

Electronic supplementary information for

**Design and Understanding of High-Performance Gas Sensing
Material Based on Copper Oxide Nanowires Exfoliated from
Copper Meshes Substrate**

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Experimental Section

Materials. Copper meshes (CM) about 400 meshes were commercially available and tailored into small size. Both the reagents employed in samples preparation (Sodium hydroxide, NaOH and Potassium peroxydisulfate, $K_2S_2O_8$) and gas sensing target analytes (ethanol, acetone, benzene, toluene, benzaldehyde and benzyl alcohol) were analytical grade and were used as received without further purification.

Fabrication of needlelike CuO. The copper meshes were sequentially cleaned with deionized water, acetone and anhydrous ethanol in an ultrasonic cleaner for 10 min to remove possible impurities. The surface of copper meshes was reconstructed by simple immersion in an aqueous solution of 1.0 M NaOH and 0.05 M $K_2S_2O_8$ at room temperature for 30 min. The copper meshes turned to blue from the shiny yellow colour. After finishing this reaction, the samples then were cleaned with deionized water, followed by drying and driven in a drying oven (150 °C and 0.5 h). The copper meshes turned to dark from blue. The process of its colour change was further shown in FIG.S1a-c. Then a 5 ml centrifugal tube was charged with anhydrous ethanol and pieces of dark meshes, followed by low-power sonication for 30 min (Branson 1510E-MT) to form dispersion. After taking out the dark meshes and solvent evaporation, the CuO powder with needlelike morphology was obtained. For the purpose of contrast, the CuO powder was also synthesized by the followed method. The 0.5 M $CuSO_4 \cdot 5H_2O$ (50 ml) and 1 M NaOH (50 ml) aqueous solutions were mixed and the blue precipitates was collected and washed with distilled water three times. Then the precipitates endure the annealing process (150 °C and 0.5 h) just as the procedure of needlelike CuO. The product obtained by this method was referenced as “ordinary CuO” and its morphology was provided in FIG.S5.

Characterization. The crystal structure of the as-prepared samples were characterized by X-ray

diffraction (XRD) analysis using a X'PERT PRO diffractometer with Cu K α radiation of 1.5418 Å wavelength at 2 θ ranging from 20° to 90°. Field emission scanning electron microscope (FESEM) were obtained on JSM-6701F both with Au-sputtered specimens. Transmission electron microscope (TEM, FEI Tecnai G2 TF20) was also employed to examine the morphology and microstructure of samples. By dropping the homogeneous suspensions on a copper TEM grid (coated with a thin amorphous carbon film), TEM samples were prepared after drying at room temperature. The ethanol suspension of blue and dark meshes was examined separately on a UV-visible spectrophotometer (Agilent Cary 60). The measurement of Thermo-Gravimetric Analysis (TGA, Instrument type: STA 449F3, NETZSCH Corp., Ltd.) was conducted in air. Test range was 25 °C - 800 °C and heating rate was 10 °C·min⁻¹. X-ray Photoelectron Spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi) measurement was carried out using the Al K α line as the excitation source. The ordinary CuO product was tested by the single point Brunauer-Emmett-Teller (BET) method through nitrogen adsorption/desorption analysis (ASAP 2010, USA Micromeritics).

Fabrication and gas sensing measurements of needlelike CuO: The powder form CuO was mixed with small mass deionized water to form a paste and then coated onto the outside surface of a ceramic tube. Then the sensors were aged at 60 °C for 7 days. A Ni-Cr alloy coil heating wire across the tube was employed as a heater to adjust the operating temperature by tuning its heating voltage. Four Pt wires connected to pair of Au electrodes were previously installed at each end of ceramic tube to collect the the signals of changes in CuO sensor's resistance value. The gas sensing apparatus (WS-60A with resolution ratio of 1 mV, Wei Sheng Electronics Science and Technology Co., Ltd.) was used to evaluate the gas sensing properties under a steady-state

condition. A given amount of analyte was injected, fully evaporated, and then mixed with air in the glass chamber. The sensors' response to certain kind of gases is defined as R_g/R_a , where R_a is the initial sensor resistance in air and R_g is the sensor resistance in a target gas. The response time was defined as the time required to reach 90% of resistance change after injecting the detected analyte and the recovery time was the time necessary for the sensor to return to 10% above the original resistance in air after releasing the test gas [1, 2].

Supplementary Figures

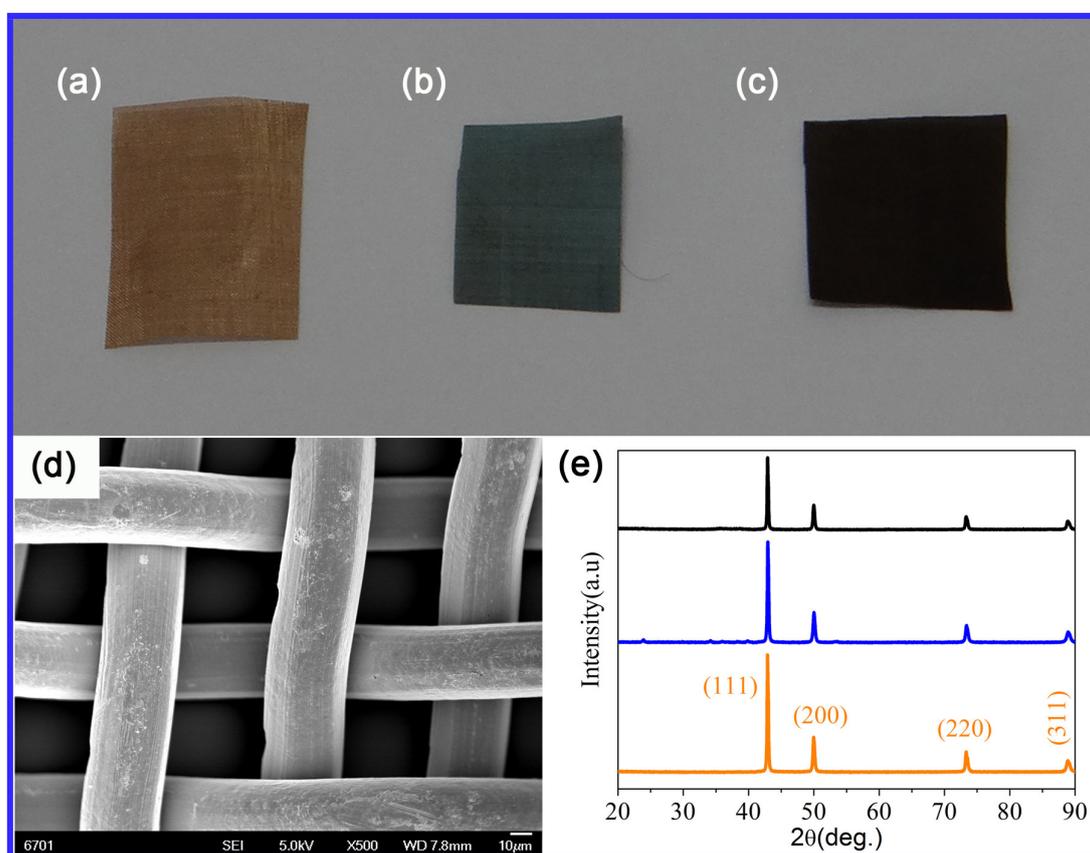


FIG. S1. The color changes of as-dried samples in the following stages: (a) original state (b) The CM after immersion in mixed solution (c) The CM after pyrolysis. (d) FESEM image of the pristine CM. (e) The holistic view XRD patterns of (a): orange line, (b): blue line and (c): dark line.

As FIG.S1e shown, all the obvious diffraction peaks correspond well with Cu (JCPDS 03-065-6065) and the 2θ positions of (111), (200), (220) and (311) diffraction peaks are located at 42.78° , 49.82° , 73.11° and 88.60° , correspondingly.

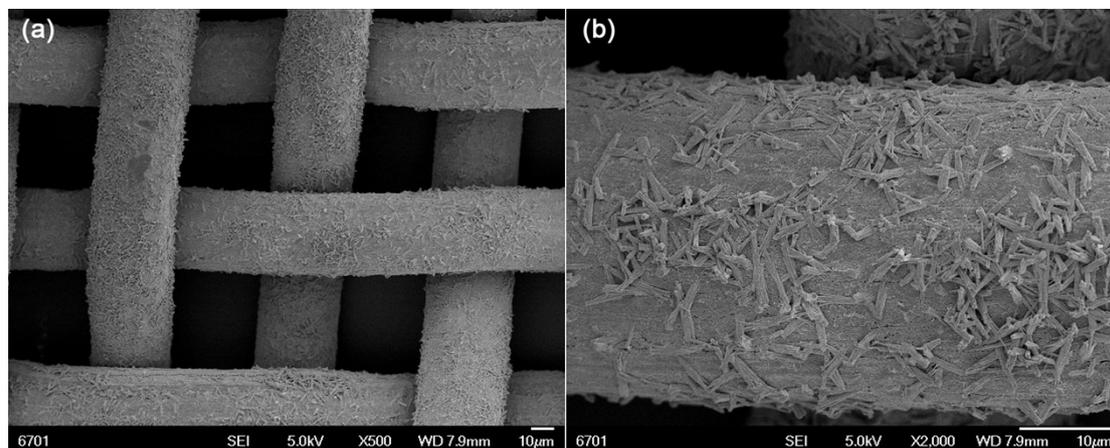


FIG. S2. FESEM images of the residual dark CM after 30 min ultrasound.

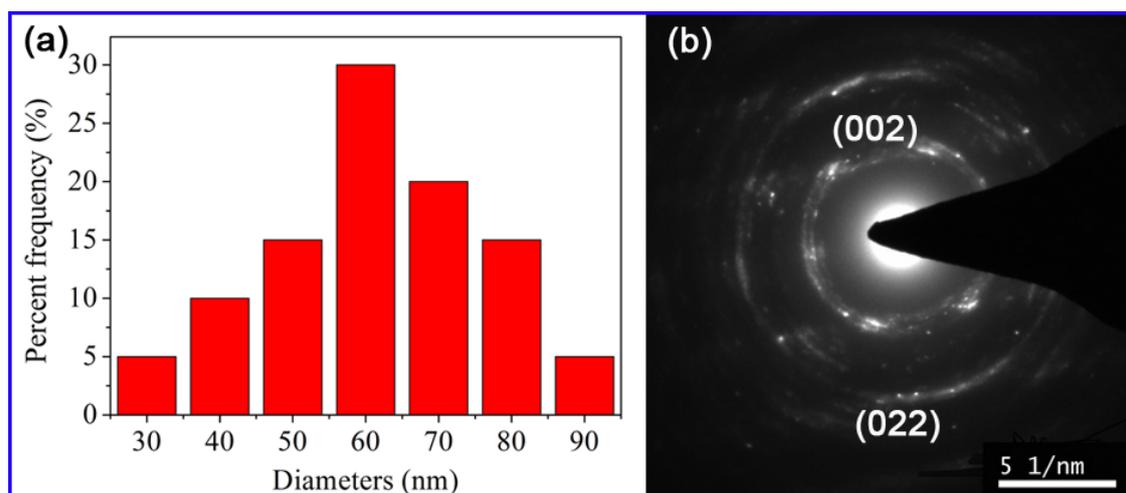


FIG. S3. (a) The diameters distribution of needlelike CuO nanowires (b) The selected area electron diffraction pattern of needlelike CuO nanowires.

In FIG.S3a, it shows the diameters distribution of needlelike CuO nanowires. The diameters of these CuO nanowires were probably estimated to be 50-70 nm (65%). In FIG.S3b, the annular structure reveals that the achieved CuO is polycrystal. The measured results of lattice spacing based on the rings in the above electron diffraction pattern is in accordance with the known lattice

spacing for CuO (JCPDS 45-0937) along with their respective hkl indexes of (002) and (022) [1,2].

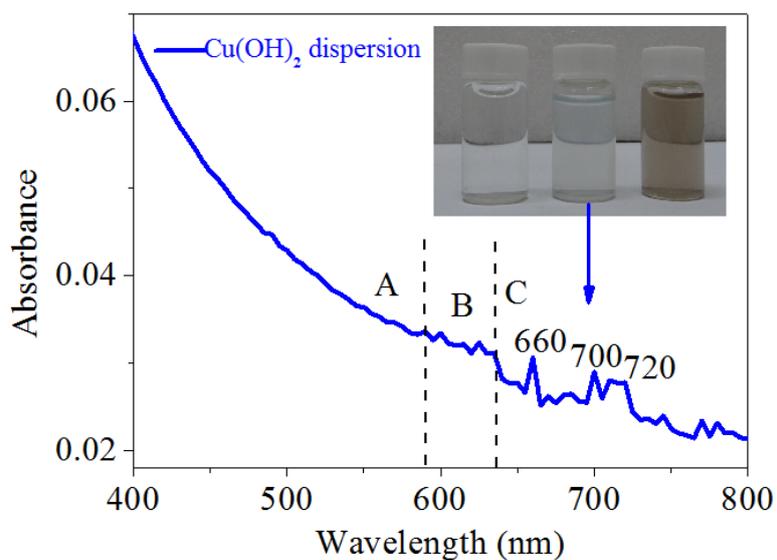


FIG. S4. The visible absorption spectra of $\text{Cu}(\text{OH})_2$ ethanol dispersion and the inset is the photograph of background (left); $\text{Cu}(\text{OH})_2$ (middle); CuO (right) ethanol dispersion.

As for region A, the smoothly rising absorbance is attributed to the high absorption peak located at ultraviolet band. As for region B, the absorption peaks are extremely weak. As for region C, several absorption peaks located at 660, 700 and 720 nm (orange-red light) can be found. So the $\text{Cu}(\text{OH})_2$ ethanol dispersion show its complementary colour: light blue.

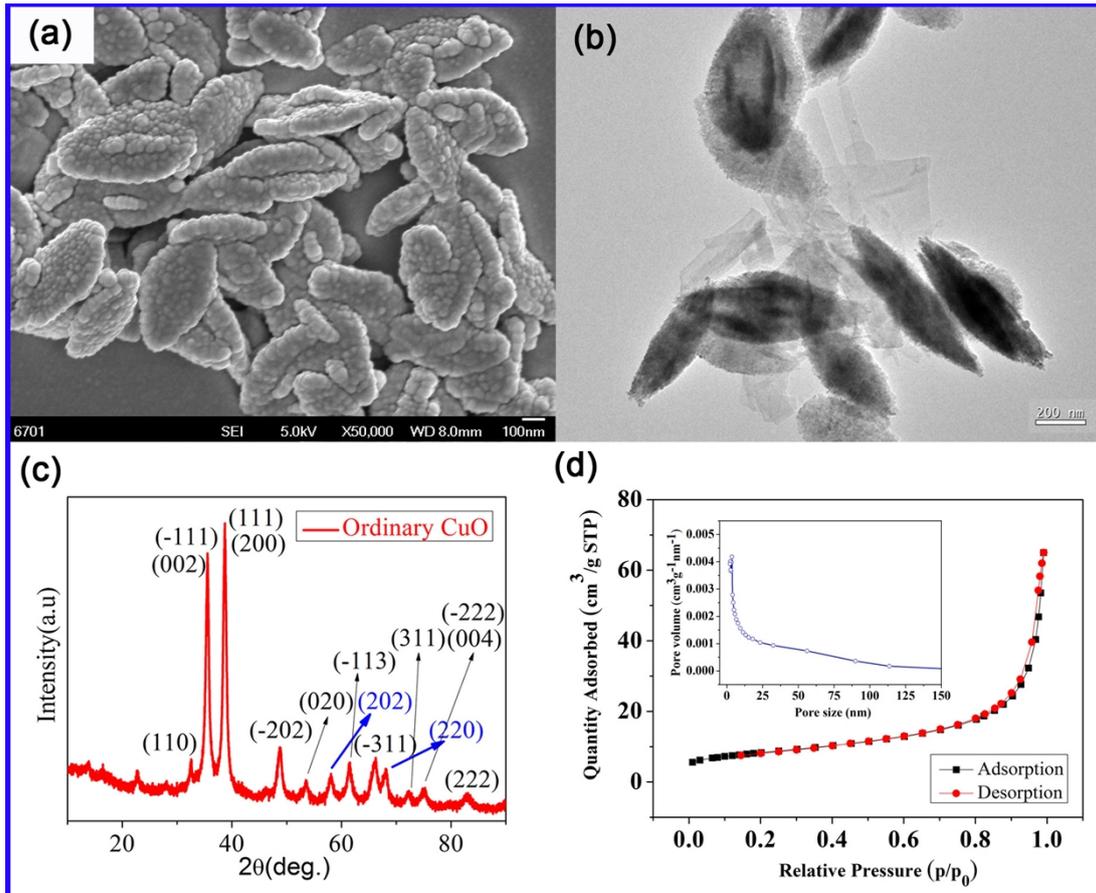


FIG. S5. The characterizations of ordinary CuO: (a) FESEM image; (b) TEM image; (c) XRD pattern; and (d) N₂ adsorption–desorption isotherm measurement.

The FESEM and TEM images show the ordinary CuO exhibit spindle-like shape with a width of 50-200 nm. As FIG.S5c shown, all the obvious diffraction peaks correspond well with CuO (JCPDS 01-089-5897) and the 2θ position of (-111) and (002) diffraction peaks are overlapped. The 2θ position of (111) and (200) diffraction peaks are also overlapped. For the standard value of (-111) and (002) diffraction peaks in this JCPDS, the 2θ positions are located at 35.56° and 35.46° , and the relative intensities are 92.3 % and 36.5 %, correspondingly. For the standard value of (111) and (200) diffraction peaks in this JCPDS, the 2θ positions are located at 38.74° and 38.93° , and the relative intensity are 100.0 % and 29.2 %, correspondingly. The XRD pattern indicate that the ordinary CuO is assigned to monoclinic crystal system (space group:C2/c). As

FIG.S5d shown, the N_2 adsorption–desorption isotherm displays no obvious hysteresis loop and its BET surface area of ordinary CuO is estimated to be $29.4 \text{ m}^2/\text{g}$.

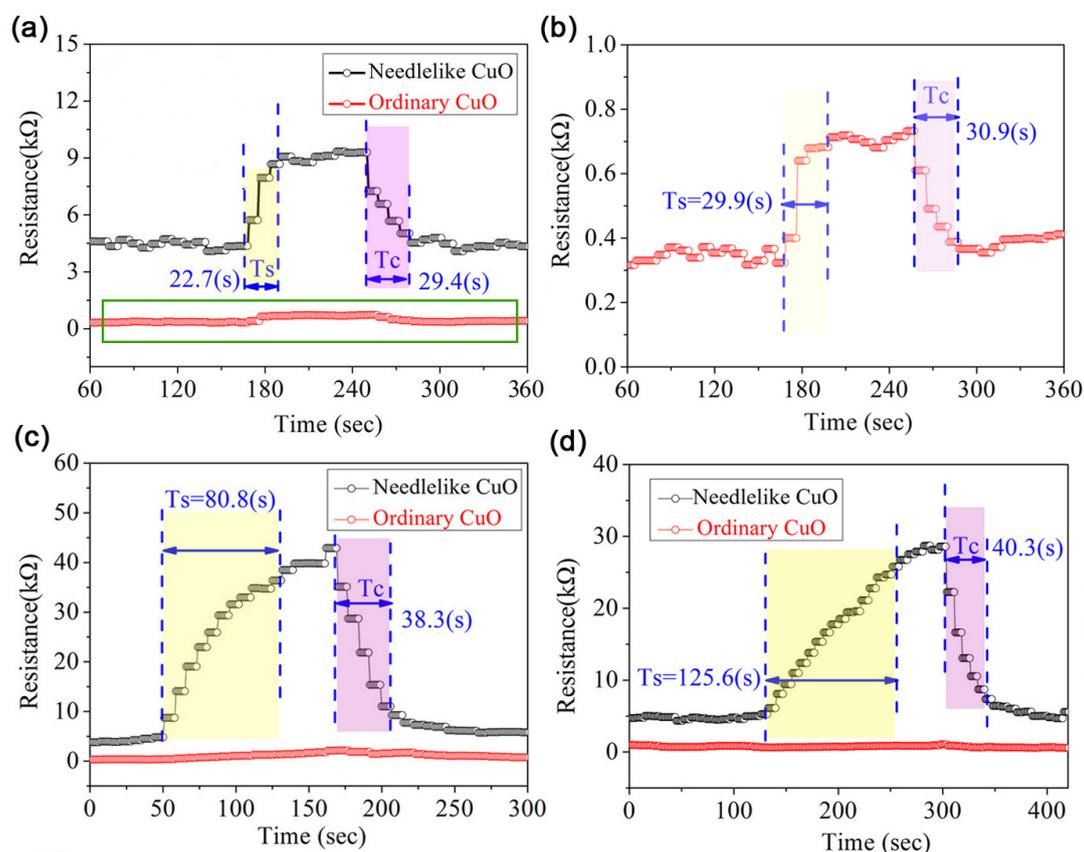


FIG. S6. The transient response–recovery curves of CuO sensors to (a) 100 ppm benzene, (b) enlarged view of green rectangle, (c) benzaldehyde, and (d) benzyl alcohol.

The method for obtaining response time (T_s) and recovery time (T_c) are given in above text, which are further illustrated by FIG. S6. The T_s and T_c of needlelike CuO sensor to 100 ppm benzene is 22.7 and 29.4 s while that of ordinary CuO is 29.9 and 30.9 s as shown in FIG. S6a-b. The T_s and T_c of needlelike CuO sensor decrease by 24.1% and 4.9%. The T_s and T_c of needlelike CuO sensor to 100 ppm benzaldehyde is 80.8 and 38.3 s and the T_s and T_c of needlelike CuO sensor to 100 ppm benzyl alcohol is 125.6 and 40.3 s. While it is hard to obtain the T_s and T_c of ordinary CuO sensor to benzaldehyde and benzyl alcohol, its response and recovery behavior are

still weak when the sensing curves are magnified.

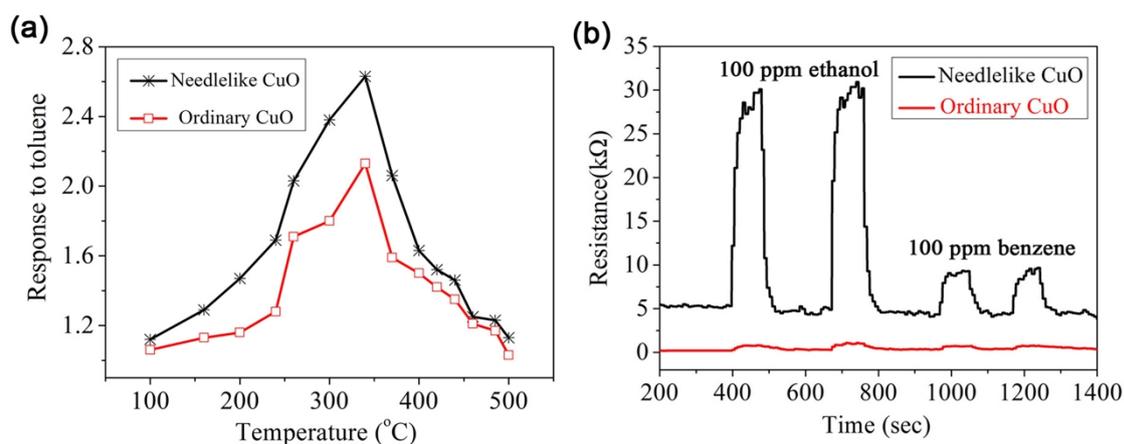


FIG. S7. (a) The response of CuO sensors to 200 ppm toluene at different testing temperatures. (b)

The reproducibility of CuO sensors to 100 ppm ethanol and benzene.

FIG. S7a shows the responses of needlelike and ordinary CuO sensors to toluene of 200 ppm as a function of the operating temperature. The sensors of needlelike and ordinary CuO exhibit the highest response to toluene gas at 340 °C. In general, the sensitivity values increase remarkably at first and then degrade dramatically with the increase of working temperature. The reproducibility of needlelike CuO sensor to 100 ppm ethanol and benzene was given in FIG.S7 b. FIG.S7 b shows the results that the peaks are found nearly constant, suggesting that the needlelike CuO sensor displays an acceptable reproducibility to ethanol and benzene [2].

References

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- [2] Z. Guo, G.Q. Chen, G.M. Zeng, L.Z. Liu, C. Zhang, Metal oxides and metal salt nanostructures for hydrogen sulfide sensing: mechanism and sensing performance, *RSC advances* 5 (2015) 54793-54805.