Electronic Supplementary Material (ESI) for CrystEngComm.

Morphology-selective crystallization of cocatalysts on cuprous oxide with improved photocatalytic activity

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Synthesis of Cu_2O cubes and octahedron

All the chemical reagents were used as obtained. In a typical procedure of synthesizing cubic Cu_2O, 10 mL of 2.0 M NaOH aqueous solution was added to 100 mL of 0.01 M $CuCl_2$ aqueous solution at 55 ℃. After stirring for 0.5 h, 10 mL of 0.6 M ascorbic acid aqueous solution was added to the above solution. The mixed solution was kept at 55 ℃ with stirring for 5 h, and then gradually became brick-red, indicating formation of Cu_2O. After that, the final products were collected by centrifugation, washing with distilled water and absolute ethanol several times and drying in a vacuum oven at 40 ℃ for 6 h. In a typical procedure of synthesizing octahedral Cu_2O, 1.67 gram of polyvinylpyrrollidone was added to 50 mL of 0.01 M

$CuCl_2$ aqueous solution at 55 ℃. After stirring for 10 min., 5 mL of 2.0 M NaOH aqueous solution was added to the above mixed solution. After stirring for 30 min., 5 mL of 0.6 M ascorbic acid aqueous solution was added. The mixed solution was kept at 55 ℃ with stirring for 5 hrs. The product was processed following the same procedure as the cubes.

Synthesis of MnO_x-Cu_2O heterostructures

The MnO_x-Cu_2O heterostructures were obtained by an oxidation route under light irradiation. First, 20 mg Cu_2O cubes were dispersed into 8 mL distilled water by sonication. And then the suspension was irradiated with a 300 W Xe lamp (PLS-SXE300) with a cutoff filter (λ<420nm). Under continuous stirring, 1.0 mL of 5.9 mM $MnSO_4$ aqueous solution and 1.0 mL of 15 mM $NaIO_3$ aquesou solution were simultaneously added to the above suspension, and the mixed solution reacted for 5 hrs. After that, the final products were collected by centrifugation, washing with distilled water and absolute ethanol several times and drying in a vacuum oven at 40 ℃ for 6 hrs.

Synthesis of NiO_x-Cu_2O heterostructures

Synthesis of the NiO_x-Cu_2O heterostructures followed the same route as MnO_x-Cu_2O except nickel precursor. First, 20 mg Cu_2O cubes were dispersed into 8 mL distilled water by sonication. Under continuous stirring, 1.0 mL of 1.3 mM $NiCl_2$ aqueous solution and 1.0 mL of 5 mM $NaIO_3$ aquesou solution were simultaneously added to the above suspension, and the mixed solution reacted for 5 hrs. After that,

the final products were collected by centrifugation, washing with distilled water and absolute ethanol several times and drying in a vacuum oven at 40 ℃ for 6 hrs.

Synthesis of Fe_xO_y-Cu_2O heterostructures

Synthesis of the Fe_xO_y-Cu_2O heterostructures followed the same route as MnO_x-Cu_2O except iron precursor. As for 5% Fe_xO_y-Cu_2O sample. First, 50 mg Cu_2O cubes were dispersed into 14 mL distilled water by sonication. And then the suspension was irradiated with a 300 W Xe lamp (PLS-SXE300) with a cutoff filter (λ<420nm). Under continuous stirring, 1.0 mL of 18 mM $FeSO_4$ aqueous solution and 1.0 mL of 15 mM $NaIO_3$ aquesou solution were simultaneously added to the above suspension, and the mixed solution reacted for 5 hrs. After that, the final products were collected by centrifugation, washing with distilled water and absolute ethanol several times and drying in a vacuum oven at 40 ℃ for 6 hrs. In 1% Fe_xO_y-Cu_2O sample preparation, 1.0 mL of 3.6 mM $FeSO_4$ aqueous solution was added while the other conditions were kept the same. Pristine iron oxide was synthesized by the same procedure except no Cu_2O addition.

Characterizations

The X-ray diffraction (XRD) patterns of the products were measured by using a BRUKER D8 Discover diffractometer with Cu-K_α radiation (λ = 0.15406 nm), and at a scanning rate of 0.02 deg/s in the 2θ range from 28° to 80°. Scanning electron microscopy (SEM) images were obtained using a Hitachi S4800 SEM.

Photocatalytic activity test

Photocatalytic studies were carried out as follows: 15 mg of catalyst sample was dispersed into a 50 mL of 2×10^{-5} M methyl orange (MO) aqueous solution. The suspended solution was magnetically stirred in the dark for 0.5 h to reach its adsorption/desorption equilibrium, and then it was irradiated with magnetic stirring in a water bath kept at 25 ℃ under a 300 W Xe lamp (PLS-SXE300, 150 mw/cm^2) equipped with UV filter (cutoff filter <420 nm) from a given distance of ca. 15 cm. At a given time interval, aliquot of the dispersion solution was taken for analysis on a spectrophotometer (PE Lambda 650s).

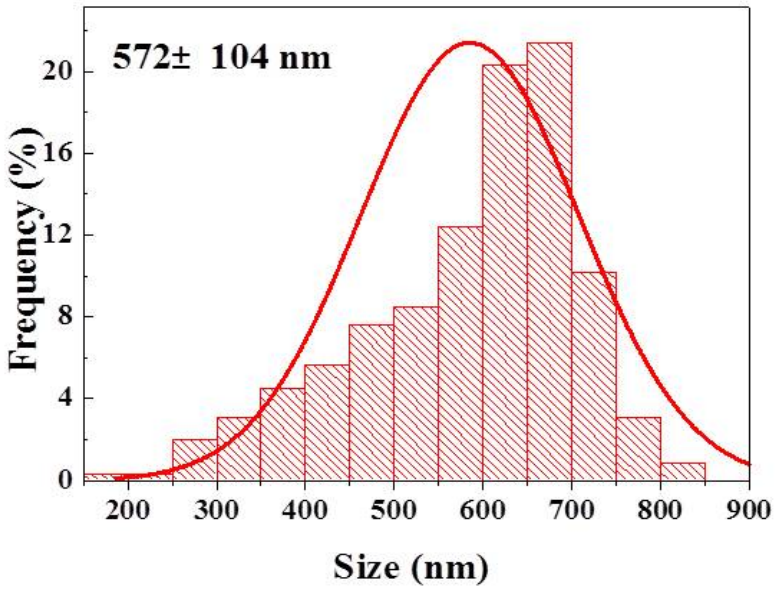

Fig. S1 Size distribution histogram of cubic Cu_2O obtained in this work.

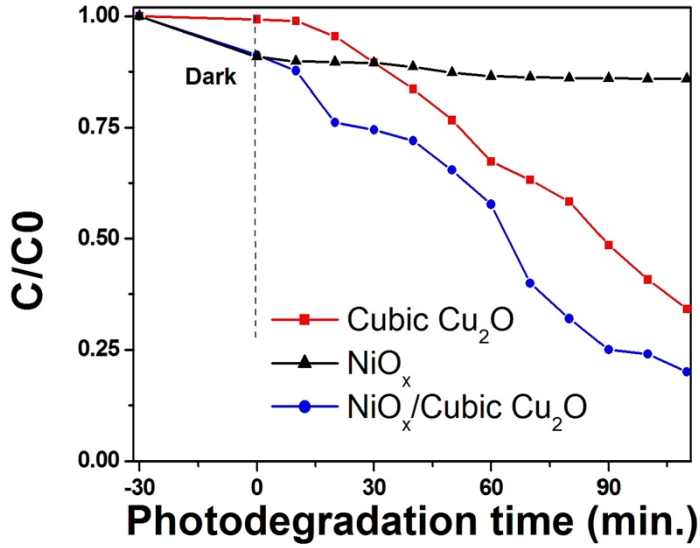

Fig. S2 Photodegradation of methyl orange by NiO_x/Cu_2O hybrid photocatalyst (blue line with round dots), pristine cubic Cu_2O sample (red line with rhombi) and pristine NiO_x sample (black line with triangles)

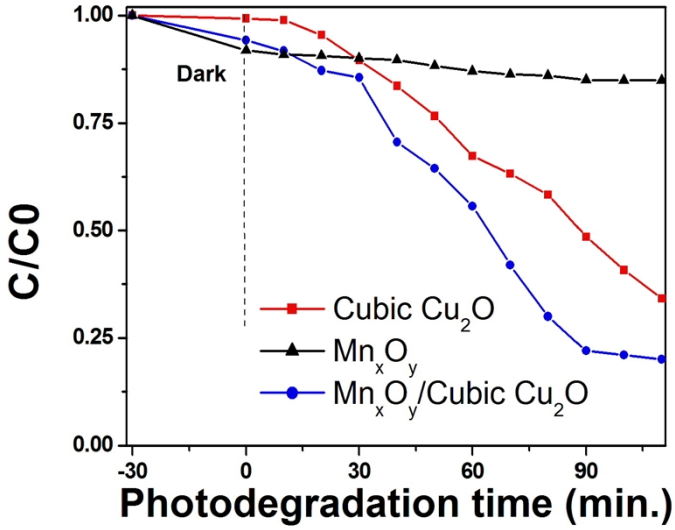

Fig. S3 Photodegradation of methyl orange by Mn_xO_y/Cu_2O hybrid photocatalyst (blue line with round dots), pristine cubic Cu_2O sample (red line with rhombi) and pristine NiO_x sample (black line with triangles)

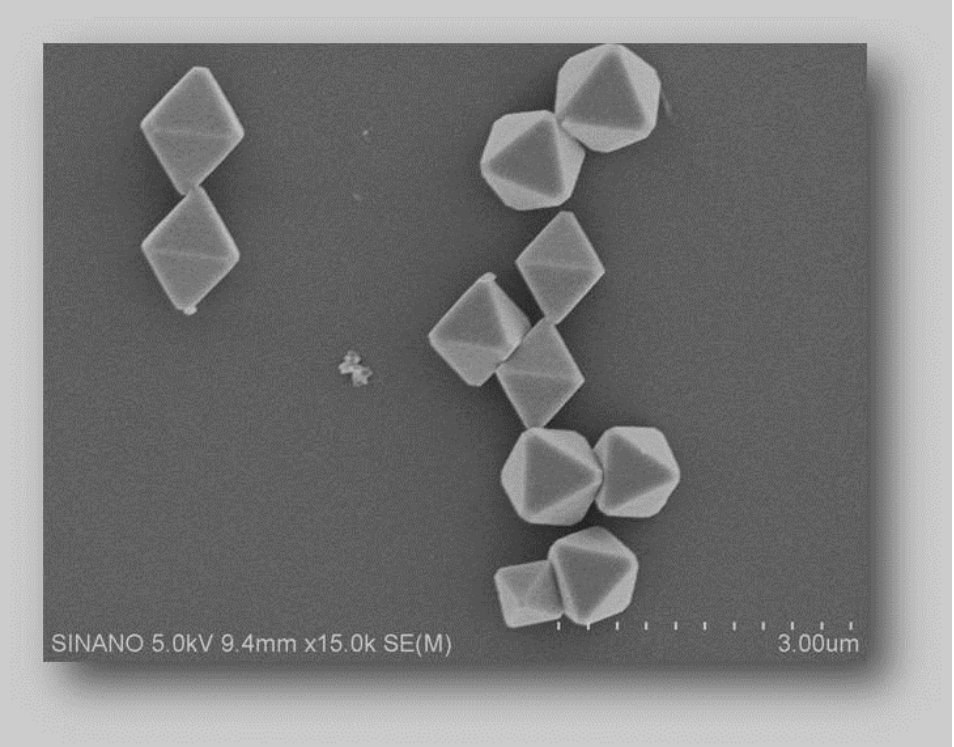

Fig. S4 SEM image of as-obtained truncated Cu_2O octahedron.

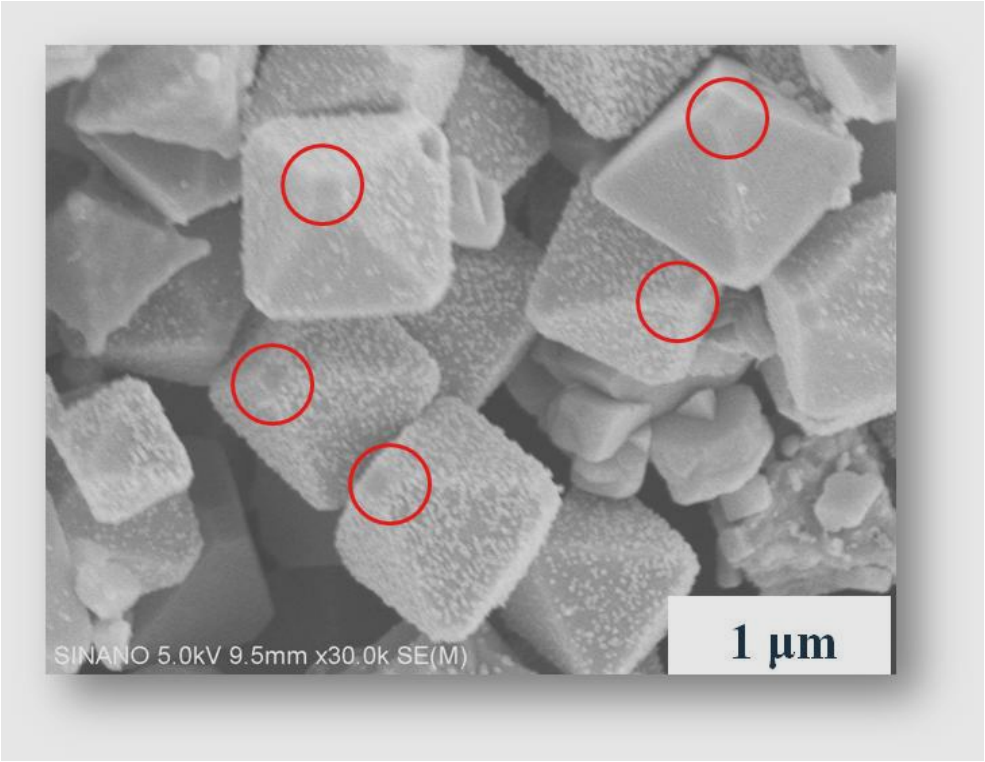

Fig. S5 SEM image of Au/octahedral Cu_2O, showing highly selective-deposition of gold on facet {111} other than facet {100}.