Supporting Information

Inside-out Core-Shell Architecture: Controllable Fabrication of Cu_2O@Cu with High Activity for Sonogashira Coupling Reaction

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Experimental Section

The phase purity and crystal structures of as-synthesized samples were detected by an X–ray diffractometer (XRD) (Xpert, Pro, Holland). The morphology was examined by transmission electron microscopy (TEM) (JEOL, JEM-2100, Japan), scanned electron microscopy (SEM) (JEOL, JSM-6490LV, Japan), and field emission scanned electron microscopy (FESEM) (JEOL, JSM-7600F, Japan).

Synthesis of spherical Cu_2O@Cu Core-Shell Structure

In a typical procedure, a solution was first prepared by mixing 0.002 mol $CuCl_2$, 20 mL ethylene glycol, and 10 mL deionized water in a two-necked flask, which was immersed in a water bath at 60 ^oC. The mixture was stirred with a magnetic stirrer for about 10 min, and then 10 mL 5 mol L^{-1} of NaOH was added dropwise. After 5 min, 10 mL 1.1 mol L^{-1} of D-glucose (2 g) was added into the solution within 30 s. An orange-red colored precipitate ensued soon. The reaction was kept at 60 ^oC for 30 min. Afterwards, the solid product was harvested by centrifugation and washed with deionized water 3 times.

Synthesis of cubic Cu_2O@Cu Core-Shell Structure

A solution was first prepared by mixing 0.002 mol $CuCl_2$, 4 mL ethanol, and 56 mL deionized water in a two-necked flask, which was immersed in water bath at 60 ^oC. The mixture was stirred with a magnetic stirrer for about 5 min, and then 10 mL 2.5 mol L^{-1} of NaOH was added in a dropwise manner.

After 5 min, 30 mL 0.18 mol L^{-1} of D-glucose (1 g) was added into the solution within 2 min. The reaction was kept at 60 ^{o}C for 10 min. Afterwards, cubic Cu_2O was harvested by centrifugation and washed with deionized water 3 times. All of the Cu_2O particles were taken in 20 mL ethylene glycol, and 10 mL deionized water in a two-necked flask, which was immersed in water bath at 60 ^{o}C. The mixture was stirred with a magnetic stirrer for about 10 min, and then 10 mL 5 mol L^{-1} of NaOH was added in dropwise fashion. After 5 min, 10 mL 1.1 mol L^{-1} of glucose (2 g) was added into the reaction mixture within 30 s. The reaction was kept at 60 ^{o}C for 30 min. Finally, the cubic core-shell Cu_2O@Cu was harvested by centrifugation and washed with deionized water 3 times.

Synthesis of hexapod Cu_2O@Cu Core-Shell Structure

A solution was first prepared by mixing 0.001 mol $CuCl_2$, 24 mL ethanol, and 6 mL deionized water in a two-necked flask, which was immersed in water bath at 60 ^{o}C. The mixture was stirred with a magnetic stirrer for about 5 min, and then 5 mL 10 mol L^{-1} of NaOH was added in dropwise manner. After 5 min, 15 mL 0.11 mol L^{-1} of D-glucose (0.3 g) was added into the solution within 2 min. The reaction was kept at 60 ^{o}C for 30 min. Afterwards, hexapod Cu_2O was harvested by centrifugation and washed with deionized water 3 times. All of the Cu_2O particles was added in the 20 mL ethylene glycol, and 10 mL deionized water in a two-necked flask, which was immersed in water bath at 60 ^{o}C. The mixture was stirred with a magnetic stirrer for about 10 min, and then 10 mL 5 mol L^{-1} of NaOH was added in drop wise manner. After 5 min, 10 mL 1.1 mol L^{-1} of glucose (2 g) was dropped into the reaction mixture within 30 s. The reaction was kept at 60 ^{o}C for 30 min. Finally, the hexapod core-shell Cu_2O@Cu was harvested by centrifugation and washed with deionized water 3 times.

Palladium- and ligand-free Sonogashira coupling using Cu_2O@Cu catalyst

In the experimental procedure for catalytic reaction, a mixture of aryl iodide (1 mmol), phenylacetylene (1 mmol), K_2CO_3 (2 mmol), and Cu_2O@Cu (20 mg) in a round-bottomed flask was heated in DMF (2 mL) at 110 ^{o}C for the required time period (Table 1). After completion of the reaction (monitored by TLC), the product was extracted into ethyl acetate following the usual work-up procedure and was purified by column chromatography. All of the products listed in Table 1 are known in the literature and were identified by comparison of their FT-IR, 1H, and 13C NMR with literature data. All the reagents were purchased from Sigma-Aldrich Chemical Co. and were used directly without further any purification. NMR spectra were obtained using the Bruker AVANCE 300MHz spectrometer using $CDCl_3$ as solvent. IR spectrum was taken on Perkin Elmer Spectrum 2000 FT-IR spectrometer.

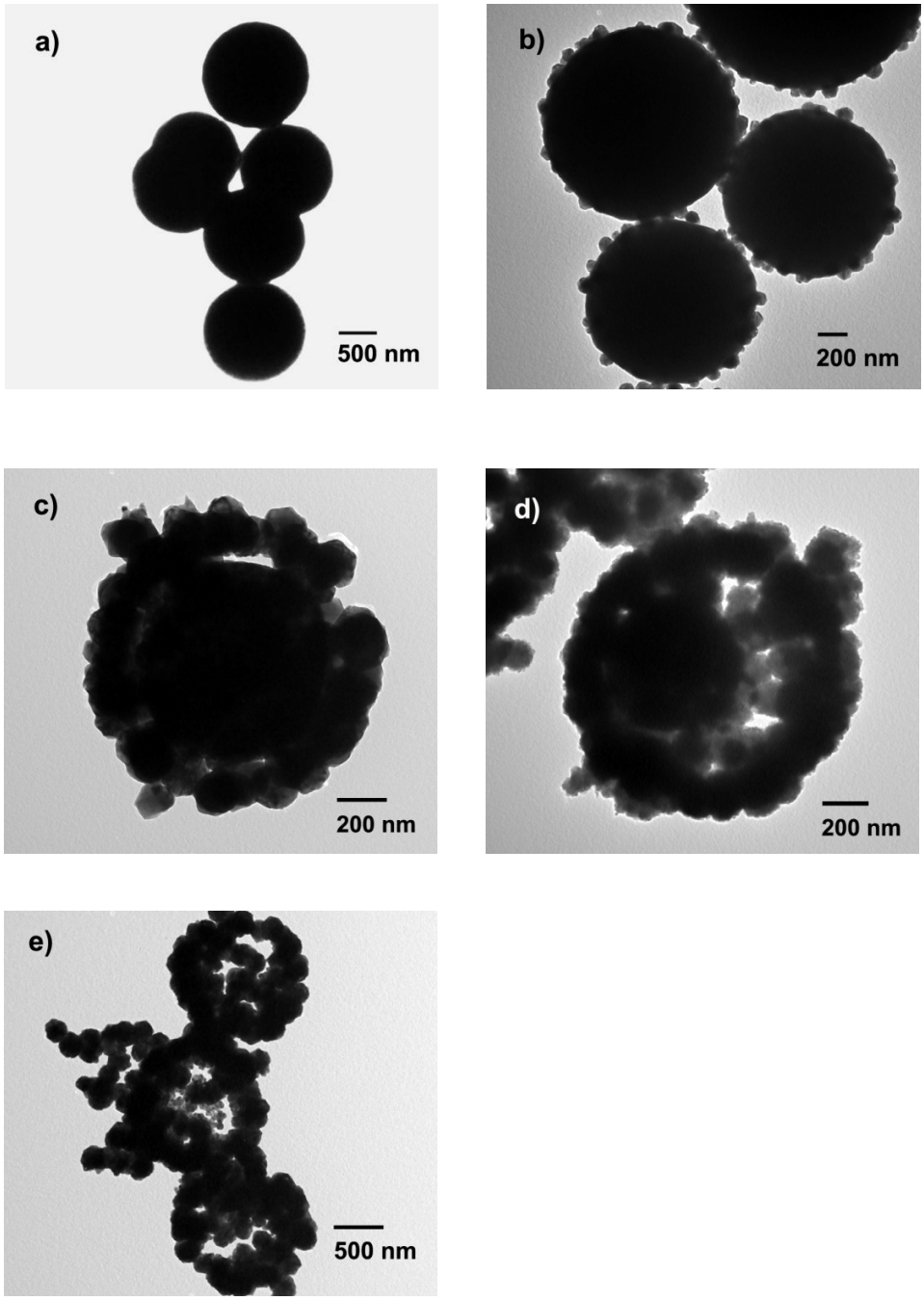


Fig. S1. TEM image of samples obtained at different time. a) 2 min; b) 10 min; c) 20 min; d) 30 min; e) 40 min.

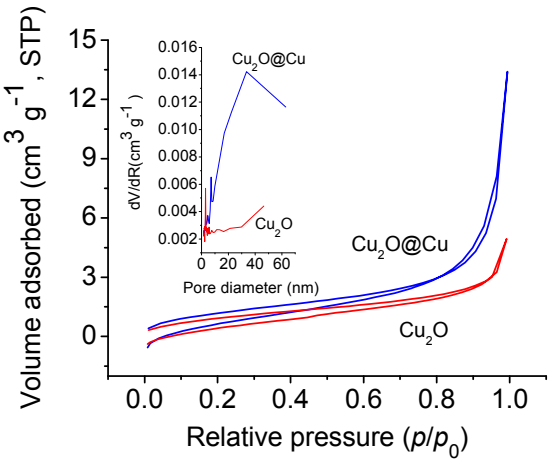


Fig. S2. N_2 adsorption–desorption isotherms of Cu_2O@Cu (prepared at 25 min) and Cu_2O (prepared at 2 min) and corresponding pore size distributions (inset).

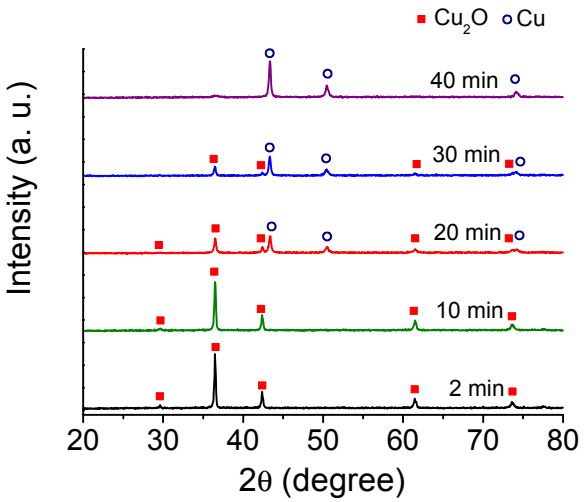


Fig. S3. XRD patterns of samples prepared at different time.

According to the Fig. 2b, some small particles are present on the surface of the solid spheres prepared at 10 min, but peaks of Cu are absent. This may be the result of the insufficient crystallinity of Cu or the accuracy limit of the instrument.

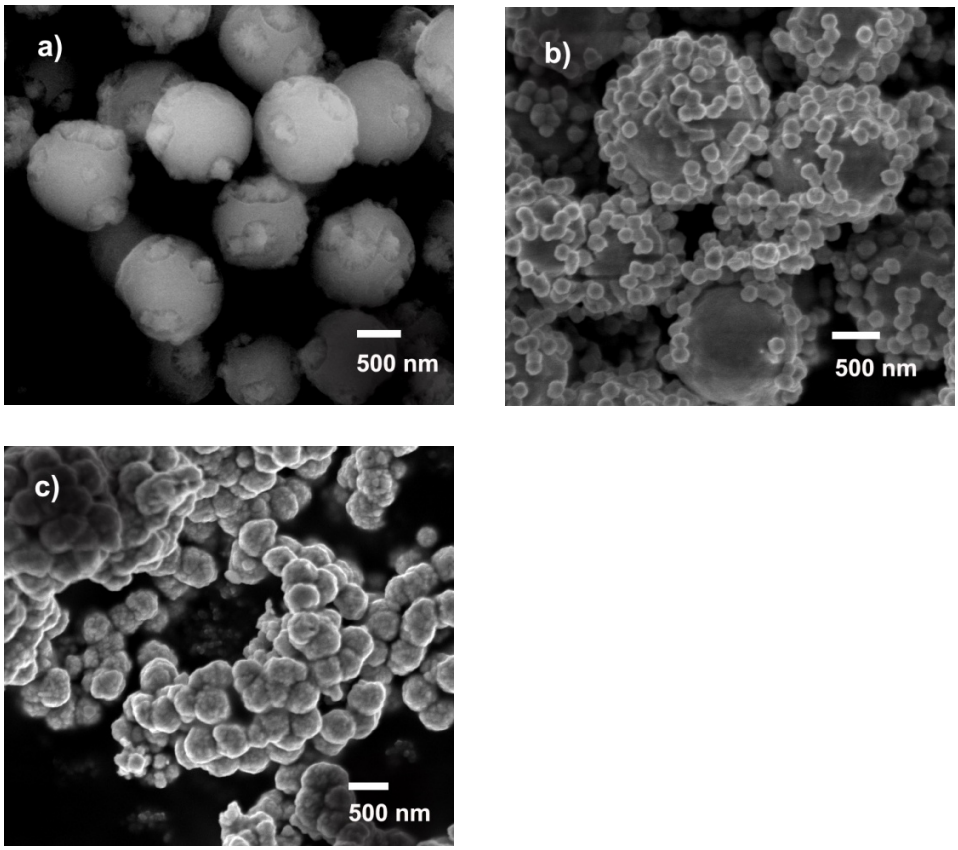


Fig. S4. SEM image of samples obtained with different NaOH amount at 30 min. a) 0.8 g; b) 1.5 g; c) 4 g.

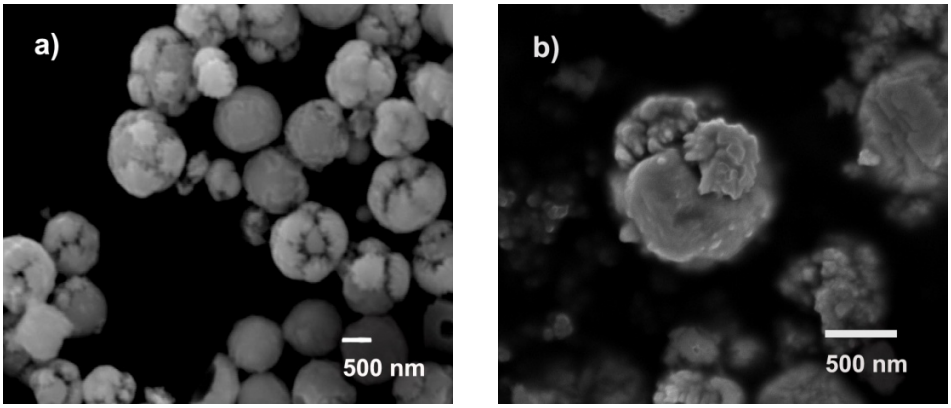


Fig. S5. SEM image of samples obtained with 0.8 g NaOH.a) 60 ^{o}C, 60 min; b) 80 ^{o}C, 30 min.

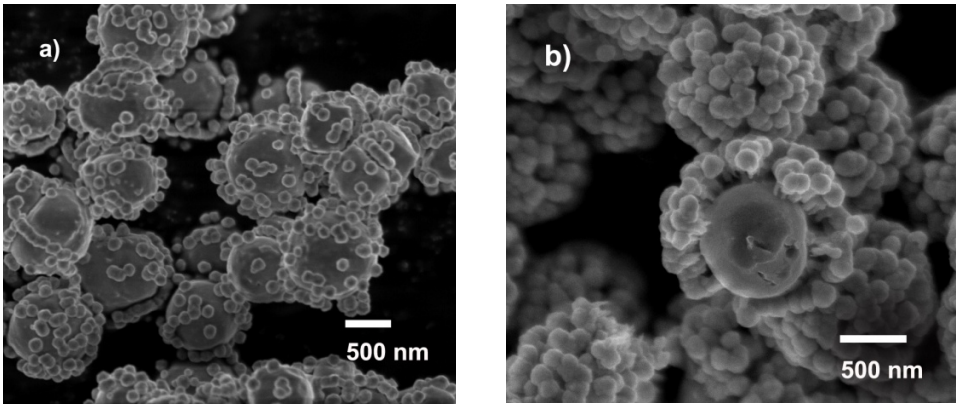


Fig. S6. SEM image of samples obtained with different glucose amount at 30 min. a) 1 g; b) 4 g.

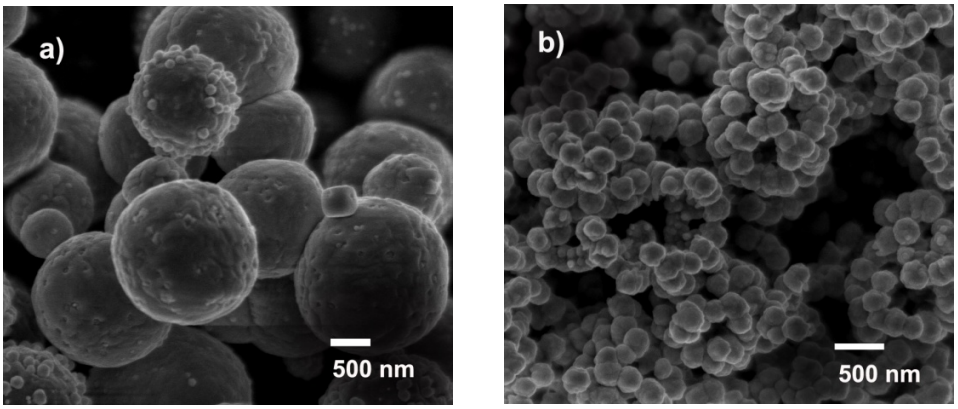


Fig. S7. SEM image of samples obtained at different temperature. a) 50 ^{o}C; b) 70 ^{o}C.

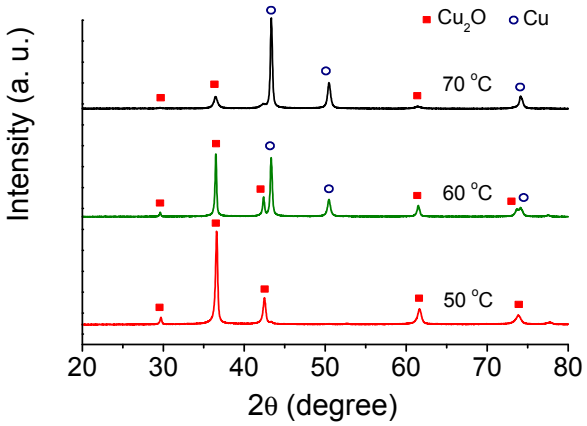


Fig. S8. XRD patterns of prepared samples at different temperature (reaction time was 25 min).

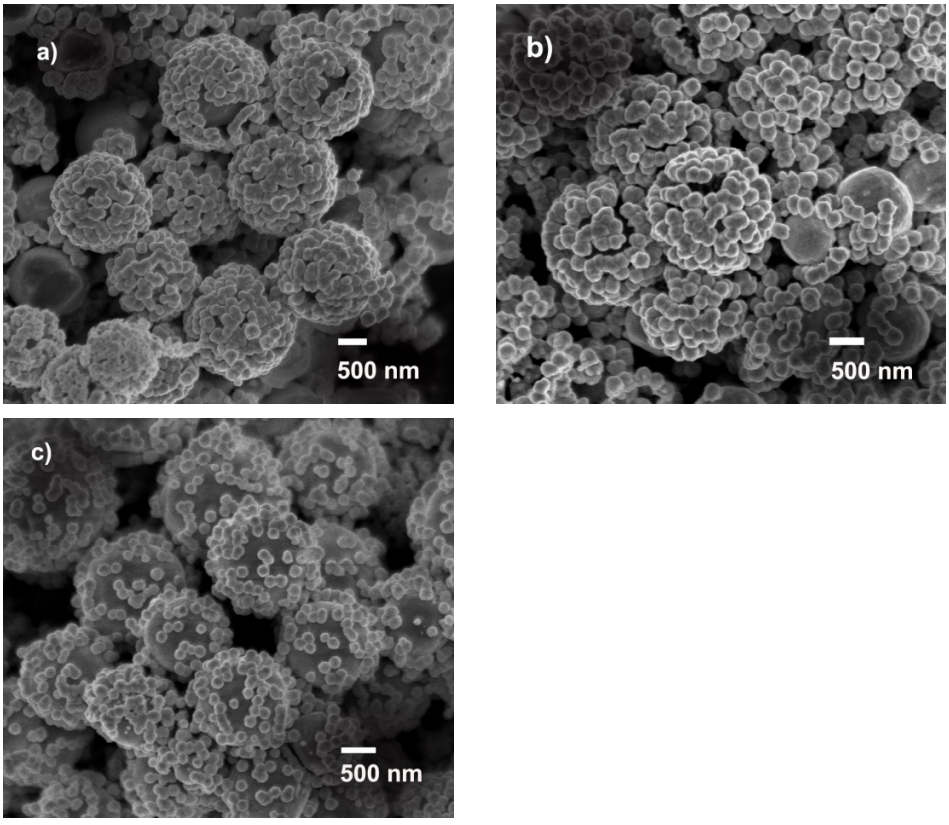


Fig. S9. SEM image of samples obtained by using different copper salt. a) $Cu(CH_3COO)_2$; b) $CuSO_4$; (c) $Cu(NO_3)_2$

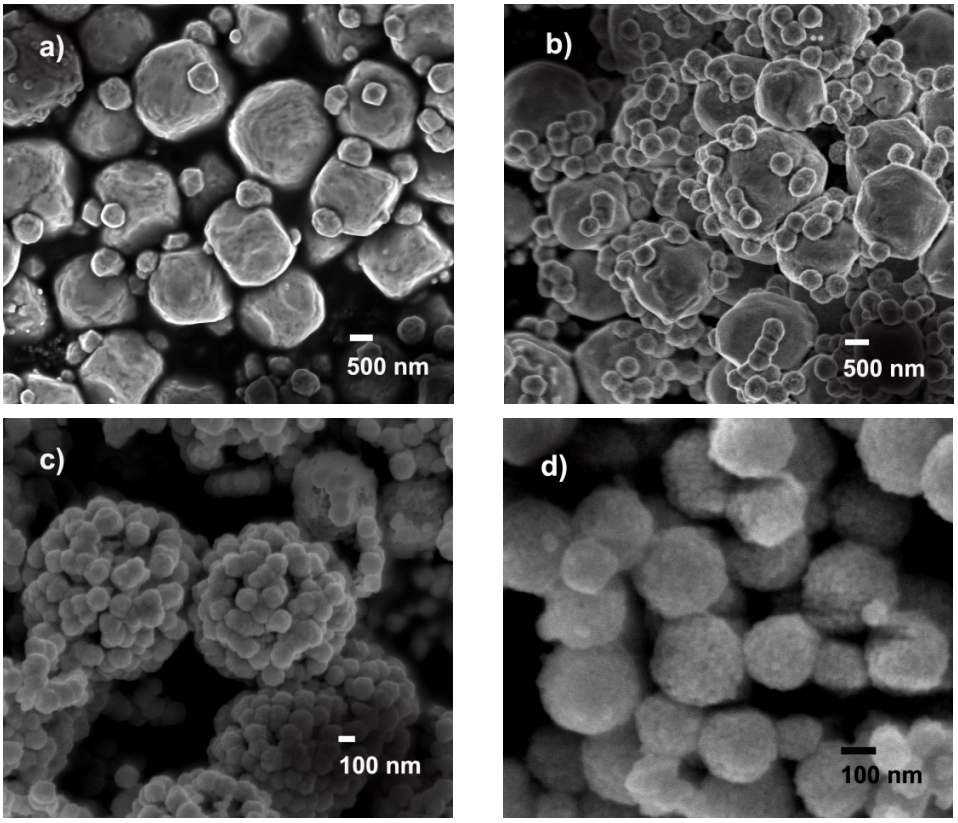


Fig. S10. SEM image of samples obtained by using different solvent. a) 50 mL water; b) 10 mL ethylene glycol and 40 mL water; (c) 30 mL ethylene glycol and 20 mL water; d) 50 mL ethylene glycol.

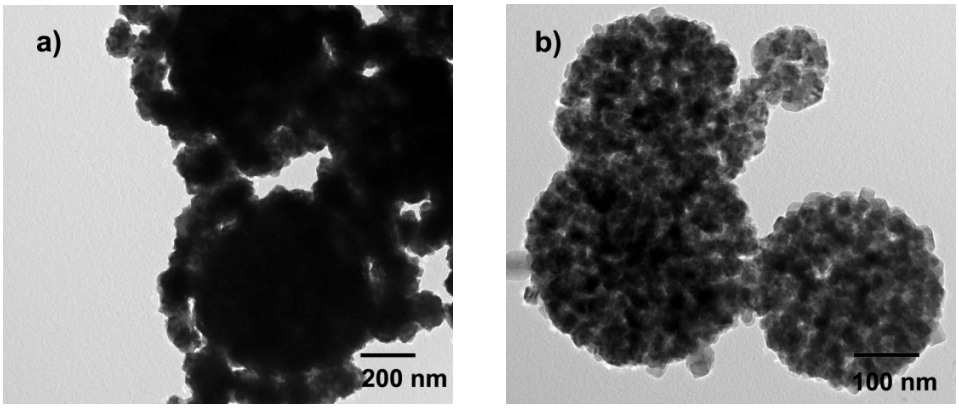


Fig. S11. TEM image of samples obtained by using different solvent. a) 30 mL ethylene glycol and 20 mL water; b) 50 mL ethylene glycol.

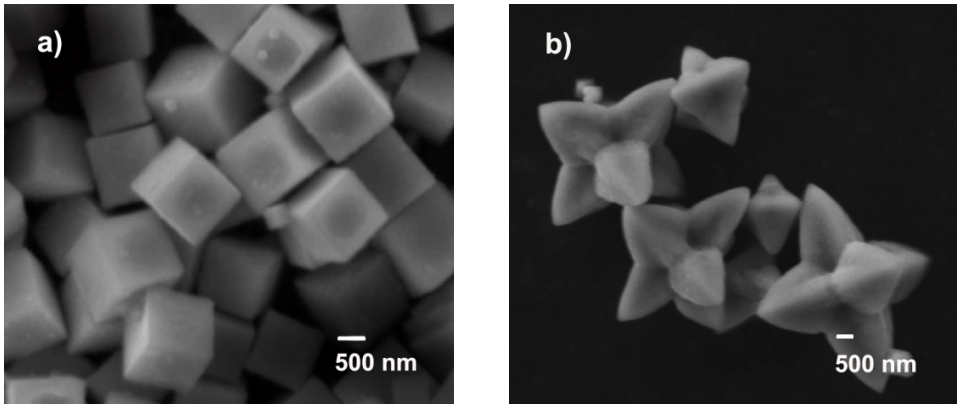


Fig. S12. SEM of a) square and b) hexapod structure.

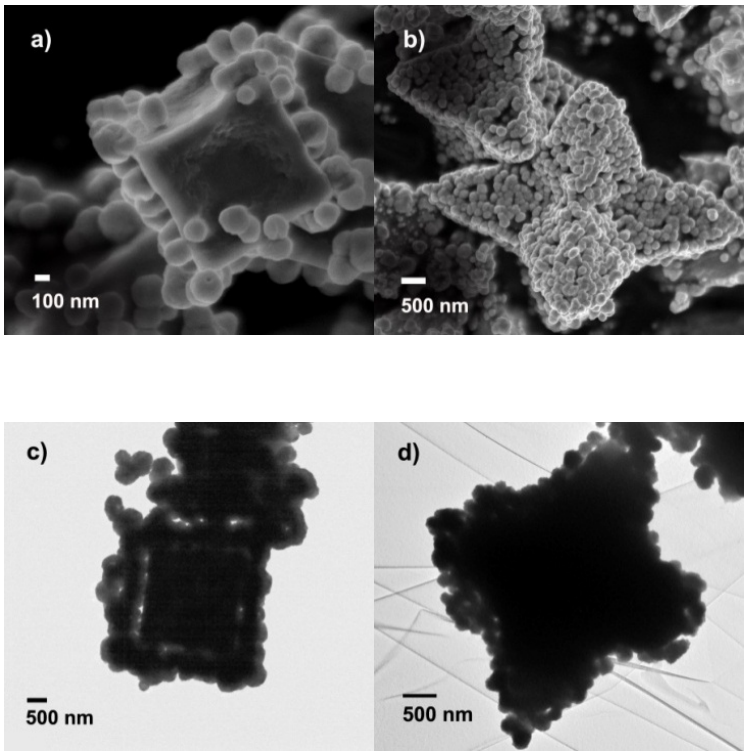
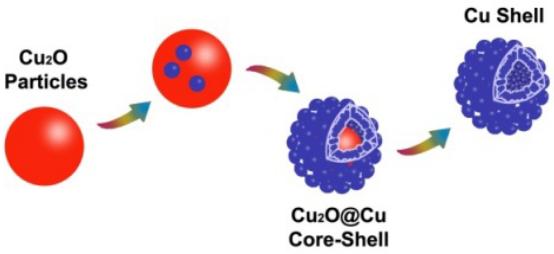


Fig. S13. SEM and TEM images of core-shell square and hexapod structures. a) SEM image of square structure; b) SEM mage of hexapod structure; c) TEM image of square; d) TEM image of hexapod structure.



Scheme S1. Schematic diagram of the synthetic procedure for the formation of Cu_2O@Cu core-shell architecture

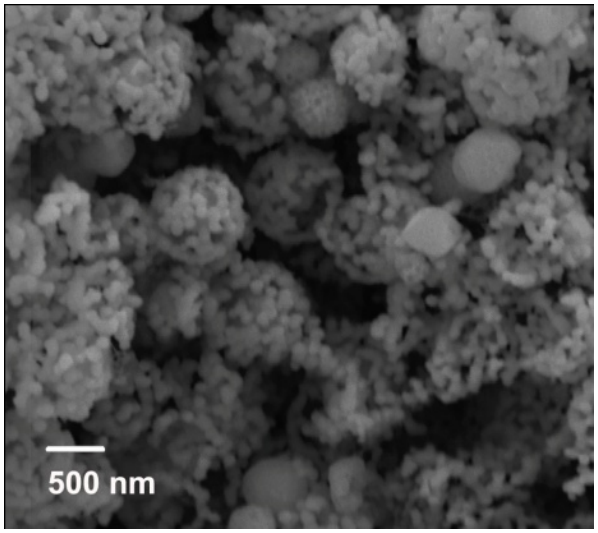


Fig. S14. SEM image of recycled sample