

Ammonia-Assistant Epitaxial Assembly of Cu₂O@Ag Yolk-Shell and Ag Cage

*Jiqiao Zhang, Cui Zhang, and Shuangxi Liu**

Institute of New Catalytic Materials Science and Key Laboratory of Advanced Energy

Materials Chemistry (Ministry of Education), College of Chemistry, Nankai

University, Tianjin 300071, People's Republic of China

E-mail: sxliu@nankai.edu.cn

Experimental Details and Data

Chemicals

Copper acetate, sodium hydroxide, ascorbic acid, aqueous ammonia, silver nitrate, and polyvinylpyrrolidone (PVP, MW~10000) were analytical grade and purchased from Tianjin Heowns Biochemical Technology Co., Ltd. Distilled water was used throughout the experiments.

Preparation of Samples

Preparation of 26-facet Cu₂O

In short, 26-facet polyhedrons Cu₂O were synthesized as a typical proposed. ^[1]

Preparation of CA₁

0.2 g silver nitrate was resolved in 20 mL distilled water, then ammonia aqueous solution (0.1M) was added drop by drop to the above solution for forming [Ag(NH₃)₂]⁺ complexant transparent solution. The as-synthesized Cu₂O dispersed in distilled water by sonication and dropped aliquot of [Ag(NH₃)₂]⁺ complexant transparent solution were mixed at room temperature with magnetic stirring for 2h under 500W Xenon lamp irradiation, the color of the solution changed gradually from brick-red to gray, indicating the formation of silver shell.

Preparation of CA₂

The experiment differed from the above CA₁ in adding molar ratio of Cu₂O and [Ag(NH₃)₂]⁺ complexant was 1:2, labelled as CA₂.

Preparation of CA₃

In dark condition, the other conditions were kept constant as the above CA₁, labelled as CA₃, to investigate the role of the Xenon lamp in the preparation process.

Preparation of CA₄

In another counterpart experiment, the same concentration of silver nitrate aqueous solution as that of the [Ag(NH₃)₂]⁺ complexant was dropped into the Cu₂O suspension by magnetic stirring under 500W Xenon lamp irradiation, noted as CA₄.

All samples were reacted for 2 h. The final product was collected, washed with ethanol and distilled water several times and dried in vacuum oven at 65°C for 12h.

Extraction Cu₂O-yolk of CA₁

The prepared Cu₂O@Ag yolk-shell composites (CA₁) were immersed in ammonia solution (12 wt%) and stirred with magnetic force for 30 min to remove the inner Cu₂O yolk. ^[2,3] The precipitates were separated by centrifugation, washed with deionized water and ethanol, and then dried in vacuum oven at 65°C for 12 h, marked as CA₅.

Characterization

Powder X-ray diffraction (XRD) patterns of catalysts were obtained on a Bruker D8 Focus diffractometer with CuK α radiation ($\lambda=1.54184 \text{ \AA}$) at scanning speed of 0.01°/s in a scan range of 20° < 2 θ < 80° operating at 40 kV and 40 mA. Scanning electron microscopy (SEM) images were obtained on a JEOL JSM-7500F field-emission scanning electron microscope at an accelerating voltage of 5 kV. High resolution transmission electron microscopy (HRTEM) measurements were carried out on a Philips Tecnai G² F20 electron microscope operating at 200 kV. N₂ adsorption-desorption analysis was performed on a Micromeritics TriStar 3000 apparatus at 77K.

Table S₁ Different samples synthesized under different conditions

Sample	Xenon lamp	NH ₃ /H ₂ O	Molar ratio Cu ₂ O to Ag ⁺
CA ₁	Y ^{a)}	Y	10:1
CA ₂	Y	Y	1:2
CA ₃	N ^{b)}	Y	10:1
CA ₄	Y	N	10:1

a) Y means used; b) N means not used.

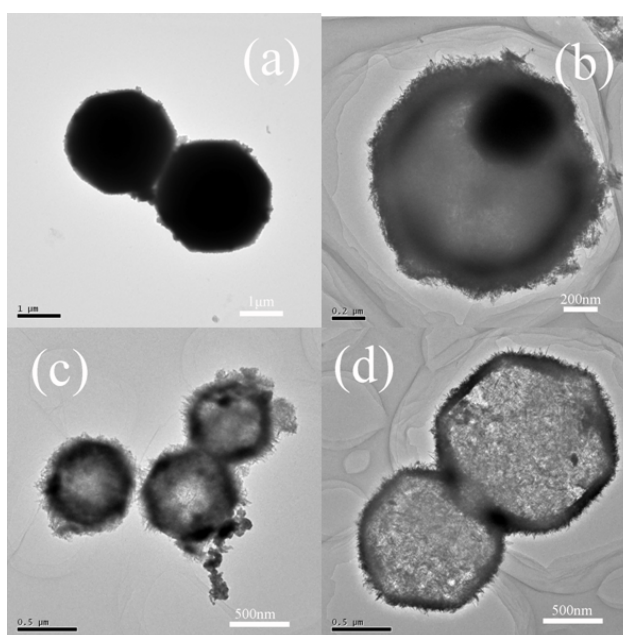


Fig. S₁ TEM images of the Ag cage synthesized processing by in site redox, epitaxial assembly with Cu₂O and [Ag(NH₃)₂]⁺ complexant: a) for half an hour; b) for 1hour; c) for 1.5h; d) for 2 hour.

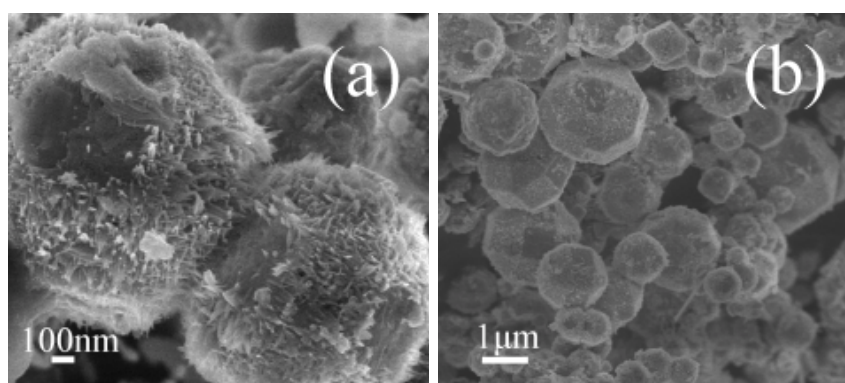


Fig. S₂ SEM images of CA₃. a)-b) are high magnification images of Cu₂O@Ag yolk-shell composite formed by reaction of Cu₂O with Ag(NH₃)₂⁺ complexant (molar ratio was 10:1) in dark.

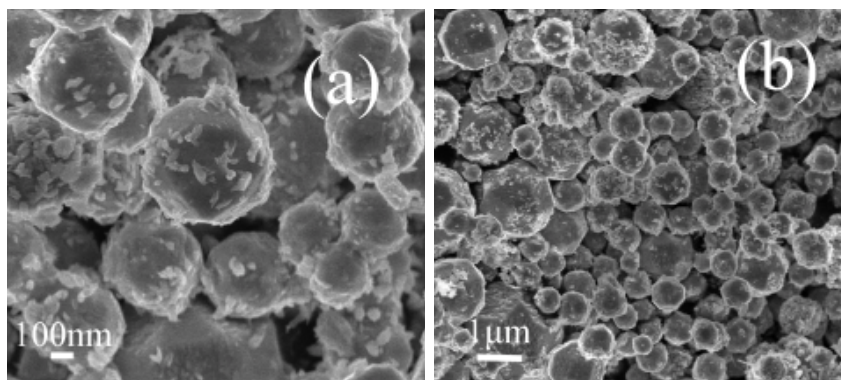


Fig.S₃ SEM images of CA₄. a)-b) are different magnification images of Ag/Cu₂O composites, by reaction of the Cu₂O with Ag⁺ from AgNO₃ (molar ratio was 10:1) under 500W Xenon lamp irradiation in air.

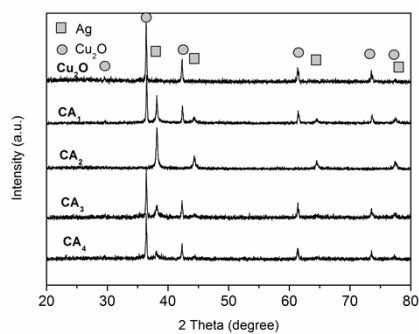


Fig. S₄ XRD patterns of all the products prepared correspondingly as the condition in Table S₁.

References

- 1 X. P. Wang, S. H. Jiao, D. P. Wu, Q. Li, J. G. Zhou, K. Jiang, and D. S. Xu, *CrystEngComm* 2013, **15**, 1849.
- 2 S. H. Jiao, L. F. Xu, K. Jiang, D. S. Xu, *Adv. Mater.* 2006, **18**, 1174.
- 3 R. N. Briskman, *Sol. Energy Mater. Sol.Cells* 1992, **27**, 361.