Supplementary Material (ESI)

Synthesis and Characterization of Multipod Frameworks of Cu_2O Microcrystals and Cu_7S_4 Hollow Microcages

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Experimental Section

All reagents and solvents were purchased from commercial sources and used as received without further purification. Chemicals used in this study included $Cu(Ac)_2 \cdot 2H_2O$ (99.5%, Guangdong Xilong Co., China), $EDTANa_2 \cdot 2H_2O$ (99.0%, Nanjing Chemical Company, China), NaOH (96%, Beijing Co., China), $Na_2S \cdot 2H_2O$ (99.5%, Guangdong Xilong Co., China), n-butyl alcohol (99.5%, Nanjing Chemical Company, China) and ethanol (AR, Beijing Fine Chemical Company, China).

Synthesis of Cu_2O templates

Three types of Cu_2O microcrystals were prepared and the reaction conditions are listed in Table 1. In a typical synthesis, 0.744 g $EDTANa_2 \cdot 2H_2O$ and 0.32 g NaOH were dissolved in 3.5 mL water, and 0.11 g $Cu(Ac)_2 \cdot 2H_2O$ and 6.5 mL n-butyl alcohol were added into the above solution. The volumes of water and n-butyl alcohol were varied to produce different microcrsystals. After sonication in water for 30 s, the solution was transferred into a Teflon-lined stainless steel autoclave. The autoclave was heated to 100°C for 5h, and then allowed to cool down to room temperature. The red products were collected and washed three times with distilled water and absolute ethanol, respectively.

Synthesis of Cu_2O–Cu_7S_4 core–shell particles

In a typical synthesis, the obtained Cu_2O templates were dispersed in an anhydrous ethanol solution (50 mL), followed by the addition of 50 mL aqueous solution composed of 0.01 M Na_2S and 0.001 M NaOH at 0 °C in an air atmosphere under magnetic stirring for 45 min. The precipitates were separated by centrifugation, and washed with deionized water and ethanol.

Synthesis of Cu_7S_4 hollow particles

In a typical synthesis, the above Cu_2O–Cu_7S_4 core–shell particles were immersed in an ammonia solution (25%)

for 48 h to remove the inner Cu_2O cores. The particles were centrifuged twice in deionized water and anhydrous ethanol, respectively. They were finally dried at 60 °C for 12 hours in a vacuum oven.

The phases of samples were characterized by X-ray diffraction (XRD, Cu Kα1 radiation, Rigaku D/max2550VB, Japan). The morphologies and structures of samples were studied using scanning electron microscopy (SEM, JSM-6700F, JEOL, Japan) and transmission electron microscopy (TEM, JSM-3010, JEOL, Japan), respectively.

No.	N-butyl alcohol (ml)	Water (ml)
a	6.5	3.5
b	4.7	5.3
c	3.2	6.8

Table 1. The volume ratios of n-butyl alcohol to water in the synthesis of sample a-c.

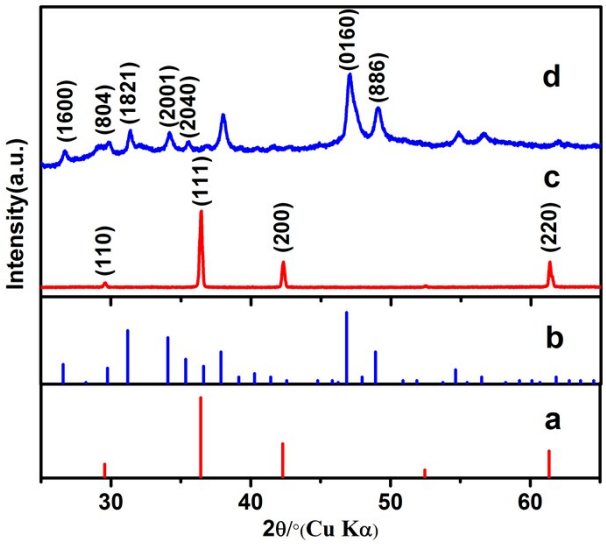

Figure S1. XRD patterns: a) Cu_2O with PDF file No. 05-0667, b) Cu_7S_4 with PDF file No. 23-0598. Patterns c,d) are the corresponding XRD patterns of 14-pods Cu_2O and Cu_7S_4 hollow cages, respectively.

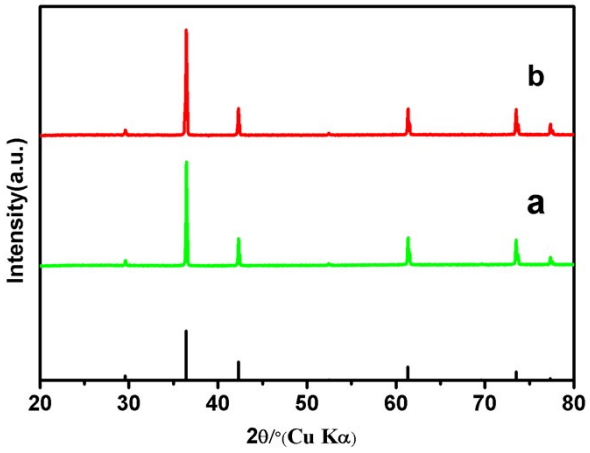

Figure S2. XRD patterns: a) 6-pods Cu_2O and b) type I 14-pods Cu_2O with PDF file No. 05-0667

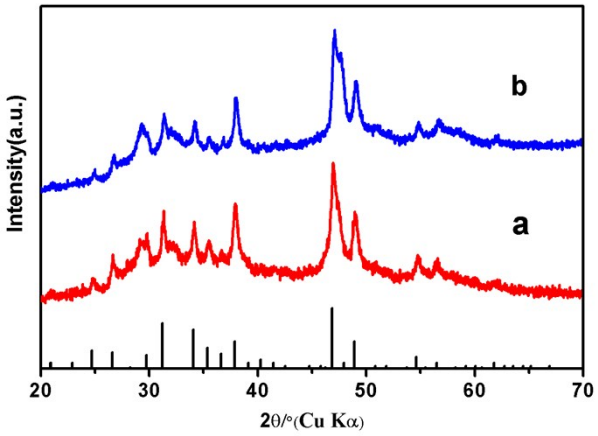

Figure S3. XRD patterns: a) 6-pods Cu_7S_4 cages and b) type I 14-pods Cu_7S_4 cages with PDF file No. 23-0598

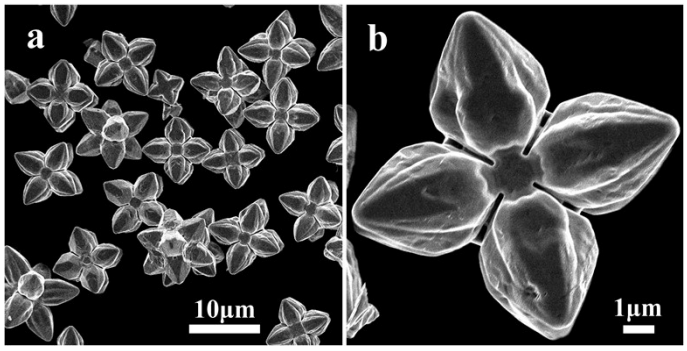

Figure S4. SEM images of 8-pods Cu_2O, (a) is the low magnification image, (b) is the high magnification image.