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Chemical synthesis, characterisation and gas sensing performance of copper oxide nanoribbons†

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Single crystalline copper oxide nanoribbons were synthesized *via* a surfactant-assisted hydrothermal route. The resulting CuO nanoribbons contain substantial amounts of nanorings and nanoloops. High resolution TEM analysis identified CuO nanoribbons growing along the [010] direction. CuO nanoribbons exhibited excellent sensing performance towards formaldehyde and ethanol vapours with rapid response and high sensitivity at low operating temperatures. We found that the loading of a small amount of Au or Pt nanoparticles on the surface of CuO nanoribbons can effectively enhance and functionalize the gas sensing performance of CuO nanoribbons.

Introduction

One-dimensional nanostructures such as nanotubes, nanowires, nanorods and nanoribbons have been extensively investigated worldwide,^{1–4} because they have many potential technological applications, including nanoelectronics, nanophotonics, nano-computing and nanoscale bio and chemical sensing. Chemical sensors play an important role in the areas of emissions control, environmental protection, public safety, and human health.^{5–7} Much more public concern today than ever before over the serious environmental issue are further promoting the development of sensors with both high sensitivity and rapid response. In addition to in-depth exploration of gas sensing mechanisms⁸ and innovative sensor device design,⁹ a variety of novel gas sensors based on metal oxide one-dimensional (1D) nanostructures, such as SnO₂,¹⁰ In₂O₃,¹¹ Fe₂O₃,¹² WO₃,⁵ V₂O₅,¹³ ZnO,¹⁴ and TiO₂¹⁵ *etc.*, have been successfully fabricated and intensively investigated. It has been well documented that the large surface-to-volume ratios of nanobelts or nanoribbons, along with the congruence of the carrier screening length with their lateral dimensions, make them excellent candidates for gas sensing applications.^{16,17} It was also found that surface doping of n-type metal oxide semiconductors with catalytic metals, such as platinum, gold, palladium, and iridium can further improve the sensitivity, reduce the response time and operation temperature, and even change the selectivity pattern.^{18–20} However, to date most efforts in the field of metal oxide gas sensors have been devoted to n-type semiconductors, while the sensing properties of the p-type one-dimensional metal oxide semiconductors have scarcely been investigated.

As an important p-type semiconductor, cupric oxide (CuO) has been extensively studied due to its diverse applications,

such as in gas sensors, catalysis, batteries, high critical temperature superconductors, solar energy conversion, and field emission emitters.^{21–23} For these potential applications, CuO micro- or nano-structures with various morphologies have been synthesized.^{24–28} Nevertheless, very little work has been directed towards fabricating gas sensors based on 1D CuO nanostructures, and there are no reports on the gas sensing properties of CuO nanoribbons. Herein, we report the chemical synthesis and the gas sensing properties of p-type CuO nanoribbons with and without noble metal additives towards formaldehyde and ethanol gases for the first time. We show that the p-type semiconductor gas sensors based on CuO nanoribbons have rapid response and high sensitivity to very low concentrations of formaldehyde and ethanol gases at low operating temperatures, and that their sensing performances can be further enhanced by functionalizing the CuO nanoribbons with small quantities of Pt or Au nanoparticles.

Experimental

CuO nanoribbons were synthesized from the hydrothermal reaction between CuSO₄ and NaOH in the presence of an anion surfactant sodium dodecylbenzenesulfonate (SDBS). In a typical procedure, 10 mL of 0.1 M sodium dodecylbenzenesulfonate (SDBS) was dropped into 10 mL of 0.1 M CuSO₄ solution with continuous stirring. Subsequently, 10 mL of 6 M NaOH solution was added dropwise into the above suspension. After stirring for another 10 min, the mixture was hydrothermally treated at 120 °C for 10 h. The black product was collected and washed with distilled water and absolute ethanol, and finally dried under a vacuum at 60 °C for 4 h.

Functionalization of the CuO nanoribbons with Pt and Au was carried out through a wet-chemical reduction method. Briefly, the as-prepared CuO nanoribbons were ultrasonically dispersed in 20 mL of H₂O, to which a given amount of H₂PtCl₆ or HAuCl₄ (1% to CuO in molar ratio) and L-ascorbic acid solution was added sequentially. After the above mixture was heated at 60 °C for 15 min under continuous stirring, the products were collected in the same way as for the pristine nanoribbons.

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The as-prepared samples were characterized by X-ray diffraction (XRD, Cu K α radiation, Philips 1730), field emission scanning electron microscopy (FESEM, JEOL 6700F) equipped with energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM, JEOL 2011).

Gas sensing measurements were carried out on a computer-controlled WS-30A system. The structure, fabrication and testing principle of our gas sensors based on the as-prepared CuO nanoribbons is similar to that for Fe₂O₃ nanotubes.⁸ For comparison, the other two types of gas sensors using the commercial CuO powders (<5 μ m) and the nanoplates, which were synthesized through a procedure similar to that for CuO nanoribbons but replacing SDBS with sodium citrate, were also fabricated and tested.

Results and discussion

The morphology of the as-synthesized CuO products was observed *via* field emission scanning electron microscope (FESEM) and is shown in Fig. 1(a). The high yield of CuO nanoribbons has been observed by SEM. The nanoribbons have varied widths and lengths extending for tens of micrometres. The chemical composition of the nanoribbons was analysed by energy dispersive X-ray spectroscopy (EDS) and is shown in Fig. 1(b)), which revealed that the nanoribbons are only composed of Cu and O, and the atomic ratio of Cu to O was very close to 1 : 1, in agreement with the stoichiometric proportion of CuO. The as-prepared CuO nanoribbons contain 2 wt% SDBS surfactant, which has been determined by thermogravimetric analysis (TGA, Fig. S1†).

The phase purity of nanoribbons was determined by powder X-ray diffraction (XRD) as shown in Fig. 2. All the diffraction peaks can be readily indexed to the monoclinic symmetry of CuO (space group *C2/c*, *a* = 4.684 Å, *b* = 3.425 Å, *c* = 5.129 Å, β = 99.47°; ICDD-JCPDS file no. 05-0661). The broadening

Fig. 1 (a) FESEM image shows the morphology of the CuO product; (b) EDS pattern reveals that the CuO products are composed of Cu and O with a ratio of 1 : 1.08. The signal of carbon came from the carbon conducting tape on which CuO samples were stuck.

Fig. 2 XRD pattern of the as-synthesized CuO nanoribbon.

of all the recorded peaks in the XRD pattern indicates that the component crystallites are of nanoscale character. No other impurities were detected by XRD analysis, indicating the phase purity of the CuO nanoribbons, which was consistent with the EDS analysis result.

The micromorphology and crystallographic structure of the CuO nanoribbons were further analysed by transmission electron microscopy (TEM) and high resolution TEM (HRTEM). Fig. 3(a) shows a low magnification TEM image of CuO nanoribbons, revealing the abundant ribbon-like 1D nanostructures.

Fig. 3 Bright field TEM images showing microstructural features of CuO nanoribbons. (a) Tangled nanoribbons at low magnification; (b) overlapping thin and thick nanoribbons; (c) CuO nanoring; (d) HRTEM image and selected area diffraction pattern (inset) showing (002) planes parallel to the growth direction of nanoribbons; (e) nanoring loops; (f) HRTEM image of region in (e) indicated by rectangle, interplanar spacings consistent with (002) planes parallel to ribbon long axis and (010) plane perpendicular to long axis.

The width of the nanoribbons is in the range of 30–100 nm and the thickness is about 2–8 nm. Among the nanoribbons, some are straight with a flat lateral face along the length direction, while the others are bent and inter-twisted, implying that the nanoribbons are highly flexible. Straight nanoribbons were frequently joined and overlapped in parallel on the flat sides, even with nanoribbons of different thickness, as shown in Fig. 3(b), indicating strong attractive forces between the flat sides of parallel nanoribbons. The bending contour of CuO nanoribbons is clearly illustrated under an electron beam. We also observed CuO nanoribbon rings (Fig. 3(c)). Those nanorings were formed by bending of 1 or 2 nanoribbons. Complex nanoloops were observed (Fig. 3(e)), which were formed by several nanoribbons joined in parallel on the flat sides and then bent into loops or looped segments. Fig. 3(d) and (f) further show the HRTEM images of a CuO nanoribbon and a nanoloop respectively. Combined with selected area electron diffraction (SAED) (the inset in Fig. 3(d)), it revealed the same growth direction for the nanoribbons, nanorings and nanoloops, *i.e.* along the [010] direction. Both HRTEM and SAED analyses confirmed the single crystalline nature of the as-grown CuO nanoribbons, nanorings and nanoloops.

or shape of the CuO nanoribbons. The XRD patterns of the Pt- and Au-loaded samples (not shown here) are in essence the same as that of the pristine CuO nanoribbons. No Pt or Au diffraction peaks have been detected due to their trace contents. However, the catalytic metals Pt and Au were quantitatively detected by EDS analysis and are shown in Fig. 4(c) and (d), respectively. Their contents were about 0.50 atm% and 0.78 atm% for the Pt-loaded sample (Pt-CuO nanoribbons) and the Au-loaded sample (Au-CuO nanoribbons), respectively. TEM, HRTEM and EDS analyses were further performed on Au- and Pt-loaded CuO nanoribbons, clearly showing the presence of Au and Pt nanoparticles (Fig. S3 and S4†).

Fig. 5(a) shows typical isothermal response curves of CuO-based sensors when cycled with increasing HCHO vapour concentrations from 5 to 500 ppm in ambient air. It can be seen that the resistance of commercial powder (black curve) showed almost no changes over the whole concentration range, indicating that the CuO commercial powder is insensitive to HCHO. In contrast, the resistance of the as-synthesized nanoplates increased even when the concentration of HCHO was very low (5 ppm), and it continued to increase gradually with increasing vapour concentration. It should be noted that the trend in the changing resistance of the p-type semiconductor sensor with the concentration of the reducing gas was completely opposite to that of an n-type sensor, implying that their sensing mechanisms are different. The major charge carriers are holes and electrons for p-type and n-type semiconductors, respectively. Upon exposure to a reducing gas, the density of p-type charge carriers (positive holes) would decrease due to surface adsorption and chemical reaction between the gas and oxide sensor (electron donation), resulting in an increase of its resistance, which is opposite to what is seen with the n-type semiconductor gas sensors.^{8,21} It was striking that all three nanoribbon-based sensors with or without noble metal additives show much better response to HCHO at any given gas concentration than the nanoplates or the commercial powders. Their resistance underwent a dramatic increase on the injection of HCHO and then rapidly recovered after the test gas was released.

Fig. 4 (a, b) SEM image of the Pt- and Au-loaded samples, respectively, indicating the loading of noble metals did not change the morphology of CuO nanoribbons. (c, d) EDS pattern of the Pt- and Au-loaded samples, indicating the content of Pt and Au is 0.50 at% and 0.78 at%, respectively.

Fig. 5 (a) Typical response curves of the CuO-based sensors during cycling between increasing concentration of HCHO and ambient air; (b) sensitivity *versus* HCHO concentration. The black, violet, red, green and blue curves denote commercial powder, nanoplates, pristine nanoribbons, Au–CuO nanoribbons and Pt–CuO nanoribbons, respectively.

The response time and recovery time (defined as the time required to reach 90% of the final equilibrium value) were only 2–4 and 3–7 s, respectively. This result indicated that the nanoribbon-based sensors have good reversibility. Compared to other reported HCHO sensors^{29,30} the CuO nanoribbons offered the fastest response and recovery capacities. The detection limit of the CuO nanoribbon-based sensor towards HCHO can be as low as 5 ppm. Furthermore, among the three nanoribbon-based sensors, the response amplitudes of the Pt–CuO nanoribbons (blue curve) and the Au–CuO nanoribbons (green curve) are always higher than that of the pristine CuO nanoribbons (red curve) at any gas concentration, indicating a promotion effect of the noble metal nanoparticles due to their catalytic capacity.^{19,20} Fig. 5(b) shows the correlation between the sensitivity of the five CuO-based sensors and the concentration of HCHO. Here the gas sensitivity was defined as the ratio of the stationary electrical resistance of each element in the test gas (R_{gas}) and in air (R_{air}), i.e., $S = R_{\text{gas}}/R_{\text{air}}$. The figure clearly illustrates that the CuO bulk powders have no sensitivity to HCHO even at the high concentration of 500 ppm, while the nanoplates showed very low sensitivity to HCHO. However, all the CuO nanoribbon-based sensors displayed high sensitivity to HCHO in the concentration range from 5 to 500 ppm. Their sensitivities took on an exponential rate of increase at first (below 100 ppm), which then changed to a linear increase in the range of 100–500

Fig. 6 (a) Typical response curves of the CuO-based sensors on cycling between increasing concentration of ethanol and ambient air at 200 °C; (b) sensitivity *versus* ethanol concentration. The black, violet, red, green and blue curve denotes commercial powder, nanoplates, pristine nanoribbons, Au–CuO nanoribbons, and Pt–CuO nanoribbons, respectively.

ppm. As a whole, the sensitivity of CuO-based sensors to HCHO increased in the following order: bulk powder < nanoplates $\ll$ pristine nanoribbons < Au–nanoribbons < Pt–nanoribbons. The Pt-doped CuO nanoribbons exhibited the best gas sensing performance.

The sensing performance of the CuO-based gas sensors to ethanol in the concentration range of 5–1000 ppm is displayed in Fig. 6. Similar to the sensing test results on HCHO, the resistances of all the sensors increased to different extents on exposure to ethanol vapour, and then recovered on the release of the test gas. The response and sensitivity of all the nanoribbon-based sensors were much better than those of the nanoplates and bulk powder, and their response and recovery times were 3–6 and 4–9 s, respectively. Compared to a recent report³¹ on the sensing properties of CuO nanorods to ethanol, which showed a sensitivity of about 2 in an atmosphere of 2000 ppm ethanol at a working temperature of 300 °C, the sensitivity of our pristine CuO nanoribbons was at least double at much lower concentration (1000 ppm) and working temperature (200 °C). This result may be attributed to the unique geometry of the CuO nanoribbons. Nanoribbons are thought to have a higher surface-to-volume ratio, and low surface-contact resistance, as well as providing a pathway for free carriers, allowing them to cross the bulk of the ribbons along the axis, much as in a field effect transistor channel.³² The surface area of CuO nanoribbons

was measured to be $126.4 \text{ m}^2 \text{ g}^{-1}$ by using a Quanta Chrome Nova 1000 Gas Sorption Analyzer. High surface area of CuO of the nanoribbons may be another important factor in allowing them to adsorb a maximum amount of gas molecules. It should be noted that the relatively low operation temperature helps to decrease the consumption of energy, and can improve the suitability of the sensor in some particular situations. Furthermore, the sensing performance can be enhanced by functionalization with a small amount of Au and Pt nanoparticles. For example, the sensitivity of Au–CuO nanoribbons improved exponentially in the low concentration range, while the sensitivity of the Pt–CuO nanoribbons distinctly increased over a wide concentration range.

We noticed that the Pt additive always showed a better effect to the sensing enhancement than Au. This may be caused by differences in their catalytic activity.⁸ At the same time, the CuO nanoribbon-based sensors always showed higher sensitivity to HCHO than to ethanol. This discrepancy may be due to their different surface reaction mechanisms. It has been reported that ethanol is oxidized to CO_2 on the surface of an oxide sensor through a series of intermediate steps including the formation of ethoxy groups and acetaldehyde. Therefore, it can be deduced that formaldehyde has a more active surface reaction than ethanol on CuO sensors, and thus results in higher sensitivity and a quicker response time.

Conclusions

In conclusion, the synthesis of CuO nanoribbons and their functionalization with nanosize noble metal particles such as Au and Pt were achieved by a wet chemical method. The as-prepared CuO nanoribbons contain nanorings and nanoloops. HRTEM and SAED analysis confirmed that CuO nanoribbons, nanorings and nanoloops all grow along the [010] direction. The gas sensing properties towards HCHO and ethanol of the resultant materials have been investigated, demonstrating that CuO nanoribbons have quicker response and higher sensitivity than those of other counterparts to both HCHO and ethanol at a low operating temperature. Furthermore, functionalizing the CuO nanoribbons with Pt or Au nanoparticles leads to a remarkable enhancement of their gas sensing performance.

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