

Structural Evolution of Cu₂O-Derived Hybrids Comprised of Cu Cores, Silica Interlayer, and Carbon as Outlayer

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Experimental Section

Synthesis of the Cu₂O nanoparticles(NPs)

The spherical Cu₂O NPs were fabricated according to a previous report. In a typical procedure, Cu(Ac)₂•H₂O (1.8 g) and PVP-55,000 (10.8 g) were first dispersed into a mixed solution, which comprising of 180 mL deionized water and 20 mL anhydrous ethanol, and ultrasonicated for 20 min at ambient temperature. Then, ascorbic acid (1.8 g) was quickly added to the mixture solution, followed by gentle stirring. The reaction was continued for 20 min at room temperature. After that, the orange-colored solution was centrifuged, then dried at 60 °C for 12 h under vacuum to acquire the Cu₂O NPs.

Synthesis of the Cu₂O@Co(OH)₂

The 20mg freshly prepared Cu₂O, 50 mg CoCl₂•6H₂O and 1.33 g PVP were dispersed in a liquid of 20 mL of ethanol and 20 mL of deionized water, then ultrasonicated for 10 minutes. Subsequently, Na₂S₂O₃ (10 mg) was added to the above solution and Continue ultrasonicated for 30 minutes. After the reaction, the suspension was centrifuged (7500 rpm, 3 min) and washed twice with distilled water and ethanol, then dried at 50 °C for 12 h.

Synthesis of the Cu₂O@SiO₂

The Cu₂O NPs (30 mg) were dispersed in a liquid of 35 mL of ethanol, 4 mL of deionized water and 0.5 mL NaOH aqueous solution (0.2 M), followed by using sonication for 20 min, and then, TEOS (0.4 mL) was slowly dropped into the mixture solution for the specified reaction time at room temperature. The resultant Cu₂O@SiO₂ particles were collected by centrifugation (7500 rpm, 3 min) and washed five times with distilled water and ethanol, and dried at 50 °C for 12 h.

Synthesis of Cu₂O@SiO₂@RF

The freshly prepared Cu₂O@SiO₂ (50 mg) was dispersed into 50 mL of an alcohol–water system with a volume ratio of ethanol to water of 9:1, then, 1 mL of 28–30% NH₃H₂O was added under ultrasound conditions. After that, resorcinol (15 mg) was dissolved in 1 mL deionized water and 2 ml ethanol, were slowly dropped into the above solution, 5 minutes later, 0.28 mL of formaldehyde was added to this solution, then continue ultrasonicated for 7 h. After that, with the help of centrifuge, the products of Cu₂O@SiO₂@RF particles were collected and washed three times with distilled water and ethanol, and dried at 50 °C for 6 h.

Synthesis of Cu@SiO₂@C

The as-prepared Cu₂O@SiO₂@RF powder was placed in a ceramic boat at the middle of a horizontal tube furnace. After heating at 150 °C for 1 h and continuously increasing to 400°C, 500°C, 700°C, 900°C, respectively, and maintaining for 5 h with a ramp rate of 2°C min⁻¹ in N₂ gas, the black powder were obtained, which were denoted as Cu@SiO₂@C/400, Cu@SiO₂@C/500, Cu@SiO₂@C/700, Cu@SiO₂@C/900, respectively.

Characterization

X-ray diffraction (XRD) patterns of each sample were recorded with a Shimadzu (Japan) D/Max-2500 diffractometer, using a monochromatized X-ray beam with nickel-filtered Cu K α radiation. Scanning electron microscopy (SEM) images were obtained on a JEOL JSM-6700 M scanning electron micro-scope. Transmission electron microscopy (TEM) images were obtained on a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV. Raman spectra were obtained using a confocal microprobe Raman system (HR800). The specific surface area was analysed by the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was calculated from the adsorption branch of the isotherm. X-ray photo-electron spectroscopy (XPS) measurements were performed on a VGES-CALAB MKII X-ray photoelectron spectrometer. Fourier-Transform Infrared (FTIR) spectra were recorded on a VECTOR-22 FTIR spectrometer with a potassium bromide pellet as the control. Inductive coupled plasma spectroscopy (700-ES, Varian, USA) is used to test the content of Cu in different samples.

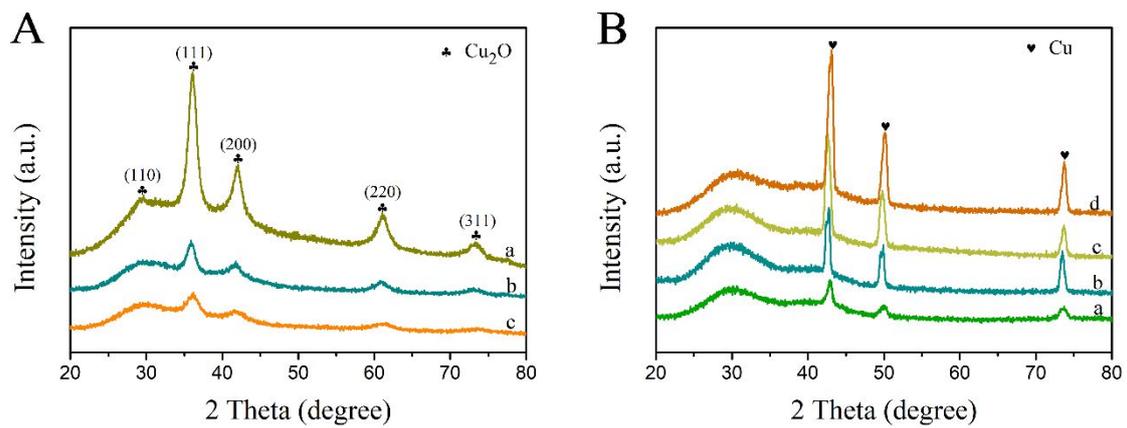


Fig. S1 X-Ray diffraction patterns of Cu_2O cubes (A-a), $\text{Cu}_2\text{O}@\text{SiO}_2$ (A-b), $\text{Cu}_2\text{O}@\text{SiO}_2@\text{RF}$ (A-c), $\text{Cu}@\text{SiO}_2@\text{C}$ submicrorattles annealed at 400 °C (B-a), 500 °C (B-b), 700 °C (B-c) and 900 °C (B-d).

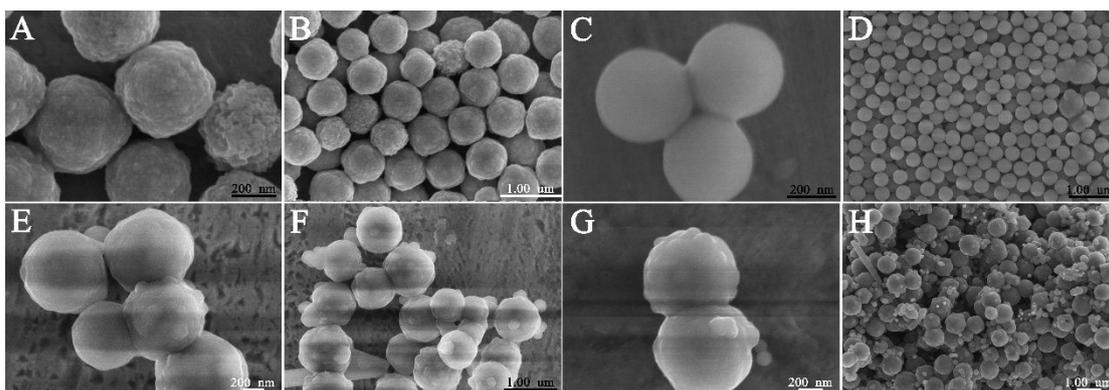


Fig. S2 (a) SEM image of $\text{Cu}_2\text{O}@Co(\text{OH})_2$ (A and B), the $\text{Cu}_2\text{O}@Co(\text{OH})_2@SiO_2$ structure (C and D), the $\text{Cu}_2\text{O}@Co(\text{OH})_2@SiO_2@RF$ structure (E and F) and $\text{Cu-Co}@SiO_2@C/700^\circ\text{C}$ structure (G and H).

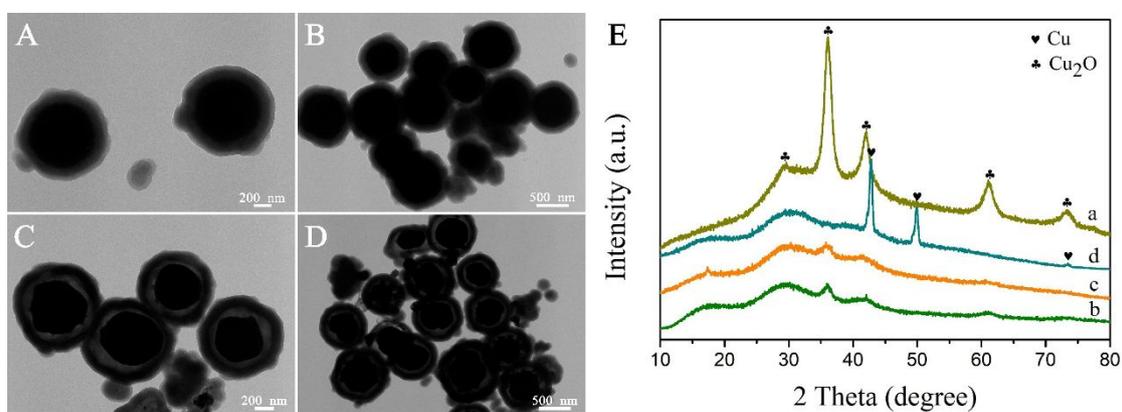


Fig. S3 TEM images of (A, B) $\text{Cu}_2\text{O}@Co(\text{OH})_2@SiO_2@RF$ and (C,D) $\text{Cu-Co}@SiO_2@C/700^\circ\text{C}$, XRD patterns of Cu_2O (E-a), $\text{Cu}_2\text{O}@Co(\text{OH})_2$ (E-b), $\text{Cu}_2\text{O}@Co(\text{OH})_2@SiO_2@RF$ (E-c) and $\text{Cu-Co}@SiO_2@C/700^\circ\text{C}$ (E-d).

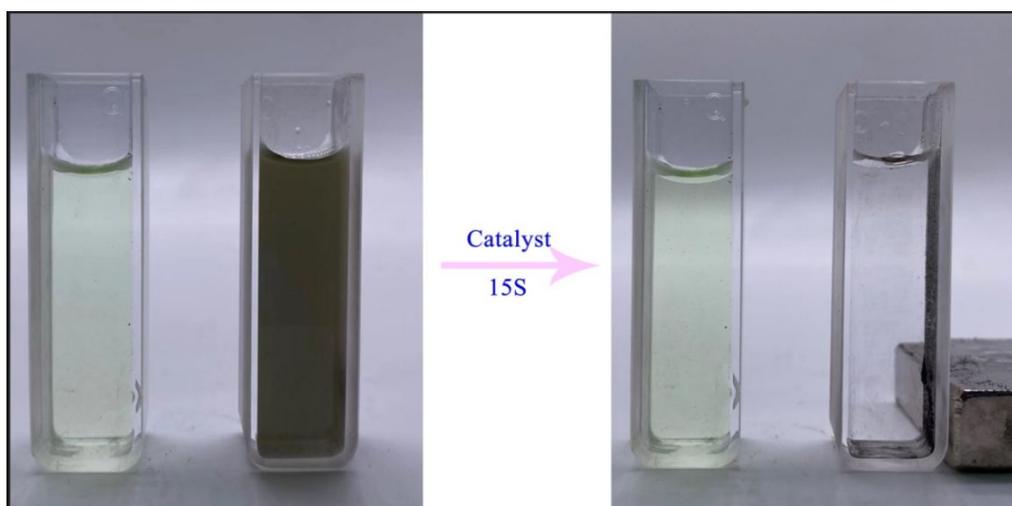


Fig. S4. The photo of $\text{Cu-Co}@SiO_2@C/700^\circ\text{C}$ magnetic separation after catalyzing 4-NP.

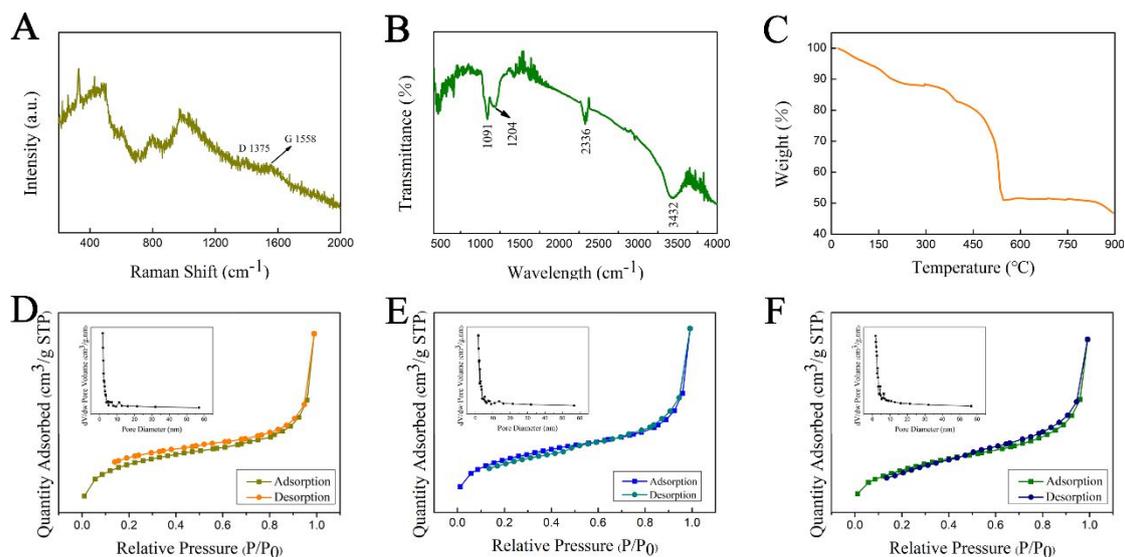


Fig. S5 (A) Raman spectra of Cu@SiO₂@C/700, (B) FTIR spectra of Cu@SiO₂@C/700, (C) TGA curve of Cu₂O@SiO₂@RF, N₂ adsorption–desorption isotherms and the pore size distribution curve of Cu@SiO₂@C after annealing at 500°C (D), 700°C (E) and 900 °C (F).

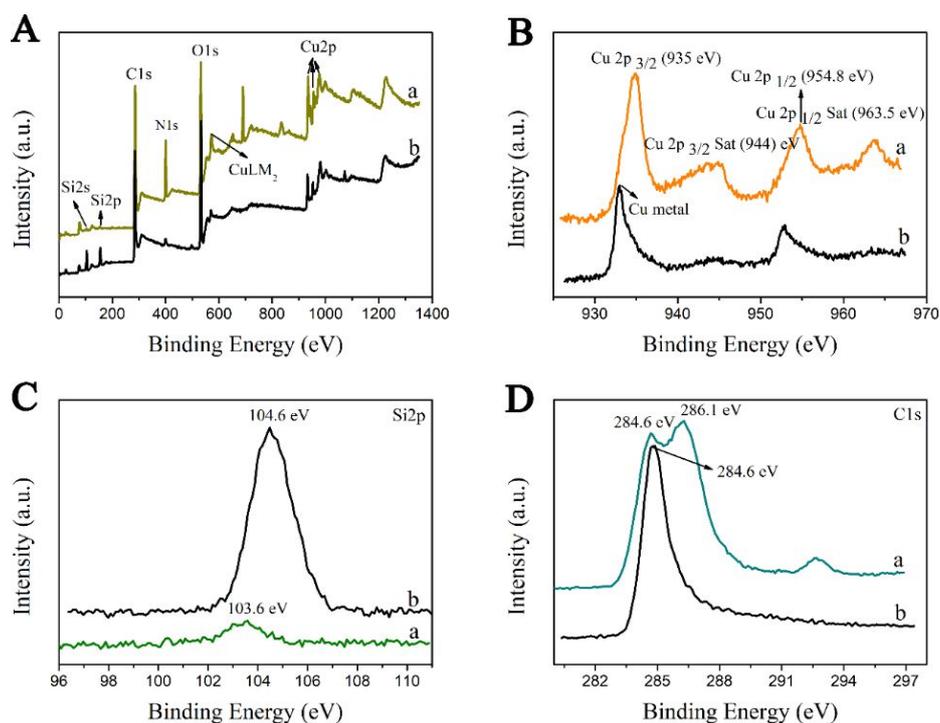


Fig. S6. (A) XPS spectra of Cu₂O@SiO₂@RF (a) and Cu@SiO₂@C/700 (b) the full survey scan, (B) Cu 2p, (C) Si 2p, and (D) C 1s.

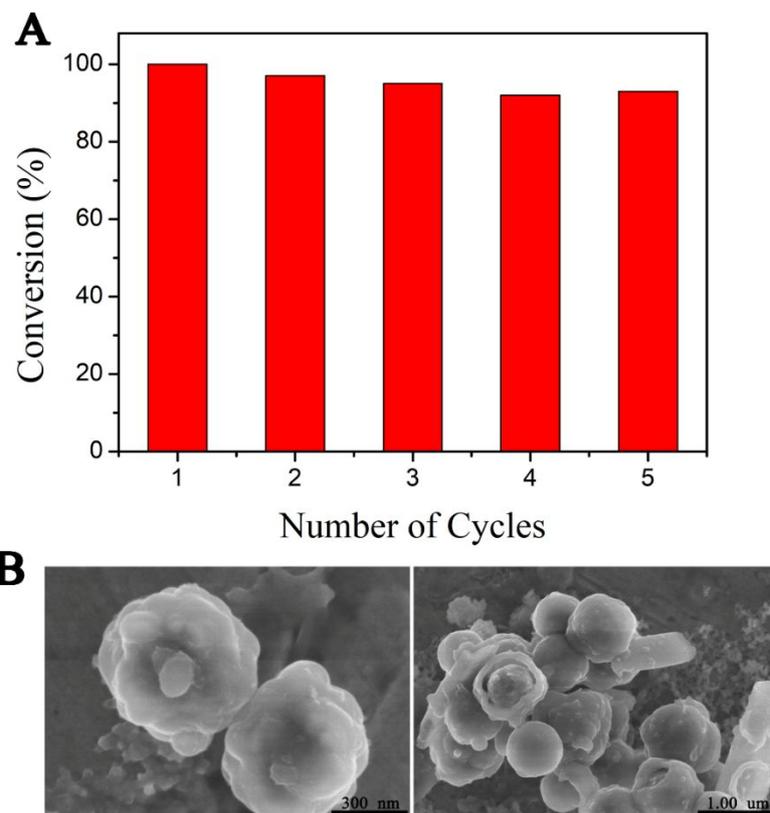


Fig. S7. (A) The reusability of Cu@SiO₂@C/700 as the catalyst for the reduction of 4-NP with NaBH₄. (B) SEM images of Cu@SiO₂@C/700 as a catalyst to reduce 4-NP with reused in 5 successive reactions.

Table S1. Surface Area, Pore Volume and Pore Size of Cu@SiO₂@C/500, Cu@SiO₂@C/700 and Cu@SiO₂@C/900 composite.

| Materials | Surface Area | Pore Volume | Pore Size |
|----------------------------|-------------------------|--------------------------|-----------|
| Cu@SiO ₂ @C/500 | 55.73 m ² /g | 0.016 cm ³ /g | 8.16 nm |
| Cu@SiO ₂ @C/700 | 38.87 m ² /g | 0.013 cm ³ /g | 8.25 nm |
| Cu@SiO ₂ @C/900 | 36.67 m ² /g | 0.017 cm ³ /g | 7.97 nm |

Table S2. ICP data of Cu@SiO₂@C/(500, 700 and 900°C)

| Catalyst | Cu (μg/mg) |
|----------------------------|------------|
| Cu@SiO ₂ @C/500 | 0.0919 |
| Cu@SiO ₂ @C/700 | 0.1043 |
| Cu@SiO ₂ @C/900 | 0.3048 |

Table S3. Comparison of the two kinds of rate constants k and κ of the Cu@SiO₂@C catalysts with the reported data for the reduction of 4-NP to 4-AP in the presence of NaBH₄

| Samples | k (*10 ⁻³ s ⁻¹) | κ (*10 ⁻³ mg ⁻¹ ·s ⁻¹) | References |
|----------------------------|--|---|----------------|
| Cu@SiO ₂ @C/500 | 5.76 | 62.2 | This work |
| Cu@SiO ₂ @C/700 | 11.38 | 109.1 | This work |
| Cu@SiO ₂ @C/900 | 18.8 | 61.7 | This work |
| CuO-Cu ₂ O/Pd | 8.722 | / | S ¹ |
| Cu cubes | 10.1 | 105 | S ² |
| Cu@Ni-NWs/G | 19.3 | 96.8 | S ³ |
| Ni/C@SiO ₂ -700 | 7.310 | 88.72 | S ⁴ |
| Ag/ZrGP | 2.92 | 19.32 | S ⁵ |
| Pd/SPB-PS | 4.4 | 116 | S ⁶ |

Notes and references

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