

Phys. Status Solidi A, 1600904 (2017) / DOI 10.1002/pssa.201600904



Facet-dependent gas sensing properties of Cu₂O crystals

Zheng Xie^{1,2}, Ning Han^{*,2,3}, Wenhui Li², Yuzhou Deng², Shuyan Gong², Ying Wang², Xiaofeng Wu², Yingxia Li^{**,1,2}, and Yunfa Chen^{2,3}

¹ State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, North Third Ring Road 15, 100029 Beijing, P.R. China

² State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, North Second Street 1, 100190 Beijing, P.R. China

³ Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Jimei Avenue 1799, 361021 Xiamen, P.R. China

Received 28 November 2016, revised 6 February 2017, accepted 6 February 2017 Published online 28 February 2017

Keywords catalysis, crystal facets, Cu_2O, gas sensing, surfaces, work function

* Corresponding author: e-mail nhan@ipe.ac.cn, Phone:+86-10-82544896, Fax: +86-10-62525716

** e-mail liyx@mail.buct.edu.cn, Phone/Fax:+86-10-64419619

Well-defined polyhedral Cu₂O exposing different crystal facets are synthesized via a facile solution-phase method, and the facet-dependent gas sensing properties are investigated. The results show that cubic Cu₂O exposing (100) facets has higher sensitivity to NO₂, acetone and benzene than octahedral Cu₂O with (111) facets. More importantly, the cubic Cu₂O has high selectivity to NO₂ and acetone at varied working temperatures by different sensing mechanisms of adsorption, chemical reaction, and intrinsic carrier excitation, as verified by the catalytic and electric property measurements. The higher sensitivity and selectivity of cubic Cu₂O is explained by the relatively lower work function of (100) surfaces than that of (111), which induces a thicker surface hole accumulation layer and thus, a higher bulk hole activation energy (0.55 eV and 0.36 eV respectively). The synergistic

effect of catalytic and electric properties gives rise to gas sensitivity decrease with the reduced percentage of (111) facets, which is beneficial to the gas sensing material design and also, is promising for the future highly sensitive and selective gas sensor fabrication.



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1 Introduction In recent years, indoor air pollution has aroused high attention due to its huge damage to people's health, such as headache [1, 2], fatigue [3], sick building syndrome [4, 5], and even cancer [6]. Metal oxide semiconductor (MOX) gas sensor is believed to be one of the most feasible detection methods because of its real-time detection and low cost [7]. As there are stringent permissive levels of the air pollutant, it is necessary for the MOX sensors to have high sensitivity. After years of development, there are several strategies established to design and synthesize highly sensitive MOX materials, with an aim to tailor the surface properties of the sensing materials. For

example, hierarchical structure design, doping by other atoms, and forming heterojunctions are all effective at enhancing the sensitivity of the oxide sensing material (e.g., SnO_2 and ZnO) by enhancing the surface interaction of the gas and the sensing materials [8–10].

On the other hand, the surface properties are also highly dependent on the exposed surface planes due to the difference in atom numbers and arrangement. Facet-dependent physical and chemical properties, such as electronic [11–13] and catalytic [14–16] properties, of polyhedral inorganic nanocrystals have caused widespread concern in recent years. Taking polyhedral Cu₂O for



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example, the (100) facets on cubes are reported to have lower electron work function than the (111) ones on octahedra [17, 18], while photocatalytic oxidation activity of (111) is higher than (100) due to the unique copper atom alignments [19, 20]. Though Cu₂O is also widely used as gas sensors because of its intrinsic p-type property, such as Cu/Cu₂O hollow spheres [21], CuO/Cu₂O composite nanowires [22], porous Cu₂O/CuO cages [23], Cu₂O nanocages [24], the relationship of the facet-dependent physical and chemical properties is not well investigated, though it is essential because gas sensing property is related to electrical resistance change caused by surface chemical catalytic reaction.

In the literature, ZnO sensing materials with different exposed planes have varied interaction properties with both NO₂ and ethanol and thus, have different sensing performances [25, 26]. In this study, (100) and (111) exposed well-shaped cubes (C), truncated cubes (TC), truncated octahedra (TO), and octahedra (O) are synthesized, and the gas sensing properties are investigated in detail taking typical air pollutants NO₂, acetone and benzene as probes. The results show that C-Cu₂O has the highest sensitivity to NO₂, acetone and benzene compared with other shapes, due to the different adsorption and catalytic properties of the facets. And more importantly, the gas sensing maxima are obtained at distinguishingly different working temperatures showing the good selectivity to NO₂ and acetone. These results highlight the compromise of the facet-dependent physical and chemical properties, and are promising for gas sensor developments.

2 Experimental

2.1 Synthesis of polyhedral Cu₂O Cu₂O with four morphologies were synthesized according to the literature [27] via a facile solution-phase method of analytical purity $Cu_2SO_4 \cdot 5H_2O$ (Xilong Chemical Reagent Co. Ltd., China), C₆H₅Na₃O₇ · 2H₂O, Na₂CO₃, $C_6H_{12}O_6 \cdot H_2O$ (Beijing Chemical Reagent Co. Ltd., China), and PVP (Sigma-Aldrich Co., USA). In a typical procedure, 1 mL 0.68 M Cu₂SO₄ · 5H₂O solution was diluted into 17 mL distilled water, and then 0.2 g PVP (K-30, Mw = 40000) was added into the solution. After being stirred with a magnetic blender for about 15-20 min at room temperature, a clear light blue solution was obtained naturally. In the meantime, 1 mL 0.74 M $C_6H_5Na_3O_7 \cdot 2H_2O$ and $1 \text{ mL } 1.2 \text{ M } Na_2CO_3$ were mixed evenly, which was then dropped into the clear light blue solution slowly under stirring constantly. The light blue turbid emerged at first stage and then transferred into clear dark blue solution, with no precipitate observed eventually. After about 10 min, 1 mL 1.4 M $C_6H_{12}O_6 \cdot H_2O$ was slowly dropped into the solution, which was then kept in a water bath at a temperature of 80 °C for 2 h, and then cooled down to room temperature naturally. The brick red precipitate was washed several times with distilled water and absolute alcohol, and separated out by centrifugation at 4000 rpm for 10 min, and finally dried in a vacuum oven at 80 °C for 6 h. Future experiments were also conducted at the same conditions except for changing the mass of PVP (0.2, 0.6, 1.0, and 3.0 g for C, TC, TO, O-shaped Cu_2O).

2.2 Characterization The crystalline phase was determined by X-ray powder diffraction (XRD, Panalytical X'pert Pro, The Netherlands, Cu K_{α} radiation of $\lambda = 0.15406$ nm, 40 kV, 30 mA). The morphologies and microstructures were characterized by a field-emission scanning electron microscope (FE-SEM, JEOL JSM-6700F, Japan 5 kV, 10 μ A) and a transmission electron microscopy (TEM, JEOL JEM-2010F, Japan, 200 kV, 100 μ A). UV-Vis absorption spectra were recorded using a spectrophotometer (Persee, TU-1901, China).

The gas sensing properties of Cu₂O with four morphologies were examined by using a homemade tubefurnace sensor test instrument, similar to our previous report [28, 29]. Briefly, two Pt wires $(0.5 \text{ mm} \times 1 \text{ m})$ were fixed on an Al₂O₃ substrate $(1 \times 2 \text{ cm}^2)$ by using a certain amount of Ag paste (Wuhan Youle Optoelectronics Technology Co., Ltd., China), which was annealed at 550 °C for 30 min in the tube furnace to make good adhesion. After that, 20 mg as-synthesized Cu₂O was ultrasonically dispersed into 2 mL ethanol and drop-coated on the Al₂O₃ substrate to form a sensor prototype. Then the sensor was placed in the tube furnace and aged at 200 °C for 24 h to ensure good ohmic contact (Fig. S1). The targeted gases with a series of concentrations from 1 to 10 ppm for acetone and benzene, 0.5-5 ppm for NO₂ were mixed with synthetic air (21.0 vol.% O2, 79.0 vol.% N2) and standard gas (49.8 ppm for benzene, 52.4 ppm for acetone, 48.4 ppm for NO₂ in synthetic air, respectively, Beijing Hua Yuan Gas Chemical Industry Co., Ltd., China) controlled by two digital mass flow controllers at a total flow rate of $300 \text{ mL} \cdot \text{min}^{-1}$. The bias on the sensor was 5 V and the current was recorded by using Keithley 2601 Sourcemeter (Keithley Instrument Inc., USA) with accuracy of $<\pm 0.1\%$. The sensor responses to benzene and acetone are defined as the ratio of sensor resistance in target gas and in air (Rg/Ra), while that for NO_2 is defined contrarily (Ra/Rg).

The catalytic activity evaluation of C-Cu₂O and O-Cu₂O was carried out in a continuous-flow fixed-bed quartz microreactor at a high space velocity (SV) of $60,000 \text{ mL} \cdot \text{g}^{-1} \cdot \text{h}^{-1}.$ The Cu_2O catalyst (50 mg, 40-60 mesh) was mixed with quartz sands (250 mg, 40-60 mesh) at a ratio of 1:5 and loaded in the quartz microreactor with quartz wool packed at both ends of the catalyst bed. Typically, the target gas with a composition of 50 ppm acetone or benzene in synthetic air was introduced into the reactor at a flow rate of $50 \,\mathrm{mL} \cdot \mathrm{min}^{-1}$. A gas chromatograph (Shimadzu GC-2014) equipped with a flame ionization detector (FID) was used to analyse the final products in the effluent gas. The concentration of CO₂ in the outlet gas was detected by another FID with a Ni conversion furnace for converting CO₂ to CH₄. The conversion of acetone or benzene was calculated as $(C_{\rm in} - C_{\rm out})/C_{\rm in}$, and CO₂ yield was calculated as $C_{CO2}/(C_{in} \times n)$, where C_{in} and

 C_{out} are the concentrations in the inlet and outlet, and *n* is the carbon numbers of acetone or benzene molecule.

3 Results and discussion

3.1 Morphology evolution and characterization of Cu₂O Generally, the kinetics and thermodynamics have been known as the key factors in controlling the crystal growth [30], the crystals with different morphologies can be obtained by adjusting the experimental parameters, such as reaction temperature [31], reaction time [20], concentration of the reactants [32] or surfactant [33], and so on. In this paper, the amount of PVP was selected as unique experimental variable to tune the morphologies of Cu₂O. Firstly, C-Cu₂O was obtained at 80 °C for 2 h using 0.2 g PVP as FESEM images and particle size distribution statistics shown in Fig. S2a. It is obvious that these particles are well-defined cubes with sharp edges and uniform shape. Meanwhile, it can be clearly seen that the particle is mainly composed of six (100) planes and the average edge length is measured to be about 0.66 µm according to the statistics of 100 C-Cu₂O particles. Further characterization by TEM (Fig. 1a) found that C-Cu₂O particle exhibited a square pattern with high symmetry, and the corresponding selected area electron diffraction (SAED) pattern reveals that it is a single-crystal structure with exposed (100) facets (Fig. 1a, insert). TC-Cu₂O could be acquired as shown in Fig. S1b when the amount of PVP is increased to 0.6 g. It can be clearly seen that eight corners of the particles are truncated to form eight triangles on these cross sections. The edge length of TC-Cu₂O with six (100) facets and eight (111) facets is 1.03 µm and has a narrow size distribution as shown in the insert pattern of Fig. S2b. The particles exhibit



Figure 1 The TEM images of different morphologies Cu_2O , (a) C-Cu₂O, (b) TC-Cu₂O, (c) TO-Cu₂O, (d) O-Cu₂O and the insets are their corresponding SAED patterns.

hexagons in TEM as shown in Fig. 1b inferring that the products align along the (111) direction normal to the substrate [27]. The corresponding SAED pattern indicates that they are single-crystal structure (Fig. 1b, insert). Further increasing PVP amount to 1.0 g, TO-Cu₂O was obtained as shown in Fig. S2c, the six corners of the particles look like being cut a bit from a octahedral and thus lead to form a truncated octahedral with six (100) facets and eight (111) facets. It is noteworthy that the sizes of the particles increase from 1.03 µm of TC-Cu₂O to 1.31 µm, and meanwhile, the particles still have a narrow size distribution. A dodecagon with two unequal adjacent lengths has been exhibited in the TEM of TO-Cu₂O as shown in Fig. 1c, the corresponding SAED pattern reveals that they are single-crystal structure (Fig. 1c, insert). Fully developed O-Cu₂O can be obtained when the amount of PVP increased to 3.0 g. From the SEM image in Fig. S2d, it can be seen that the Cu₂O particles have almost perfect octahedral morphology with 12 well-defined edges and 6 sharp corners without truncating, and the length of the octahedra is 1.49 µm with a narrow size distribution. Corresponding TEM pattern as shown in Fig. 1d exhibits a hexagon with a high symmetry, and meanwhile, SAED pattern indicates that the obtained O-Cu₂O is a single-crystal structure (Fig. 1d, insert).

The crystal structures of products synthesized at different conditions are examined by XRD as shown in Fig. 2a, which reveal that all Cu₂O particles belong to cubic phase (Cu₂O PDF 00-005-0667) without any impurity, such as copper and cupric oxide. Obviously, the strong and sharp peaks indicate that obtained Cu₂O particles are with high crystallinity. To further explore the bandgaps of the products, UV-Vis absorption spectra of Cu₂O with different morphologies are measured as shown in Fig. S3, where a broad absorption bands is clearly seen ranging from 500 to 650 nm. According to Tauc equation, bandgaps are calculated from the plots of $(\alpha h\nu)^2$ versus $h\nu$ curves of UV-Vis absorption spectra (Fig. 2b), indicating that the band gaps decrease from 2.0 to 1.9 eV with the percentages of (100) plane diminishing, that is the morphology of Cu₂O transfer from cube to octahedral, in good accordance with the literature [34, 35]. To confirm PVP on the Cu₂O surface have been removed clearly, the TG curves of C-Cu₂O and O-Cu₂O were carried out as shown in Fig. 2c. From the figure, weight loss observed in O-Cu₂O-six and not in C-Cu₂O-six for the major weight loss around 400 °C as revealed which can be attributed to normal thermal decomposition of PVP [36], meanwhile, it can be seen that the weight loss disappeared in O-Cu₂O-ten when the numbers of ultrasonic treatment increased to ten. The above results reveal that ten times ultrasonic washing could remove the adsorbed PVP on the Cu₂O crystal surface and exclude the impact on performance of Cu₂O facets.

3.2 Growth mechanism of Cu_2O As for the reaction process, the initial polyhedral Cu_2O particles evolve into Cu_2O with different morphologies as a result of anisotropic growth of the polyhedral particles, due to the



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(a)

(b)

Intensity(a.µ.)



 $(ahv)^2 (eV \cdot cm^{-1})$ **Ĭ.6** 2.8 2.0 2.4 hv (eV) (c) O-Cu2O six wash 110 Cu2O six wash 108 O-Cu2O ten wash Mass (%) 106 104 102100 98 200 400 600 800 Temperature (°C)

Figure 2 The XRD patterns (a) and the tangent pattern of UV-vis absorption spectra (b) for C-Cu₂O, TC-Cu₂O, TO-Cu₂O, O-Cu₂O (PDF 00-005-0667), and TG curves (c) for C-Cu₂O and O-Cu₂O with varied washing times.

different surface energies of varied planes [37]. In this paper, PVP, is a surfactant that may have two roles. One is to prevent the aggregation of the Cu₂O particles and the other is to act as a shape-controller to facilitate the formation of Cu₂O crystals with different morphologies [27].

As a capping or dispersant agent, PVP molecule with a long chain can be adsorbed to the surface of Cu_2O particles via physical and chemical adsorption. It is believed that PVP tends to interact more strongly with the (111) facets than with the (100) facets and thus lead to suppressed growth of (111) facets compared with (100) facets [33]. In the initial stage, when 0.2 g PVP is added into the reaction system, the capping effect of PVP to Cu_2O polyhedron is not enough or weaker, which cannot hinder the growth of (111) facets

obviously, and C-Cu₂O are produced eventually. When the amount of PVP increases to 0.6 g, the interaction strength is enhanced and the surface energy of (111) facets is decreased effectively at the same time, which is beneficial to lower the growth rate of (111) facets. As a result, (111) facets can be able to retain a bit in the final morphology of Cu₂O and that is the TC-Cu₂O. Further increasing the amount of PVP to 1.0 g, the interaction strength is greatly enhanced and the growth of the (111) facets is significantly reduced, while the growth rate of (100) facets is maintained relatively unchanged, such that TO-Cu₂O are formed with a high percentage of (111) facets. When the amount of PVP is 3.0 g, truncated corners belong to (100) facets disappear gradually, perfect O-Cu2O with well-defined edges and sharp corners are generated eventually due to further decreased growth on (111) facets compared to the (100) facets. In a word, PVP as an effective capping agent can change the surface energy of (111) facets or (100) facets, Cu₂O crystals with different morphologies evolved from cube to octahedral are synthesized successfully at last.

3.3 Gas sensing properties of Cu₂O As MOX sensors are working at high temperatures and Cu₂O is easily to be oxidized into CuO at elevated temperatures, it is therefore essential to determine the highest working temperature of Cu₂O. From the TG curves and XRD patterns before and after 250 °C annealing in Fig. S4, Cu₂O will not turn into CuO when the temperature is below 250 °C, which can be chosen as a maximum operating temperature. Figure 3a shows the electrical resistance response of four kinds of Cu₂O morphologies versus operating temperature when exposed to 10 ppm benzene. Obviously, it can be seen that all responses of four morphologies increase with the enhanced temperature and get the highest response at 250 °C. It is noted that the response of Cu₂O decrease with the reduced percentage of (100) facets from cube to octahedra at the same operating



Figure 3 The responses of Cu_2O crystals with different morphologies to (a) 10 ppm benzene, (b) 10 ppm acetone, (c) 5 ppm NO₂, and (d) C-Cu₂O crystals to three gases at 5 ppm at a series of temperatures.

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temperatures, so that the C-Cu₂O behaves with the best sensing performance to benzene among the four kinds of morphologies, and the response reaches 1.24-10 ppm benzene under 250 °C. On the other hand, the responses to 10 ppm acetone in Fig. 3b and to 5 ppm NO_2 in Fig. 3c showed similar response relationships that the response increases first and descends later as the temperature increases, with the highest responses of C-Cu₂O obtained at 200 and 100 °C for acetone and NO₂, respectively. It can be clearly seen again that the response decreases with the reduced percentage of (100) facets and C-Cu₂O shows the highest response among the four kinds of Cu₂O polyhedrons. All the response results are summarized in Fig. 3d, which show the good selectivity of C-Cu₂O to the NO₂ and acetone. Specifically, C-Cu₂O exhibits a far higher response to NO₂ at 100 °C than those of other two gases (nearly zero). So does the good selectively to acetone at 200 °C. To exclude the particle size effect on the performance of sensor response, 1.13 µm cubic Cu₂O was prepared as shown in Fig. S5a according to the literature [38]. Figure S5b shows the responses to 5 ppm acetone where it is clearly seen that the responses are similar for both cubic Cu₂O with the sizes of 1.13 and 0.66 µm. The theoretical surface area can be calculated by $6L^2/L^3\rho$, where L is the size of C-Cu₂O and ρ is the density (6.0 g cm⁻³). The specific surface areas of 1.13 and 0.66 µm C-Cu₂O are 0.88 and $1.52 \text{ m}^2 \text{g}^{-1}$, which are very small as compared with the nm scale crystals. Therefore, the main reason for the performance difference is the crystal facets rather than the particle size.

The dynamic sensing response curves of C-Cu₂O toward benzene, acetone, and NO₂ at a series of concentrations at their optimized working temperatures are shown in Fig. 4a–c. The response and recovery times are shown to be less than 1 min, considering the time for the incoming benzene to reach the stabilized concentration [10]. Further, the gas responses and concentrations are plotted at

their optimum operating temperatures in Fig. 4d, which shows a quasi-linear relationship for benzene and acetone. As for NO₂, it is a curve relationship at low concentration with a larger tangent slope and it will transfer into a quasi-linear relationship with a smaller slope nearly to saturation when the concentration exceeds 2.5 ppm.

3.4 Catalytic performance of Cu₂O To explore the origin of the different gas sensing properties of the Cu₂O polyhedrons with varied shapes and catalytic properties were assessed using a fixed-bed reactor as showed in Fig. 5. The samples were mixed with quartz sands and quartz wool with neglectable effect on acetone and benzene degradation at operating temperatures below 250 °C [39]. Figure 5a and c shows the conversion of benzene and acetone as a function of reaction temperature over C-Cu₂O and O-Cu₂O catalysts, respectively. Apparently, the catalytic activity to benzene and acetone increases with the enhanced reaction temperature. It is noteworthy that the catalytic activity of C-Cu₂O is higher than that of O-Cu₂O at the same temperature, which would contribute greatly to the higher gas response of C-Cu₂O than O-Cu₂O. In the meanwhile, the conversion of acetone by both C-Cu₂O and O-Cu₂O is higher than that of benzene, which is nearly 100% for acetone at 250 °C but only 30-40% for benzene. This might be the reason why both C-Cu₂O and O-Cu₂O have higher response to acetone than to benzene as shown in Figs. 3d and 4d. On the other hand, the acetone conversion is only $\sim 40\%$ at 200 °C where the highest response is obtained, and there is also high response at 150 °C, where there is nearly no catalytic activity to both acetone and benzene. Therefore, the adsorption of acetone and benzene also contributes to the gas response at lower working temperatures of Cu₂O. This is also applicable to the gas sensing of NO₂ with gas response maxima at $100 \,^{\circ}$ C, where there would only be the adsorption process because NO2 cannot be converted at such low temperature. On the



Figure 4 The dynamic sensing characteristics of C-Cu₂O crystals to different concentrations of (a) benzene, (b) acetone, (c) nitrogen dioxide, and (d) the responses of C-Cu₂O to three gases at their optimum operating temperatures.



Figure 5 A conversion of (a) benzene or (c) acetone as a function of reaction temperature and Arrhenius plots for the oxidation of (b) benzene or (d) acetone over the C-Cu₂O and O-Cu₂O.



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contrary, the gas response is relatively lower at the highest conversion temperature of acetone (i.e., 250 °C) as compared with that at optimum 200 °C, which infers the resistance change is not only determined by the surface adsorption/reaction process, but also by the intrinsic electrical property changed, as discussed in the following section.

To further demonstrate the facet-dependent catalytic properties of C-Cu₂O and O-Cu₂O, the activation energy of benzene and acetone are calculated on the kinetics of catalytic oxidation of benzene [40, 41], toluene [40], carbon monoxide [42], and so on, according to the literature. Figure 5b and d shows the Arrhenius plots for the oxidation of benzene and acetone over C-Cu₂O and O-Cu₂O, respectively. Their apparent activation energies are calculated from the conversion rate γ (mol \cdot g⁻¹ \cdot s⁻¹) of benzene and acetone below 20%. All the correlation coefficients (R^2) of the fitting lines for the test samples are close to 1.0, which indicates the excellent linear relationship of lny versus 1000/T. The activation energies for C-Cu₂O and O-Cu₂O to benzene and acetone are 131.21, 156.55, 52.18, 61.01 kJ \cdot mol⁻¹, respectively. Such a result is in good consistency with the higher conversion for C-Cu₂O than O-Cu₂O to both benzene and acetone. According to the comprehensive analysis of the above, the C-Cu₂O has a better catalytic performance than O-Cu₂O, which may be an important explanation for the corresponding sensing properties of benzene and acetone.

3.5 Mechanism analysis Generally, it is believed that the sensing mechanism is controlled by the chemical and electrical properties of the sensing material [43]. Obviously, the chemical [14–16] and electrical [11–13] properties of polyhedron with different crystal facets, as well as exposed percentage of certain crystal facets, are not the same due to the difference of atom numbers and arrangements on its surface. Figure 6a shows the response of four morphologies Cu_2O with different exposed percentages of (100) facet to different gases at their optimum operating temperatures. It can be clearly seen that the responses to benzene, acetone, and NO_2 are decreased with the reduced percentages of (100) facet, namely, with the transformation of C-Cu₂O to O-Cu₂O.

Surface adsorption and catalytic reaction play important roles in gas sensing processes. Firstly, the oxygen molecule chemisorbs on the surface of Cu_2O particle and traps electrons to form ionized oxygen species as shown in Eqs. (1–3) [22]:

$$O_2(gas) \rightleftharpoons O_2(ads.) \tag{1}$$

$$O_2(ads.) + e^- \rightleftharpoons O_{2^-}(O_{2^-} \text{ dominate at } 25 \text{ }^\circ\text{C} - 150 \text{ }^\circ\text{C})$$

(2)



Figure 6 The (a) response of four morphologies Cu_2O with different exposed percentages of (100) facet to different gases at their optimum operating temperatures at certain concentration and (b) their corresponding Arrhenius plots for electrical current.

$$O_{2^-} + e^- \rightleftharpoons 2O^-(O^- \text{ dominate at } 150 \text{ }^\circ\text{C} - 500 \text{ }^\circ\text{C})$$
(3)

Similar chemisorption occurs when NO₂ is introduced with higher electron affinity than oxygen, and the reactions can be written as Eqs. (4) and (5). As for reducing gases, benzene and acetone are electron donors which will donate electrons by chemisorbed onto the surface or competitive adsorptions with ion-sorbed oxygen, as shown in Eqs. (6) and (7). These processes will contribute to the gas response at low temperatures (i.e., <150 °C) where benzene and acetone are not catalytically oxidized. However, when the temperature is higher, they begin to be converted to CO₂ as shown in Fig. S6, which plots the CO₂ yield as a function of reaction temperature for the oxidation of benzene and acetone over the C-Cu₂O and O-Cu₂O. Then, the reactions of (8 and 9) start to occur [21, 29].

$$NO_2(gas) + e^- \rightarrow NO_{2^-}(ads.)$$
 (4)

$$\begin{array}{l} NO_2(gas) + O_{2^-}(ads.) + 2e^- \\ \rightarrow NO_{2^-}(ads.) + 2O^-(ads.) \end{array}$$
(5)

$$C_{6}H_{6}(gas) + O_{2^{-}}(ads.) \rightleftharpoons C_{6}H_{6}(ads.) + O_{2}(gas) + e^{-}$$
(7)

$$C_{6}H_{6}(gas) + 15O^{-} \rightleftharpoons 6CO_{2}(gas) + 3H_{2}O(gas) + 15e^{-}$$
(8)

$$C_{3}H_{6}O(gas) + 8O^{-} \rightleftharpoons 3CO_{2}(gas) + 3H_{2}O(gas) + 8e^{-}$$
(9)

Though the catalytic activity becomes higher at elevated temperatures, the gas response begin to decrease after the maxima is obtained at medium temperature, inferring that another dominant process is governing the resistance of the material. Therefore, electrical properties of Cu₂O with different crystal facets are then further explored to demonstrate the intrinsic resistance changes. The curves of resistance logarithmic versus temperatures for C-Cu₂O, TC-Cu₂O, TO-Cu₂O, and O-Cu₂O as shown in Fig. S7 and Fig. 6b, show the corresponding Arrhenius plots for electrical current of four morphologies of Cu₂O, and it can be calculated that the hole activation energy [44] decreases with the percentage of (100) facet reducing. C-Cu₂O with six (100) facets possess a maximum value of 0.55 eV, while O-Cu₂O with eight (111) facets gets a minimum value of 0.36 eV. These results show that intrinsic bulk carriers are easily excited at elevated temperatures for O-Cu₂O. Consequently, if the bulk hole concentration induced by thermal excitation is much higher than that induced by surface adsorption/ reaction, the resistance will change a little, meaning a small gas response.



Figure 7 The schematic diagrams (a) for the structure of $C-Cu_2O$ and $O-Cu_2O$ after oxygen species adsorbed and (b) their corresponding energy band diagrams.

All these results are schematically shown in Fig. 7. The (100) facets have lower work function than (111) facet, which is theoretically calculated by density function theory and observed by Kelvin probe force microscopy [17, 18, 45]. This lower work function of (100) facets means more oxygen would be adsorbed on (100) facets trapping more electrons according to reactions (2) and (3), and thus, constructing a thicker surface hole accumulation layer and a higher surface potential barrier. This higher surface potential is in good accordance with the higher thermal activation energy of holes in C-Cu₂O as schematically shown in Fig. 7b. However, as a typical p-type semiconductor, the majority of the concentration is dominant in the resistance because there is neglectable barrier for holes to transport from particle to particle. In this case, C-Cu₂O changes its resistance easily because of the relatively lower work function and thus the higher concentration ion-sorbed oxygen with higher catalytic activity. These results not only show the facet dependent chemical and electrical properties, but also promising for the highly selective MOX sensor tailoring in p-type semiconductors for the future high response and selectivity sensors and noses.

4 Conclusions Cu₂O polyhedrons with four morphologies are successfully synthesized via a facile solution-phase method, and the facet-dependent gas sensing properties are investigated in detail. C-Cu₂O with six (100) facets shows higher responses to benzene, acetone, and NO₂ than O-Cu₂O exposing eight (111) facets, which is in good consistence with their catalytic activities to benzene and acetone. More importantly, the gas sensing maxima are obtained at different working temperatures illustrating good selectivity to NO₂ and acetone. Catalytic property measurements reveal a lower apparent catalytic activation energy of (100) facets than (111) ones, while electrical characterization demonstrates a higher thermal excitation energy of bulk holes on (100) facets than (111) ones, in good agreement with the relatively lower work function of (100) compared to (111). Therefore, the synergy of chemical and physical properties gave rise to a better sensing property for C-Cu₂O than O-Cu₂O eventually, and the C-Cu₂O has good selectivity to NO₂ and acetone at varied working temperatures, promising for future highly selectively gas sensor development.

Supporting Information Additional supporting information may be found in the online version of this article at the publisher's web-site.

Acknowledgements This research was financially supported by the National Key Research and Development Program (2016YFC0207101), the National Natural Science Foundation of China (51272253), and the State Key Laboratory of Multiphase Complex Systems (MPCS-2014-C-01).



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