Electronic Supplementary Information

Nanoparticle-Aggregated Hollow Copper Microcages and their Surface-Enhanced Raman Scattering Activity

Chuncai Kong, [‡] Shaodong Sun, [‡] Xiaozhe Zhang , Xiaoping Song and Zhimao Yang*

School of Science, MOE Key Laboratory for Non-Equilibrium Synthesis and Modulation of Condensed Matter,

State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, ShaanXi,

People's Republic of China

*Author to whom correspondence should be addressed; E-mail: zmyang@mail.xjtu.edu.cn
‡These authors contributed equally to this work.

Experimental Section

All chemicals used in our experiment were of analytical grade and used without further purification.

Synthesis of 26-facet Cu_2O crystals. In a typical procedure for the synthesis of 26-facet Cu_2O crystals,[1, 2] 2.9946 g of $Cu(CH_3COO)_2 \cdot H_2O$ was dissolved in 50 mL deionized water using a beaker under constant stirring at 70 ℃ for 5 min. A dark precipitate was produced when 30 mL of NaOH (3.6 g) aqueous solution was added dropwise to the above solution. After being stirred for 5 min, 0.6 g of glucose powder was added into the dark precursor with constant stirring for another 30 min at 70 ℃. Then, the obtained red particles were cleaned with deionized water and ethanol by repeated centrifugation, and dried at 70 ℃ for 12 h in a vacuum oven. Thus, polyhedral 26-facet Cu_2O crystals were prepared.

Synthesis of hollow copper microcages. The hollow copper microcages were synthesized as follows: 0.012 g of 26-facet Cu_2O crystals were dispersed in 30 mL ethylene glycol (EG) in a conical flask, after the mixture was stirred for 10 min in a water bath at 60 ℃, 10 mL of NaOH aqueous solution (5 M) was added dropwise. 5 min later, 10 mL of glucose aqueous solution (1.1 M) was added into the above solution. The reaction was kept at 60 ℃ for 120 min. Afterwards, the product was cleaned with deionized water and ethanol by repeated centrifugation. Thus, the hollow copper microcages were obtained and kept in etanol for further characterization.

Characterization. The crystal phase of the as-prepared product was characterized by an X-ray diffractometer (Bruker-AXS D8 ADVANCE) using Cu-Ka radiation (λ= 1.54 Å) in the range (20–80°). The morphology of the samples was investigated by field-emission scanning electron microscopy (FESEM) using JEOL (JSM-7000F). The transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) analysis as well as selected-area electron diffraction (SAED) pattern analysis were performed on a JEOL JEM-2100 transmission electron microscope operating at an accelerating voltage of 200 kV. Thermalgravimetric analysis (TGA)of the production was carried out on a STA 449C (NETZSCH) simultaneous thermogravimetric/differential thermal analyzer under Ar and O_2 atmosphere, respectively. The range of temperature was from 30 ℃ to 600 ℃ with heating rate of 10 ℃ min^{-1}.

Surface-enhanced Raman spectra: SERS of the as-prepared products were acquired using an HR 800 Raman spectrometer (HORIBA JOBIN YVON) with a CCD detector

and He-Ne laser (633 nm). The SERS spectra were collected at 100x objective and an accumulation time of 5 s. In addition, the grating was 600 g mm^{-1} and the filter in the SERS spectra was D1. The as-prepared Cu hollow hierarchical architectures were added into 2 ml of R6G or 4-mercaptobenzoic acid ethanol solution with different concentration. The solutions were sonicated for 3 min and left undisturbed for another 2 h, 20 µl of the solution droped on a silicon subtrate and then dried for SERS measurements.

The enhancement factor (EF) was calculated following the Equation:[3]

$$EF = I_{SERS}C_0 / (I_0C_{SERS})$$

where C_{SERS} and I_{SERS} are the concentration and peak intensity of Raman under SERS conditions. C_0 and I_0 are the concentration and peak intensity of the normal Raman measurement, with R6G ethanol solution of 10^{-1} M on a Si wafer. The EF was calculted based on the peak at 1364 cm^{-1}, according to the equation, the EF was calculted to be 0.6×10^5, 0.96×10^5, and 1.9×10^5 according to the R6G conentrations of 10^{-5} M, 10^{-6} M and 10^{-7} M respectively.
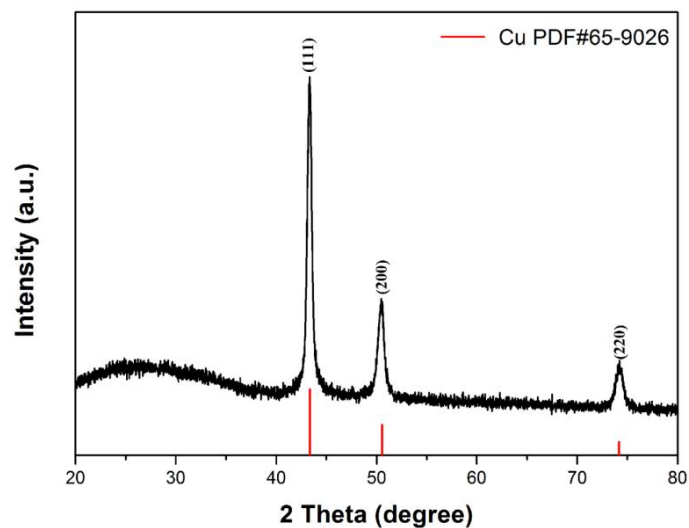
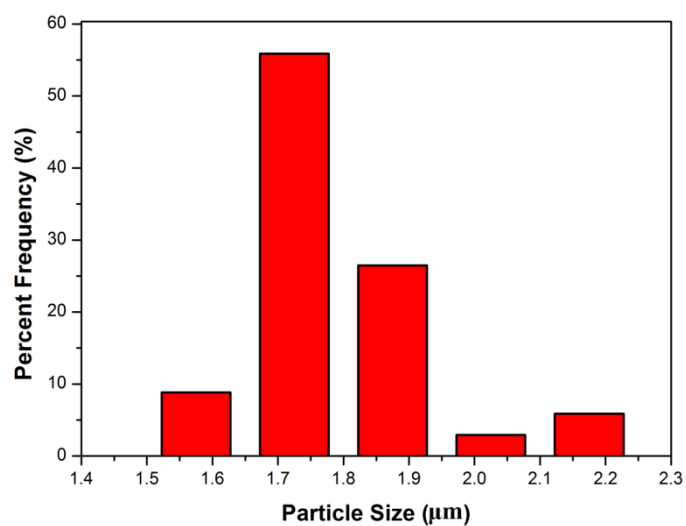**Fig. S1** XRD pattern of the as-prepared products.

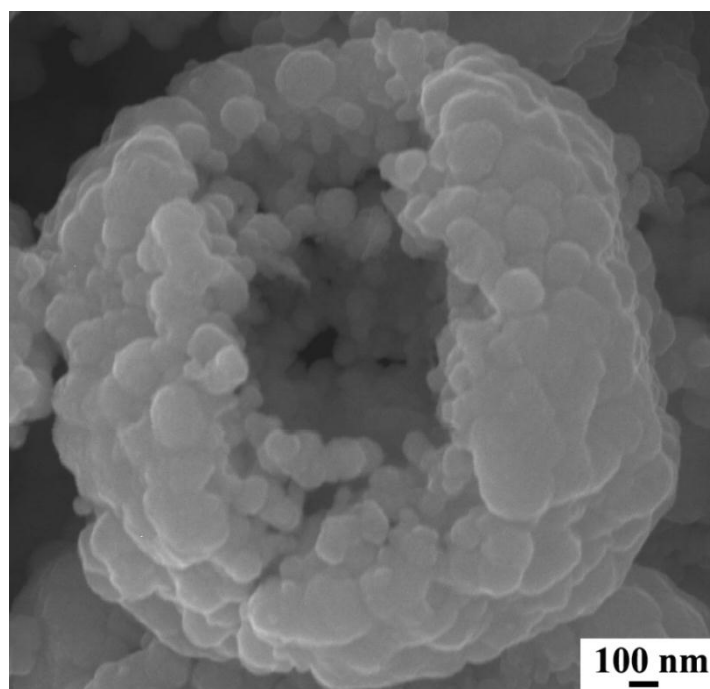**Fig. S2** The size-distribution diagram of as-prepared products.

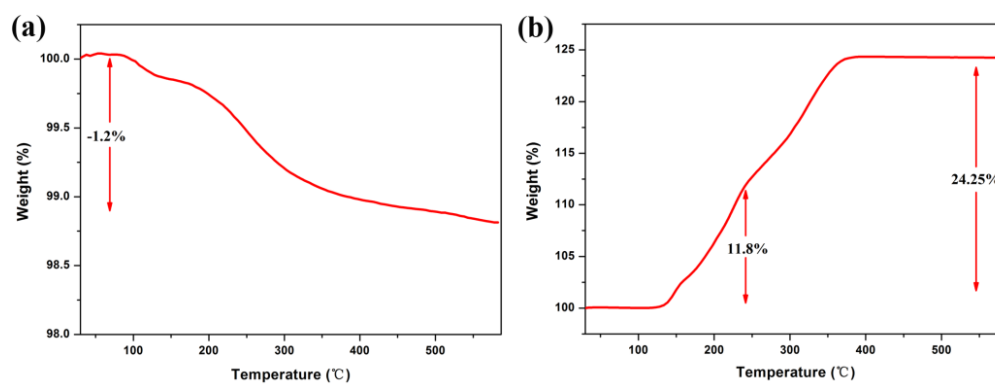**Fig. S3** FESEM image of the broken as-prepared products.

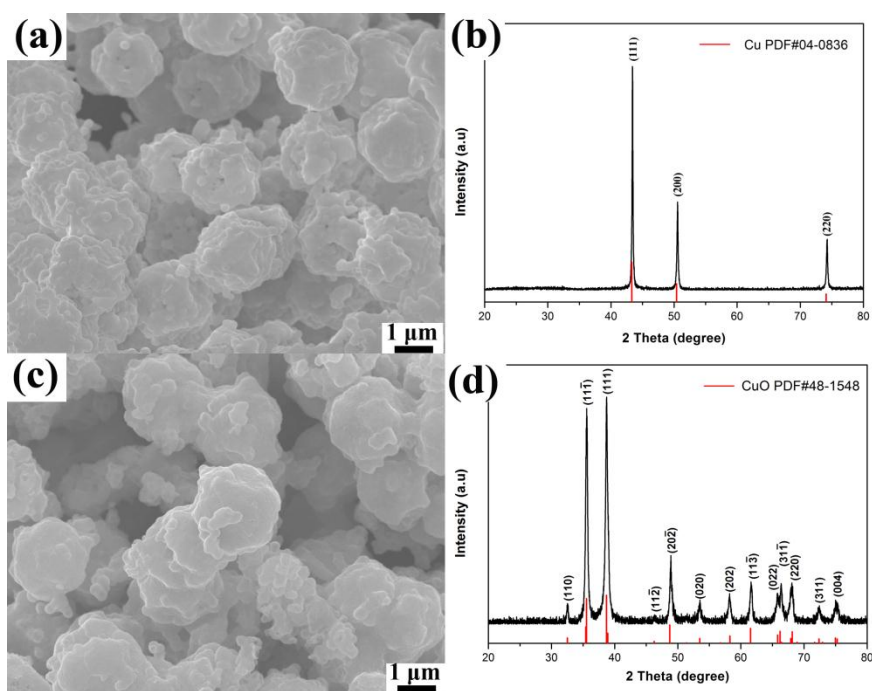**Fig. S4** TGA curve of hollow Cu microcages in different atomsphere: (a) Ar and (b) O$_2$.

Fig. S5 (a) SEM and (b) XRD of the hollow Cu microcages after measurement of TGA in Ar;

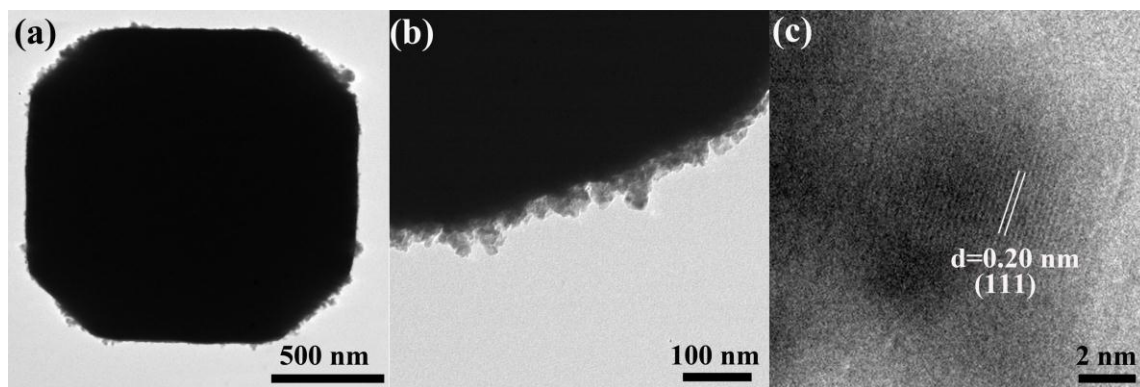(c) SEM and (d) XRD of the hollow Cu microcages after measurement of TGA in O_2.

Fig. S6 TEM and HRTEM images of products obtained at 5 min.

1. S. D. Sun, X. P. Song, C. C. Kong, S. H. Liang, B. J. Ding and Z. M. Yang, *CrystEngComm*, 2011, **13**, 6200-6205.

2. S. D. Sun, F. Y. Zhou, L. Q. Wang, X. P. Song and Z. M. Yang, *Crys. Growth Des.*, 2009, **10**, 541-547.

3. Q. Shao, R. H. Que, M. W. Shao, L. Cheng and S. T. Lee, *Adv. Funct Mater.*, 2012, **22**, 2067-2070.