Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

Copper oxide hierarchical morphology derived from MOF precursors for enhancing ethanol vapor sensing performance

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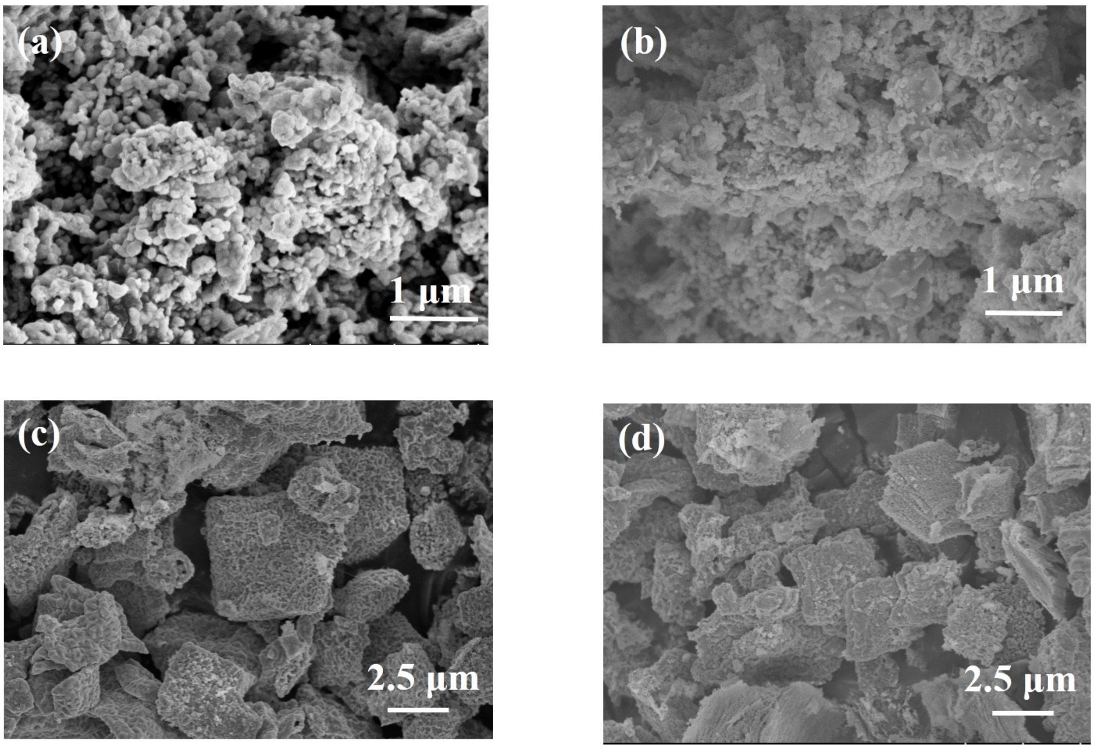


Figure S1 SEM images of (a) Rod-like CuBDC precursors calcined at 450 ^{o}C for optimum calcination time of 100 min. (b) Rod-like CuBDC precursors calcined at optimum calcination temperature of 350 ^{o}C for 250 min. (c) Cube-like Cu(BDC)(DMF) precursors calcined at 450 ^{o}C for optimum calcination time of 100 min. (d) Cube-like Cu(BDC)(DMF) precursors calcined at optimum calcination temperature of 350 ^{o}C for 250 min.

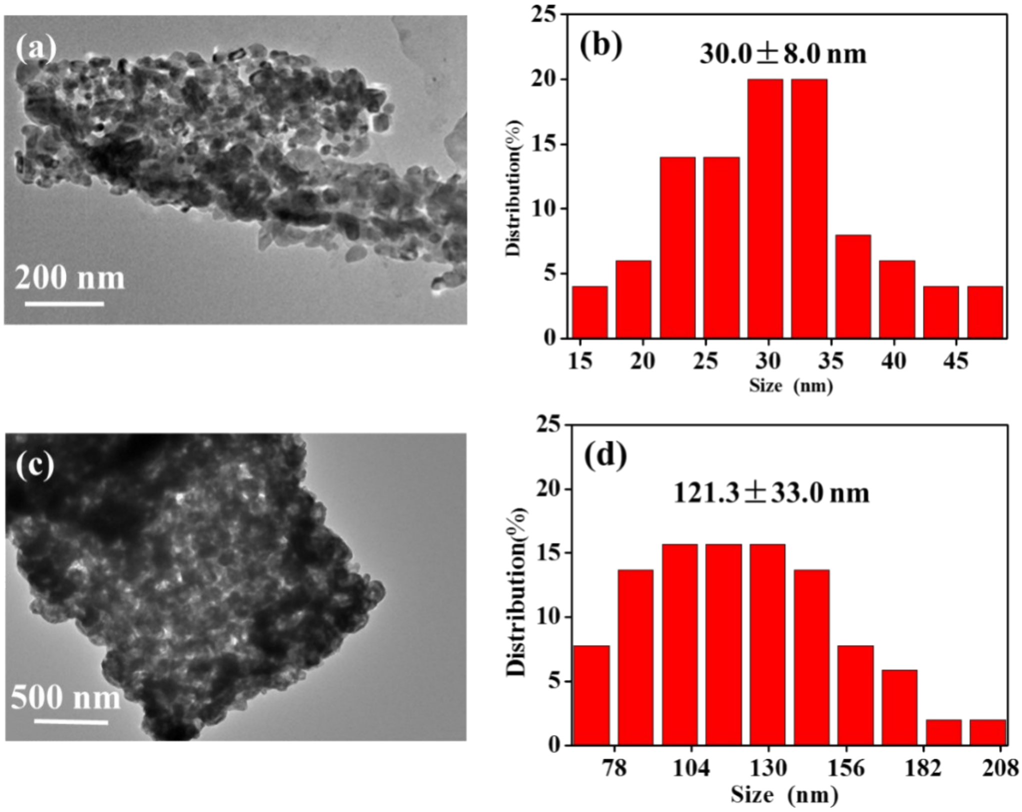


Figure S2 (a) TEM image of rod-like CuO with 30.0 nm particle sizes. (b) Particle size distributions of rod-like CuO in TEM (a) image. (c) TEM image of cube-like CuO with 121.3 nm particle sizes. (d) Particle size distributions of cube-like CuO in TEM (c) image.

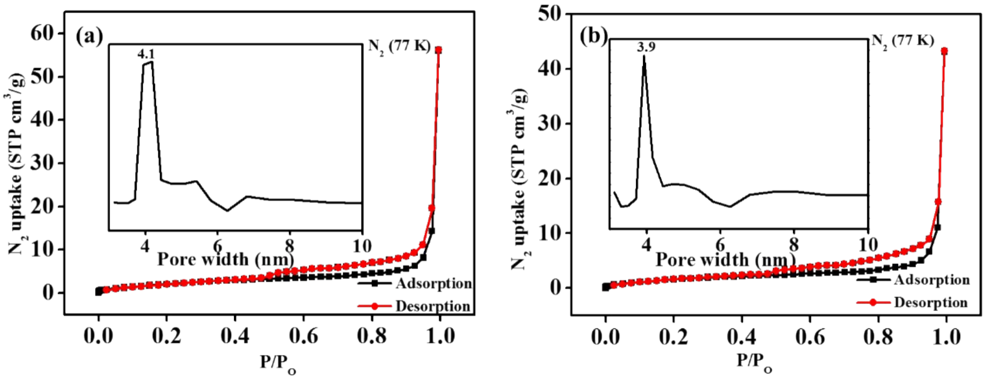
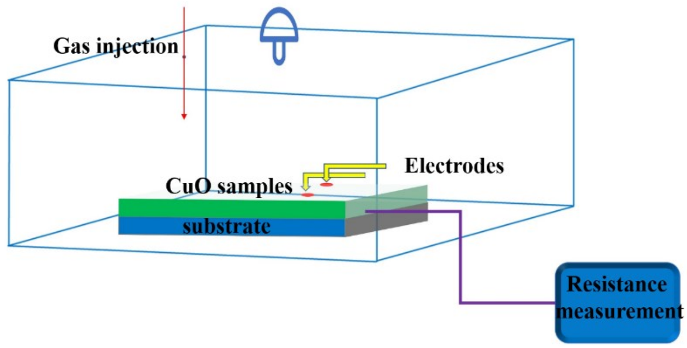


Figure S3 (a) N_2 adsorption-desorption isotherm at 77 K of rod-like CuO. The inset shows pore-size distribution of rod-like CuO (b) N_2 adsorption-desorption isotherm at 77 K of cube-like CuO. The inset shows pore-size distribution of cube-like CuO.



Scheme S1. Schematic drawings of gas sensing measurement system of rod-like and cube-like CuO.

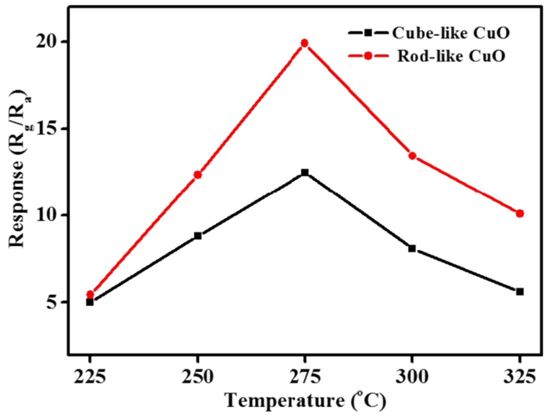


Figure S4 Different gas response for the as-prepared rod-like and cube-like CuO sensor to 200 ppm ethanol at different operating temperatures.

Table S1 Summary of ethanol gas sensors based on different copper oxide morphologies.

Structure/ morphology	C_2H_5OH conc. (ppm)	Gas response (R_g/R_a)	Operating Temperature (℃)	Year of publication	Ref.
nanoparticles	100	2.39	200	2012	[9]
Nanoleaves	1500	8.22	260	2015	[10]
Nanorod (film)	100	~5	210	2011	[11]
Wormlike CuO (film)	100	~4.7	220	2012	[30]
nanoribbons	100	~2.2	200	2008	[31]
nanoplates (film)	100	4.11	200	2012	[32]
Nanowires	1000	1.5	240	2009	[33]
Nanoplates	500	~7	150	2014	[34]
Nanocubes	300	1.51	300	2014	[35]
rod-like CuO	100	12.1	275	This work	
	200	19.9	275		
	300	24.1	275		
	400	28.9	275		
	500	37.4	275		
cube-like CuO	100	8.7	275	This work	
	200	12.5	275		
	300	15.2	275		
	400	19.4	275		
	500	22.9	275		

Table S2 Summary of ethanol gas sensors based on different materials.

Materials	C_2H_5OH conc. (ppm)	Gas response (R_g/R_a)	Operating temperature	Year of publication	Ref.
ZnO nanowires	100	5.07	240	2008	[36]
V_2O_5/SnO_2 Nanowires	1000	14	25	2015	[37]
In_2O_3 nanowires	100	~2	370	2004	[38]
Co_3O_4	500	18.8	210	2018	[39]
Fe_2O_3	200	~6	300	2016	[40]
NiO/SnO_2 thin film	100	7.9	250	2017	[41]
NiO /MWCNTs	100	2	180	2015	[42]
CuO@ZnO microcubes	100	~5.5	240	2016	[43]
rod-like CuO	100	12.1	275	This work	
	200	19.9	275		
	300	24.1	275		
	400	28.9	275		
	500	37.4	275		
cube-like CuO	100	8.7	275	This work	
	200	12.5	275		
	300	15.2	275		
	400	19.4	275		
	500	22.9	275		

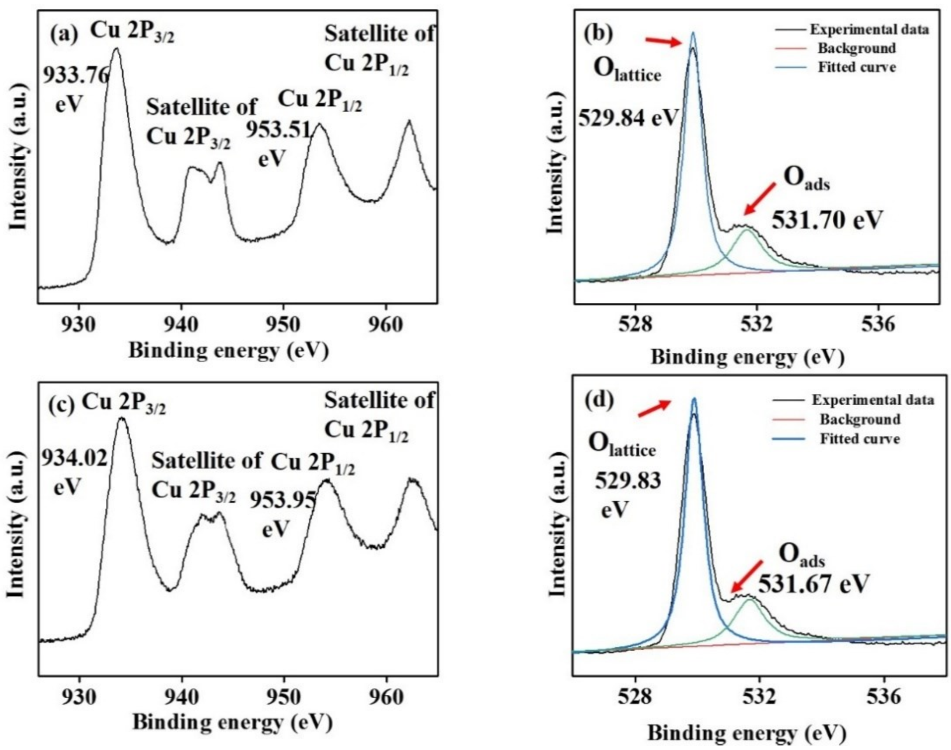


Figure S5 The high-resolution XPS spectra of (a) Cu 2p of rod-like CuO. (b) O 1s of rod-like CuO. (c) Cu 2p of cube-like CuO. (d) O 1s of cube-like CuO.

Equation S1:

$$\log(S_g-1)= b\cdot\log(C_g)+\log(a) \quad (1)$$

Where

a, b, S_g and C_g are the prefactor, absorbed oxygen species charge parameter, the response and tested gas concentration, respectively. The b value is 0.5 or 1, which indicates that the absorbed surface oxygen species on the surface of sensing materials is O^{2-} or O^{-}, respectively.

Equation S2:

$$S_g=\frac{R_{gas}}{R_{air}} = \frac{\frac{L_D}{D_C}\exp(-\frac{qV_{air}}{2kT})\exp(-\frac{\Delta\phi}{2kT}) + \frac{1}{1+\frac{L_D}{D_G}\exp(-\frac{qV_{air}}{2kT})\exp(-\frac{\Delta\phi}{2kT})}}{\frac{L_D}{D_C}\exp(-\frac{qV_{air}}{2kT}) + \frac{1}{1+\frac{L_D}{D_G}\exp(-\frac{qV_{air}}{2kT})}}$$

In which, qV_{air} is the surface potential barrier in air reference, $\Delta \Phi$ is the difference in the surface potential barrier when exposed to the tested gas versus the value in air, T is absolute temperature, k is the Boltzmann constant, Debye-layer length (L_D) is active sensing length, D_C is effective contact area and D_G is grain diameter.

Table S3 Response and recovery time of rod-like and cube-like CuO hierarchical morphology sensor to different ethanol concentrations.

CuO morphology	Gas concentration (ppm)	Response time (s)	Recovery time (s)	Response
rod-like CuO	100	102	40	12.1
	200	89	35	19.9
	300	84	34	24.1
	400	89	37	28.9
cube-like CuO	100	152	59	8.7
	200	154	51	12.5
	300	103	47	15.2
	400	121	45	19.4

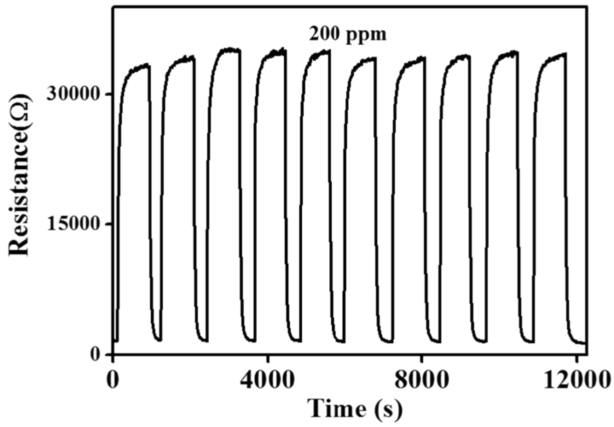


Figure S6 Gas response of rod-like CuO to 200 ppm ethanol after 10 runs at 275 °C and 43 % RH.