of monoclinic crystal phase of CuO (Figure 3a). The selected electron diffraction (SAED) confirms that monocrystalline CuO particles have octahedra structure, and the discrete diffraction cycles can be assigned to (202) and (111) crystal planes of CuO (Figure 3d). The selected area electronic diffraction and high-resolution TEM of other two CuO samples are shown in Figure 3b–f. The phase composition and the purity of the as-prepared CuO samples have been characterized by powder X-ray diffraction (XRD). Figure S2 shows the XRD patterns of HKUST-1 crystallite, while the diffraction peaks of the five as-synthesized CuO samples could be perfectly indexed as CuO (JCPDS card No. 48-1548), which not only is in agreement with the above-mentioned assignments in SAED cycles but also indicates their high purity (Figure 4).

XPS was applied to identify the surface chemical compositions and element analysis of CuO-400.\textsuperscript{25} In the survey area (0–1200 eV), elements C, O, and Cu are investigated to coexist in the same material (Figure 5a). The peaks at 933.9 eV (Cu 2p$^3/2$) and 953.6 eV (Cu 2p$^1/2$) are contributed from Cu. This result is higher than the peak positions for Cu (0) metal, which suggests that Cu has been oxidized (Figure 5b). The oxidation state of CuO can be further confirmed by two satellite peaks at 943.8 and 962.4 eV. Additionally, the C(1s) spectrum displays three peaks at 284.5, 285.5, and 288.2 eV in CuO sample, which can be assigned to C−C, C−O, and C≡O, respectively (Figure 5c). Although CuO-300 and CuO-350 samples give the high peak intensities of C−O and C≡O as shown in Figures S3 and S4, these peak intensities in XPS spectra tremendously decrease with the

![Figure 2](image2.png)

Figure 2. (a) SEM images of HKUST-1 precursors. (b,c) SEM images of the as-prepared CuO-300. (d–f) SEM images of the as-prepared CuO-350. (g–i) SEM images of the as-prepared CuO-400.

![Figure 3](image3.png)

Figure 3. HRTEM image, lattice distance, and SAED pattern of (a,d) CuO-300, (b,e) CuO-350, and (c,f) CuO-400, respectively.
increase of calcination temperature. All these results reveal that most of the oxygen-containing functional groups are successfully removed after calcination. Finally, The O 1s peak at 530.5 eV matches the oxygen species in CuO (Figure 5d). The O 1s peaks at 531.4 and 532.6 eV can be identified as oxygen vacancy (OV) and adsorbed oxygen. Hence, the as-synthesized CuO products should be CuO compounds.

N₂ adsorption–desorption isothermal was used to evaluate surface factors of the as-prepared CuO particles (Figure 6). The as-measured surface areas of five CuO products (octahedral, sponge-like, spherical CuO, CuO-450, and CuO-500) are 6.644, 9.640, 20.912, 10.304, and 7.1889 m²/g, respectively. The BJH method has been used to determine pore size distributions from the desorption branch of the isotherm (Figure 6, the inset). The octahedral CuO-400 has two pore size distributions with the maximum peaks at 2 and 20 nm, which favors mass transportation. In addition, the maximum peak of pore size distributions for the sponge-like CuO-350 is at 12 nm, while the peak for the spherical CuO-400 is at 20 nm. By comparison, CuO-400 has a larger surface area than other samples, which may contribute positively to the sharp leap as gas sensors.

**Gas Sensing Properties of CuO Products.** CuO has been widely used in humidity sensing, lithium-ion batteries, CO₂ photoreduction, and gas sensors (Table 1). Key factors to be considered in optimizing the performance and utility of chemical sensors are response time, sensitivity, selectivity, reusability, and stability. In order to prove the possibility of CuO particles as gas sensors, different CuO samples abstained from different calcination temperature have been tested for comparison. It is well-known that the response of a chemiresistor-type gas sensor strongly depends on the working temperature. Thus, the responses to diverse gases (formaldehyde, acetone, ether, or triethylamine) at 200 ppm as the function of temperature have been investigated to obtain the optimized operational temperature. As shown in Figure 7a, the responses of all sensors remarkably changed with the variation of the working temperature, and generally, higher working temperature gave poor responses. Taking CuO-300 as an example, the optimized operating temperatures for sensing formaldehyde, ether, acetone, and trimethylamine are 230, 240, 240, and 230 °C, respectively. Although high temperature could lead to the short response/recovery time due to the higher diffusion and adsorbed rate of gas molecules as well as quick reactions between TEA vapor and oxygen adsorbed on the surface, the low concentration of the adsorbed O₂ will result in the decreased responsivity. Thus, from Figure 7b, it is easy to conclude that all responses of CuO-300 samples arise with the increasing temperature at the first stage and will approach its peak (about 20) at ∼230 °C. After passing this temperature, a little bit of a decrease can be seen, suggesting that there exists an optimized working temperature.

There responses of the four CuO products was also investigated (Figure S5b–i). Intriguingly, the CuO-400 sensor showed the maximum responsibility (102) at 230 °C (Figure S5d), which might be attributed to the particles size, the special surface area, and the porosity of the as-prepared CuO-400 materials. These factors eventually have a big effect on the adsorption, the diffusion, and the desorption of gas molecules, and finally affect the optimized working temperature as well as the oxygen state. Comparably, the response sensitivity of CuO-400 sensor is almost double comparing with that of TiO₂/ SnO₂ nanosheets for sensing TEA under the same concentration, while, the working temperature for CuO-400 is lower.
than that of TiO$_2$/SnO$_2$ nanosheets$^{36}$. Based on the above considerations, we choose 230 °C as our working temperature to compare the selectivity of different gas sensors at a concentration of 200 ppm (Figure 8a). Surprisingly, the CuO-400 sensor possesses excellent selectivity to TEA in comparison to other tested gases, which strongly suggest that the mesoporous morphology of CuO-400 sample have great effect on their gas-sensing behaviors. To further study its stability, three successive sensing tests in 100 ppm TEA were performed on the as-prepared CuO-300 sensor. As is shown in Figure 8b, the original sensitivity and reproducibility of CuO-300 samples have been maintained without an obvious decrease.

Additionally, we systematically investigated the sensing performance of five CuO samples and commercially available CuO particles. Compared with commercially available CuO sample, the gas sensor performance of five CuO materials is much better than that of the commercially available one, not only in the responses to TEA but also in the reproducibility and stability. In order to further understand the relation between the concentration variation of TEA and the response ability of six CuO samples, dynamic responses at 230 °C have been conducted. From Figure 9, one can easily find that the response is nearly close to the baseline level when the CuO-300 sensor is exposed to air. However, when it is exposed to TEA vapor, the response reaches a maximum value, which suggests that CuO-300 sensor has an excellent response to TEA vapor. The evidence is that the resistances of the tested CuO samples increased when the analytic gases was reduced. As indicated in the inset curve, a monotonous responsiveness is suggested because the response increases with the increased concentration. Especially in a lower concentration (from 5 to 100 ppm, Figure 9, inset), the relationship between the concentration and the responsibility is almost linear. The responsivity of other six CuO samples to different concentration of TEA at 230 °C have also been conducted (Figure S6), and these results clearly suggest that these samples also can be served as sensors to detect TEA. Their sensitivity is five times better than that of...
pure brick-shaped SnO$_2$ material under same concentration of TEA.$^{37}$

The response—recovery feature of gas sensors is an essential parameter, which is determined by temperature-dependent reaction kinetics including the amount of the adsorbed gas and the reaction speed between O$_2$ and gases.$^{35}$ According to literature, the response—recovery time of one sensor to 100 ppm of gas is defined as the time required to reach 90% of the final equilibrium value.$^{35}$ As shown in Figure 10, although the response time is very rapid, the recovery time is relatively longer, which needs to be further improved in the future. For the comparison with different CuO samples in triethylamine vapor (100 ppm), the recovery times are 80, 103, 150, 200, and 256, respectively (Table 1). As for the CuO-400, the fast response time might come from the loose surface as well as its uniform sphere structure, which is helpful to the mass transport and gas diffusion.

Because the stability is another crucial property for a gas sensor, we conducted the explosion of CuO-400 samples to 100 ppm TEA atmosphere at 230 °C for every 7 days. Strikingly, the gas response (during 30 days) shows a slight decrease from 102 to 86.4 (Figure 11), which indicates its long-term stability and excellent reproducibility.

**Sensing Mechanism.** As a typical p-type semiconducting oxide, the sensing mechanism of CuO has been explained in detail through the changes of its conductivity caused by the reaction between the detected gas and the surface-adsorbed oxygen.$^{8,10,29,30,33}$ This mechanism can also be applied in our system. As presented in Figure 12a, when the surfaces of p-type CuO mesospheres are exposed in air, O$_2$ will be adsorbed on the surface of CuO gradually. Then, one electron in the conductive band of CuO will be captured by the adsorbed O$_2$, which leads to the changes of O$_2$ into O$_2^-$ and O$_2^{2-}$ ionic species through electron transfer; at the same time, one hole will be produced in CuO samples, which results in the variation of the conductivity of CuO sensors.

Similarly, when the surfaces of p-type CuO mesospheres is exposed in TEA vapor (Figure 12b), a virtual reaction occurs between O$_2^-$ and TEA and some holes will be consumed, which results in the change of electrical conductivity of CuO samples; at the same time, the reaction products including N$_2$, CO$_2$, and H$_2$O will be released into the air. Furthermore, more negatively charged oxygen ions on the surface can result in the formation of hole accumulation layer (HAL), which further decrease the resistance of sensors.$^{38}$ The overall reaction can be described with the following equations:

\[
\begin{align*}
O_2^{\text{(free state)}} & \rightarrow O_2^{\text{(adsorbed state)}} \\
O_2^{\text{(adsorbed state)}} & \rightarrow O_2^-^{\text{(adsorbed ionic state)}} + h^+ \quad (h^+\text{represents hole}) \\
O_2^-^{\text{(adsorbed ionic state)}} & \rightarrow 2O_2^{2-}^{\text{(final adsorbed ionic state)}} + 3h^+ \\
N(C_2H_5)_3 + O_2^{2-} + 2h^+ & \rightarrow N_2 + H_2O + CO_2
\end{align*}
\]

Through the above process, one can conclude that the surface reactions play a key role to determine the gas-sensing process. Moreover, oxidation catalytic activity is also strongly determined by the morphologies of metal oxides. Obviously, larger surface area will provide the high sensitivity of metal oxides because these materials can provide large reaction-contacting area.$^{37}$ Also, the sensitivity can be enhanced by the usage of particles with small mesosphere size.

**CONCLUSION**

A series of mesostructure CuO with different morphologies have been successfully synthesized through thermal decomposition of HKUST-1 at different temperatures. The as-prepared particles have been innovatively applied as gas sensors. These materials exhibited high sensitivity and selectivity to TEA vapor, good reproducibility, and long-term...
stability as well as a low working temperature (~230 °C). Note that the sensitivity strongly depends on the morphology of materials, proper pore distribution, and surface area. Our research clearly not only provides a promising method to prepare novel porous metal oxides with MOFs as templates but also demonstrates that porous metal oxides can be acted as a potential platform to detect TEA vapor during industrial processes and fish-processing industries.

### ASSOCIATED CONTENT

- **Supporting Information**
  
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.7b00102.

  Experimental section, table, PXRD curve, SEM images of the CuO, XPS spectra, response—recovery curve, linear dependence of response curves (PDF)

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**Notes**

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### REFERENCES