

Supplemental Information for:

Multicomponent (Ce, Cu, Ni) oxides with cage and core-shell structures: tunable fabrication and enhanced CO oxidation activity

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Experimental Section

All chemicals were used as received without further purification. The composition and crystal structures of the Cu₂O and composites **1–3** were determined by powder X-ray diffraction using a Bruker AXS GADDS X-ray diffractometer with Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$). FESEM images were collected using a JEOL 6700 SEM system equipped with Oxford EDX detector. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) experiments were performed on a FEI Titan 80/300 high-resolution transmission electron microscope (200 kV), and elemental mapping images were acquired using an EDAX accessory. The existence of surface elements and their valence states were confirmed using Thermo Fisher Scientific Theta Probe XPS measurements. The N₂ sorption isotherms were measured on a micromeritics automatic high resolution physisorption micropore/mesopore analyzer (QuadraSorb SI and ASAP2020MP).

Synthesis of Cu₂O cubes: Cu₂O cubes were synthesized using a modified procedure.^[1] In a typical experiment, Cu(OAc)₂·H₂O (0.144 g) and PVP (0.8 g) were dissolved in ethanol (65 mL). The mixture was stirred for 30 min at room temperature and the transparent solution transferred to a 100 mL-Teflon-lined autoclave and heated at 180 °C for 8 h. The autoclave was allowed to cool to room temperature. The orange product was collected and washed with ethanol in rinse-centrifuge cycles, then dried at 60 °C in an oven overnight.

Synthesis of composites **1–3:** The Cu₂O cubes synthesized above were suspended in a mixture of ethanol (40 mL) and NaCl aq. (1.71 M, 0.500 mL) at room temperature. The mixture was heated in an oil bath at 55 °C with continuous stirring for 10 min, then a measured amount of different metal precursor dissolved in an ethanol solution (20 mL) was added into the mixture dropwise. The reaction was allowed to proceed until the solution changed from orange to the expected colour (**1** and **3**: yellow green; **2**: pale orange). The products were collected by centrifugation and washed three times with water and ethanol, then dried at 60 °C in an oven overnight. Comparative reaction conditions for **1–3** are listed in Table S1.

Catalytic testing: Testing of catalysts for CO oxidation using the as-synthesized samples (~25 mg, Cu₂O and composites **1–3**) was conducted with a continuous flow, fixed-bed microreactor operating at atmospheric pressure. The gas mixture (1% CO, 10% O₂, 89% N₂) was passed through the reactor at a rate of 60 mL·min⁻¹. An online infrared gas analyzer (Gasboard-3121, China Wuhan Cubic Co.) recorded the exiting gas composition with a detection limit of 10 ppm. The activation energies of Cu₂O and composites **1–3** were calculated using the equations^[2]:

$$\ln k = \ln A - E_a/RT \quad (1)$$

$$k = (F/W) \cdot x \quad (2)$$

where F is the flow of the gaseous molecules in mol/s, which is constant in the CO oxidation test, W is the weight of the catalyst sample and x is the fractional CO conversion.

Table S1 Comparative reaction conditions for the formation of composites **1–3**

Composite	Template	Metal precursor / mmol	Reaction time / min
1	Cu ₂ O	Ce(NH ₄) ₂ (NO ₃) ₆ , 2.7	30
2	Cu ₂ O	NiCl ₂ , 3.0	30
3	2	Ce(NH ₄) ₂ (NO ₃) ₆ , 1.8	10

Table S2. XPS data for Cu₂O and composites **1–3**

Sample	Cu 2p (eV)	O 1s (eV)	Ce 3d (eV)	Ni 2p (eV)
Cu ₂ O	932.4; 934.5	530.4; 531.5	-	-
1	932.7; 934.4	529.8; 531.6	882.8; 889.2 898.6; 900.9 908.2; 917.0	-
2	933.0; 935.0	531.3	-	855.7; 861.1 882.5; 889.1
3	933.1; 934.9	529.7; 531.5	898.5; 901.0 907.9; 916.9	856.2; 861.5

Table S3 Comparison of surface areas, T_{100} , activation energies for CO oxidation over different catalysts

Sample	S_{BET} (m^2/g)	T_{100} ($^{\circ}\text{C}$)	E_a (kJ/mol)	Ref
Cu_2O	4.15	320	101.0 ± 8.0	
1	36.08	240	30.0 ± 1.9	this work
2	3.47	305	87.3 ± 2.8	
3	21.46	250	41.5 ± 1.7	
$\text{Ce}_{0.65}\text{Fe}_{0.33}\text{Pd}_{0.02}\text{O}_{1.815}$	169	85	~ 38	[2]
CeO_2	19.0	398	124.5 ± 9.4	
$\text{Cu}_{0.05}\text{Ce}_{0.95}\text{O}_2$	28.2	300	55.2 ± 1.8	[3]
$\text{Cu}_{0.10}\text{Ce}_{0.90}\text{O}_2$	26.8	275	34.2 ± 2.0	
$\text{Sn}_{0.95}\text{Cu}_{0.05}\text{O}_{2-\delta}$	33	225	50	[4]
$\text{Ni}/\text{CeO}_2\text{-r}$	64	130	~ 55.4	[5]

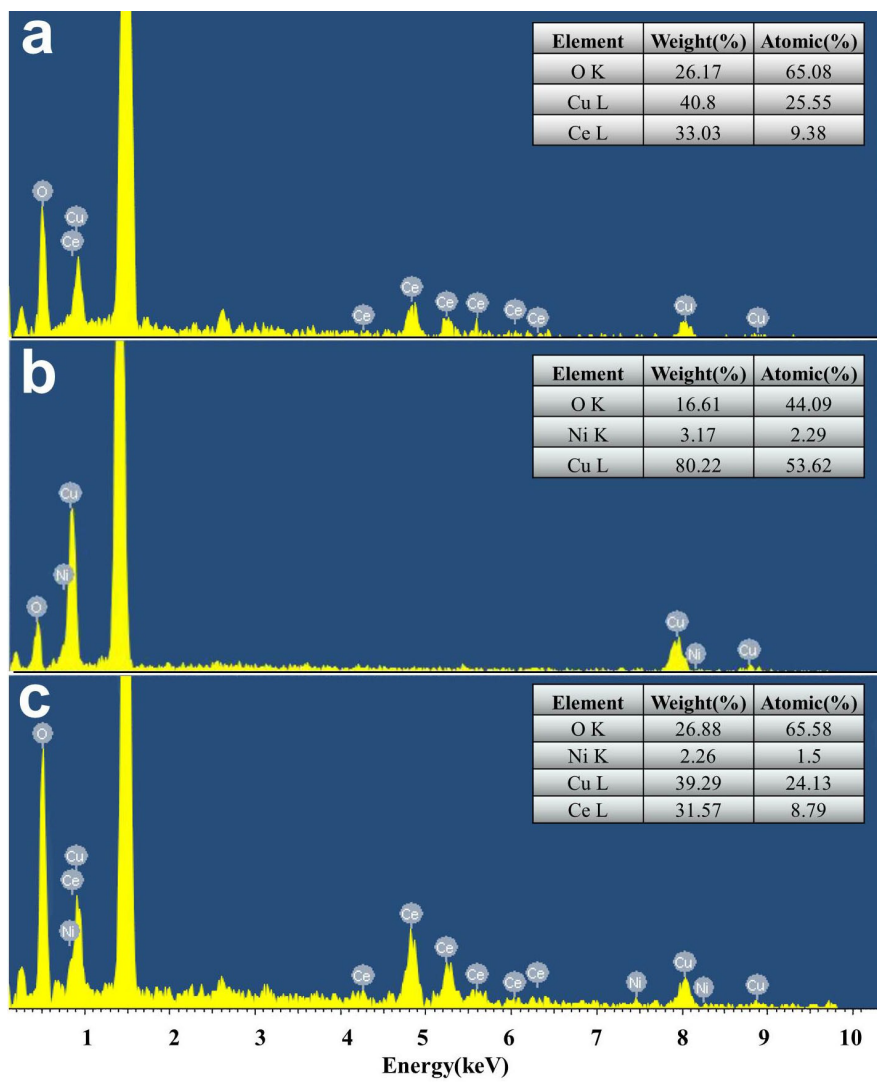


Fig. S1 EDX spectra of composites 1–3 (a–c).

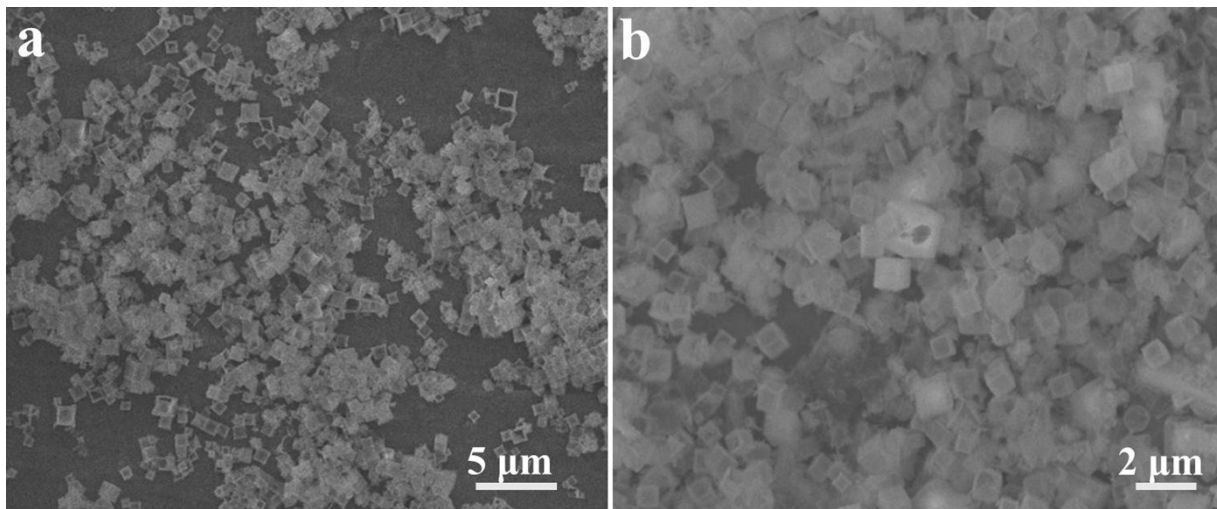


Fig. S2 Low magnification SEM images of composites **1(a)** and **3(b)**.

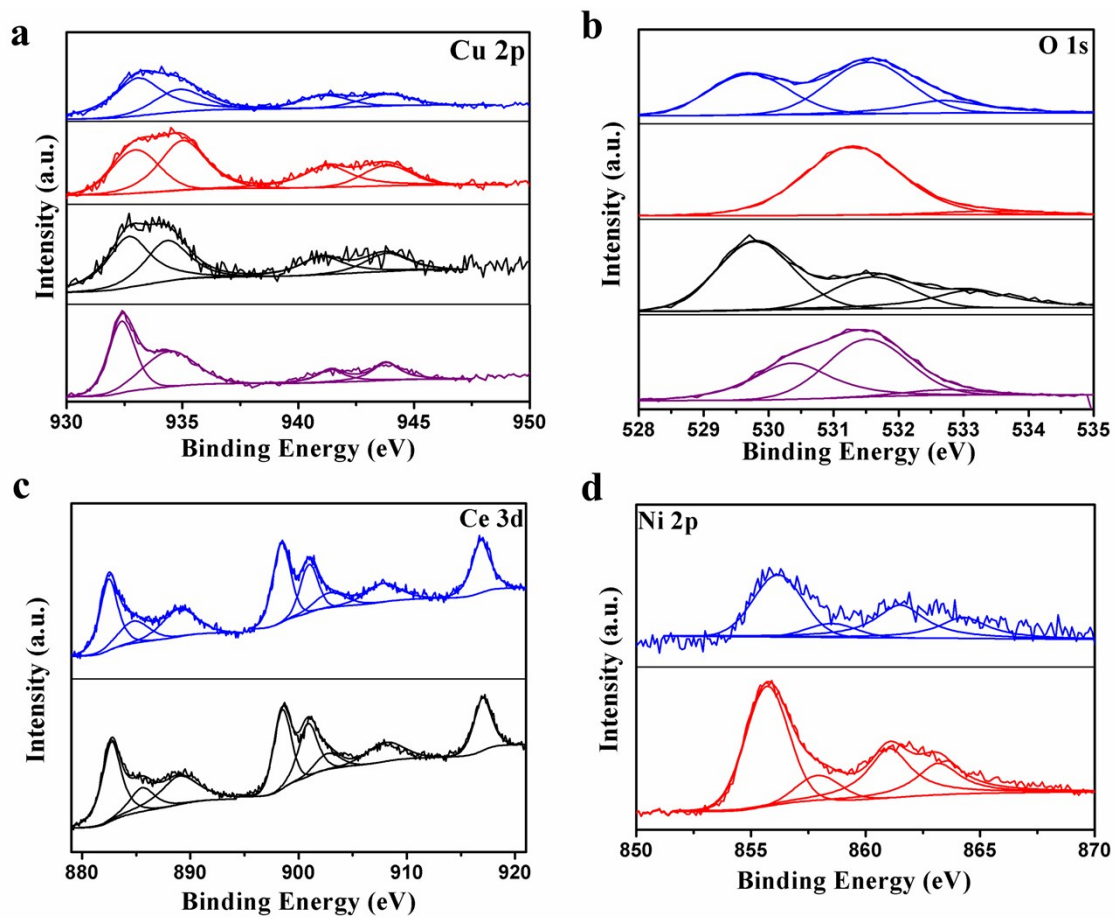


Fig. S3. XPS spectra of Cu₂O and composites 1-3 (purple, Cu₂O; black, 1; red, 2; blue, 3).

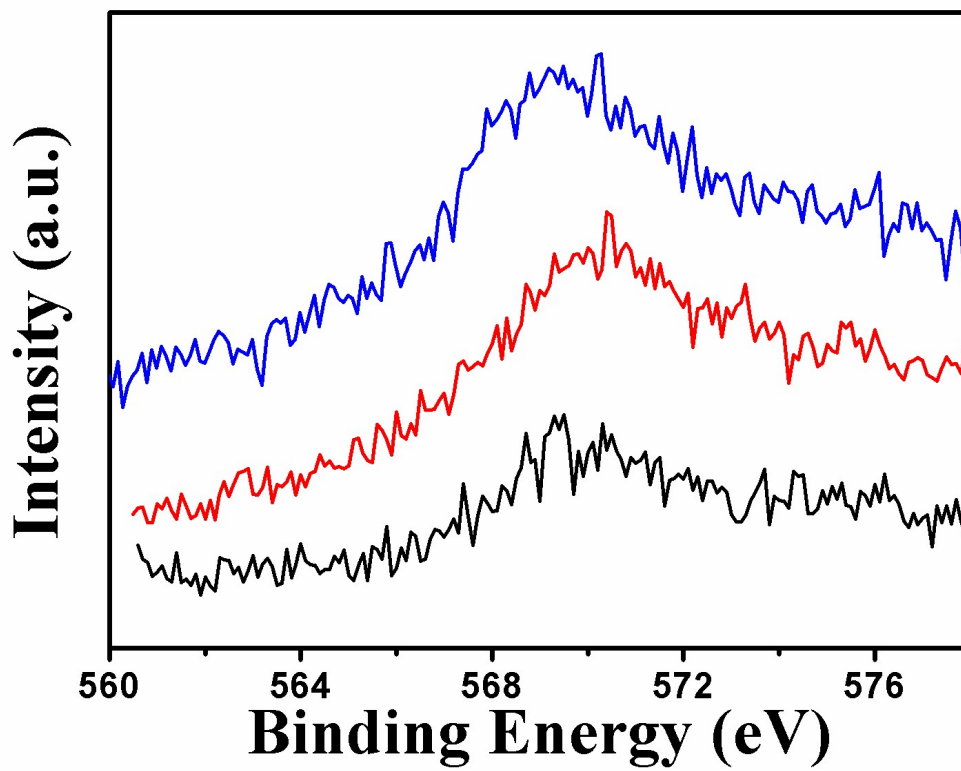


Fig. S4 Cu LMM Auger peaks of 1–3 (1-black, 2-red and 3-blue).

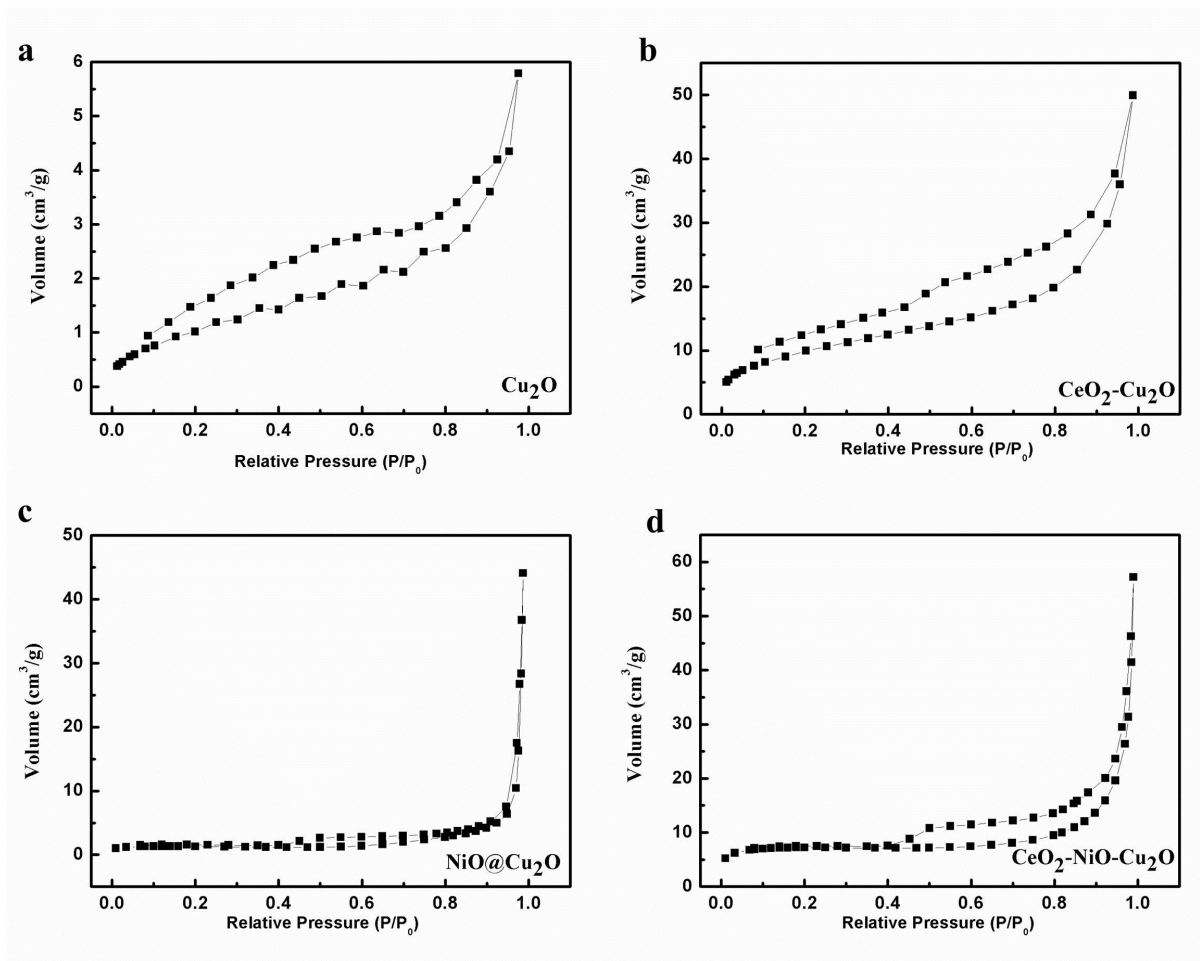


Fig. S5 N_2 sorption isotherms of Cu_2O and composites 1-3.

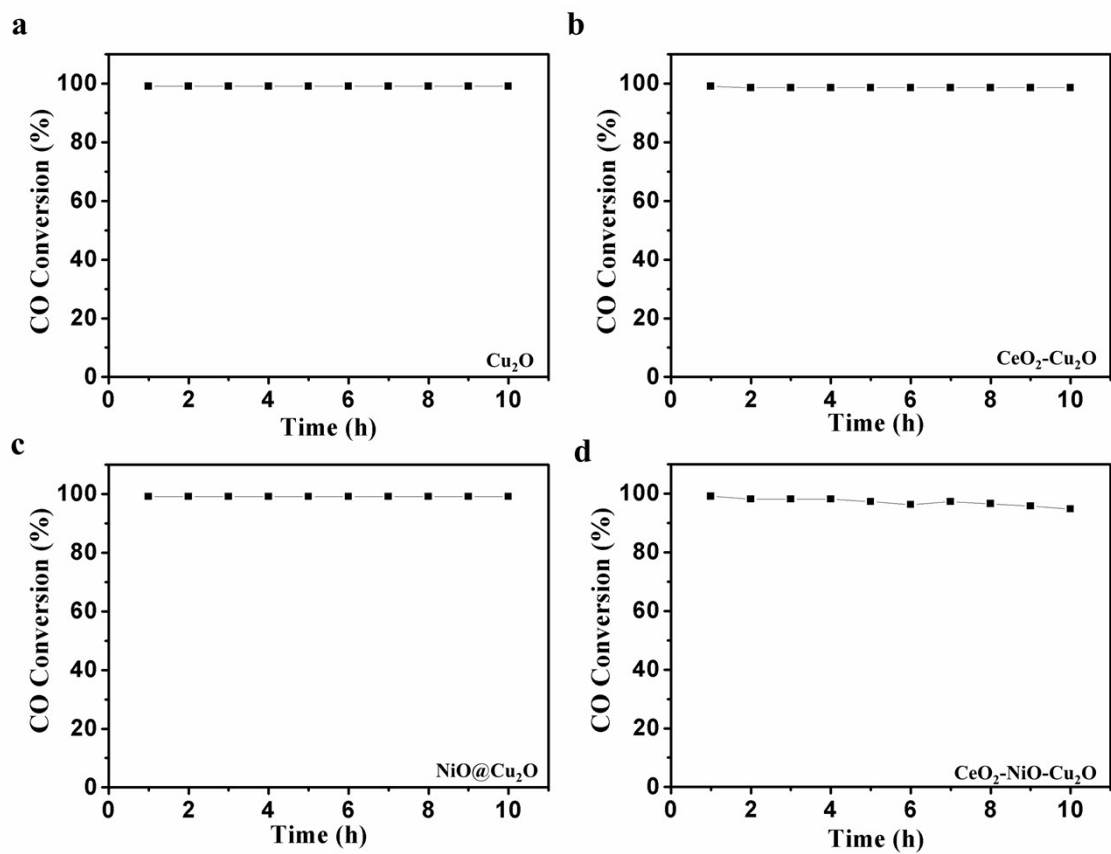


Fig. S6 Thermal stability tests of Cu_2O and **1–3**. Reaction conditions: at T_{100} after the third run.

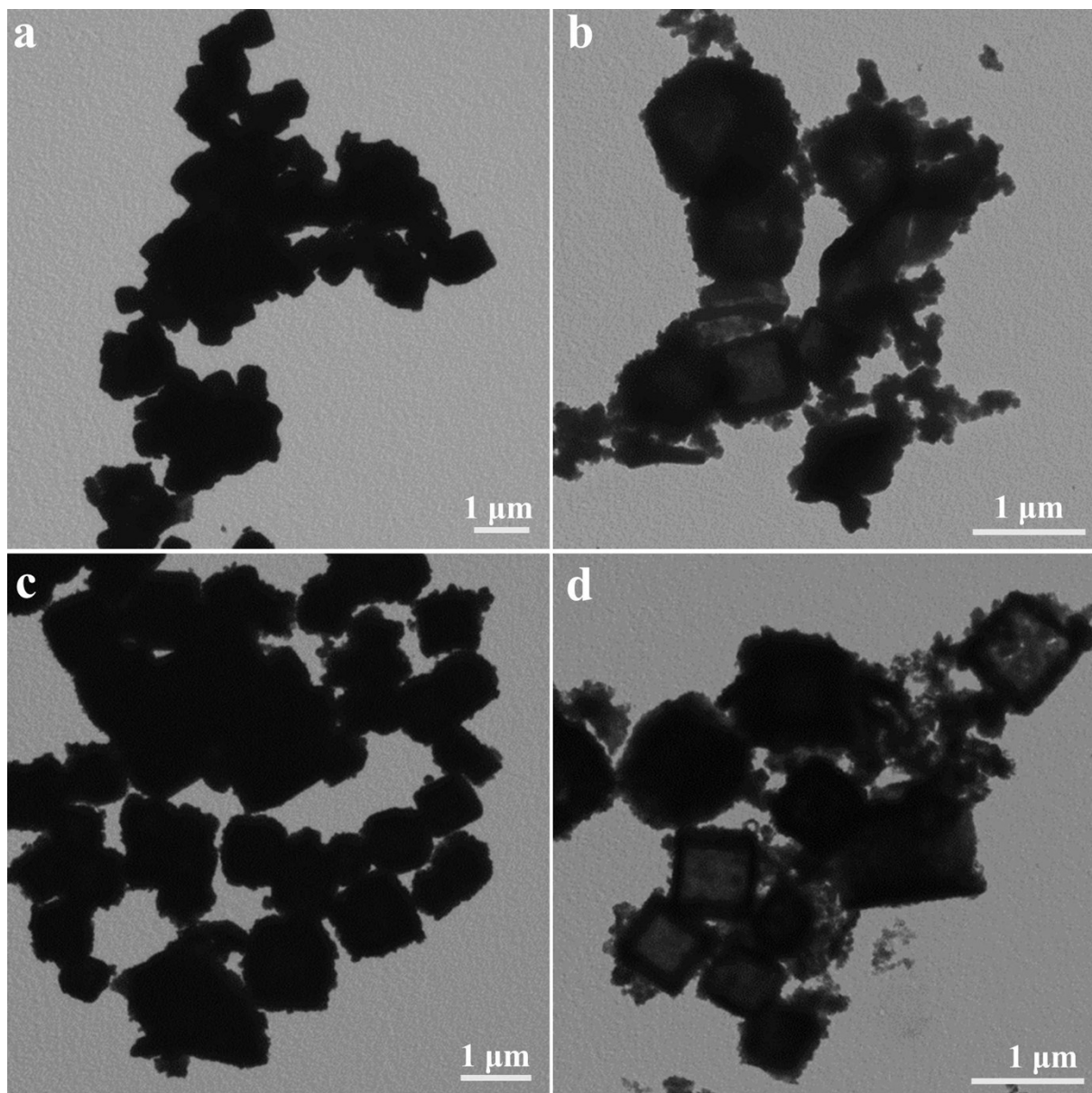


Fig.S7 TEM images of catalysts Cu_2O (a), 1–3 (b–d) after cycle tests and thermal treatment.

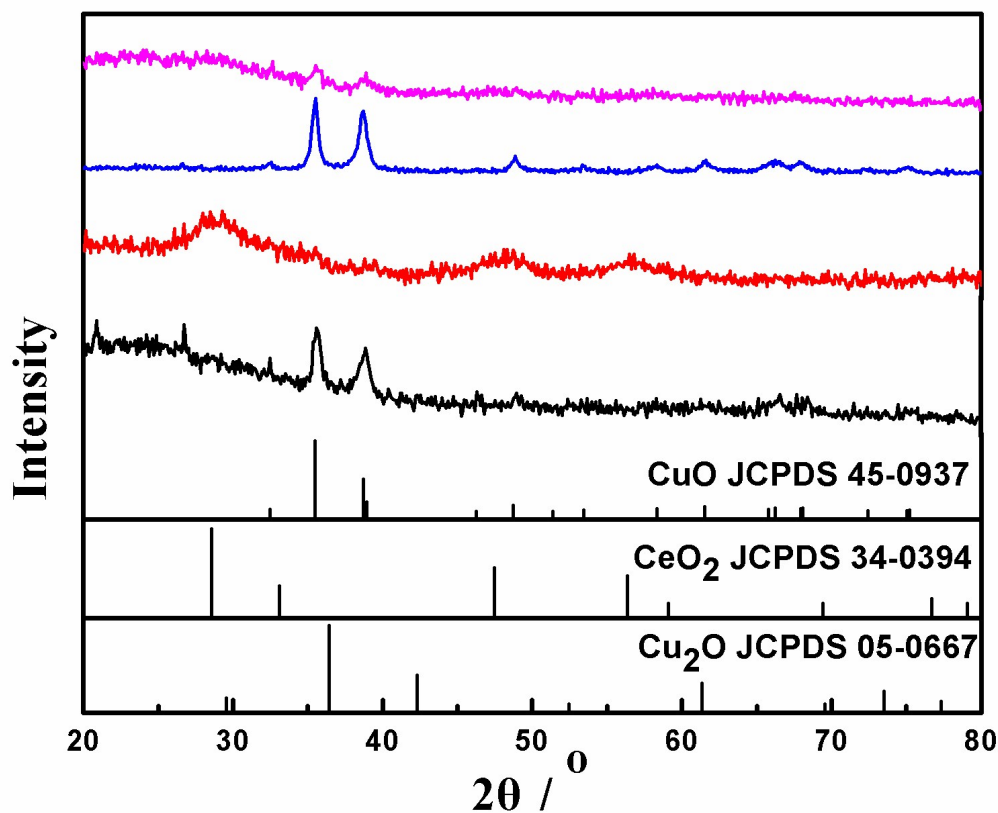


Fig. S8 XRD patterns of catalysts Cu₂O (black), **1** (red), **2** (blue) and **3** (magenta) after cycle tests and thermal treatment.

References

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