

Electronic Supplementary Information

Designing Hierarchical Hollow Nanostructures of Cu_2MoS_4 for Improved Hydrogen Evolution Reaction

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Preparation of Cu_2O nanocrystals

The synthesis of Cu_2O nanocrystals was similar to the previous reports with minor modifications.¹ Typically, 0.342 g $\text{CuCl}_2\cdot\text{H}_2\text{O}$ and 6.666 g poly (vinyl pyrrolidone) (PVP) were dissolved in 100 mL deionized water, then NaOH aqueous solution ($2.0 \text{ mol}\cdot\text{L}^{-1}$, 10.0 mL) were added to the solution. After 30 mins' stirring, ascorbic acid aqueous solution ($0.6 \text{ mol}\cdot\text{L}^{-1}$, 10.0 mL) were added with an intensive magnetic stirring for 1 h. Then orange liquid was obtained. The product was collected by centrifugation and subsequently washed several times by deionized water and absolute ethanol. Finally dried for several hours. Cu_2O nanocrystals with different morphologies and sizes were obtained in different conditions. The corresponding parameters are listed in SI Table 1.

SI Table 1. The reaction parameters for different Cu_2O nanocrystals.

Morphology	PVP	Reaction		Dropping speed	Size/nm
		temperature/ °C			
Nanosphere	Yes	20		quick	60~80
Nanosphere	Yes	20		slow	200~300
Octahedron	Yes	40		slow	500~600
Cube	No	40		slow	400~500

Yes: PVP was added in the reaction system;

No: PVP was not added.

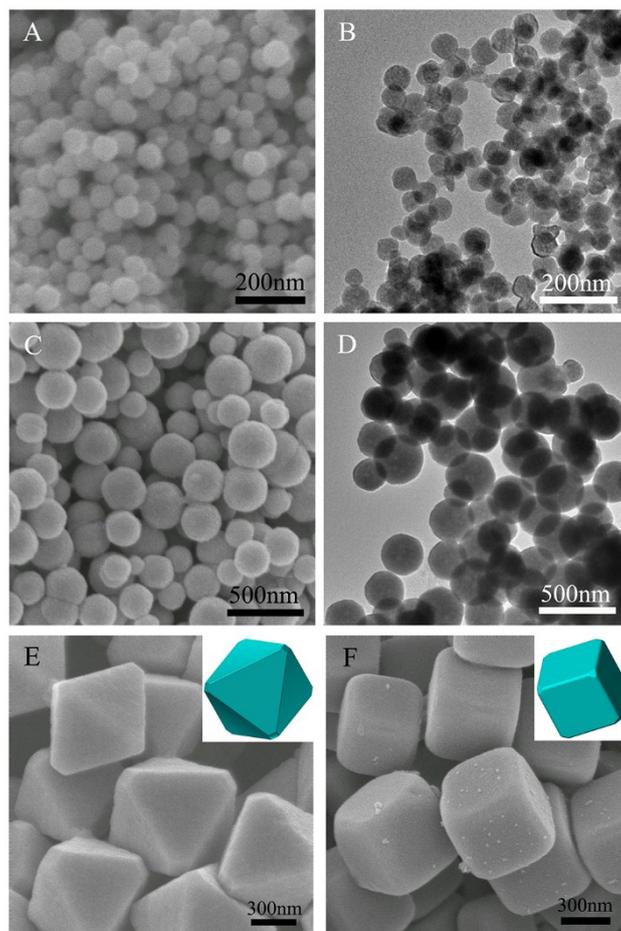


Fig. S1. SEM and TEM images of Cu_2O crystals with different morphologies and sizes. A and B are images of sphere-like Cu_2O nanocrystals with size about 60~80 nm, while C and D are images of Cu_2O spheres with size range from 200~300 nm. E shows truncated-octahedral Cu_2O crystals with size about 500~600 nm and F shows truncated-cubic Cu_2O crystals with size about 400~500 nm.

Preparation of Cu_2MoS_4 nanosheets and nanoparticles

The synthesis of Cu_2MoS_4 nanosheets is described in our recent work (Small, 2014, 10, 4637.). When the solvothermal reaction is carried out at 160 °C for 12 h, Cu_2MoS_4 nanoparticles with size about 40~60 nm are obtained (AIP Advances, 2015, 5, 077130).

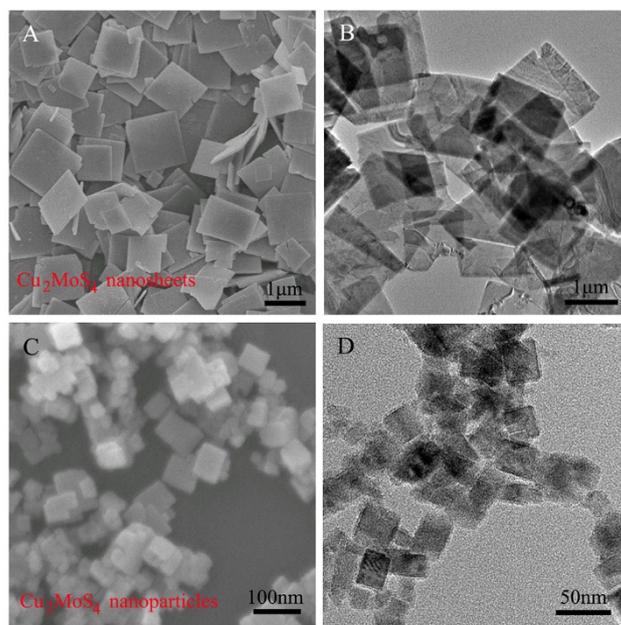


Fig. S2. SEM and TEM images of Cu_2MoS_4 at different morphologies. A and B are Cu_2MoS_4 nanosheets, while C and D are Cu_2MoS_4 nanoparticles.

EDX spectrum of Cu_2MoS_4 hollow nanoflowers

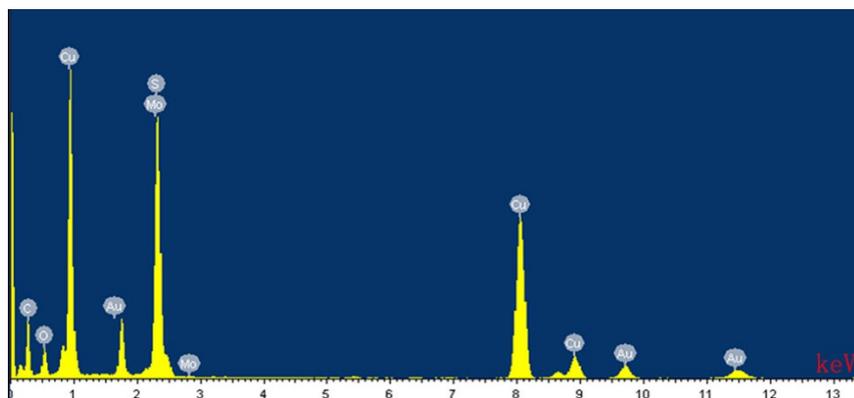


Fig. S3. EDX spectrum of Cu_2MoS_4 hollow nanoflowers.

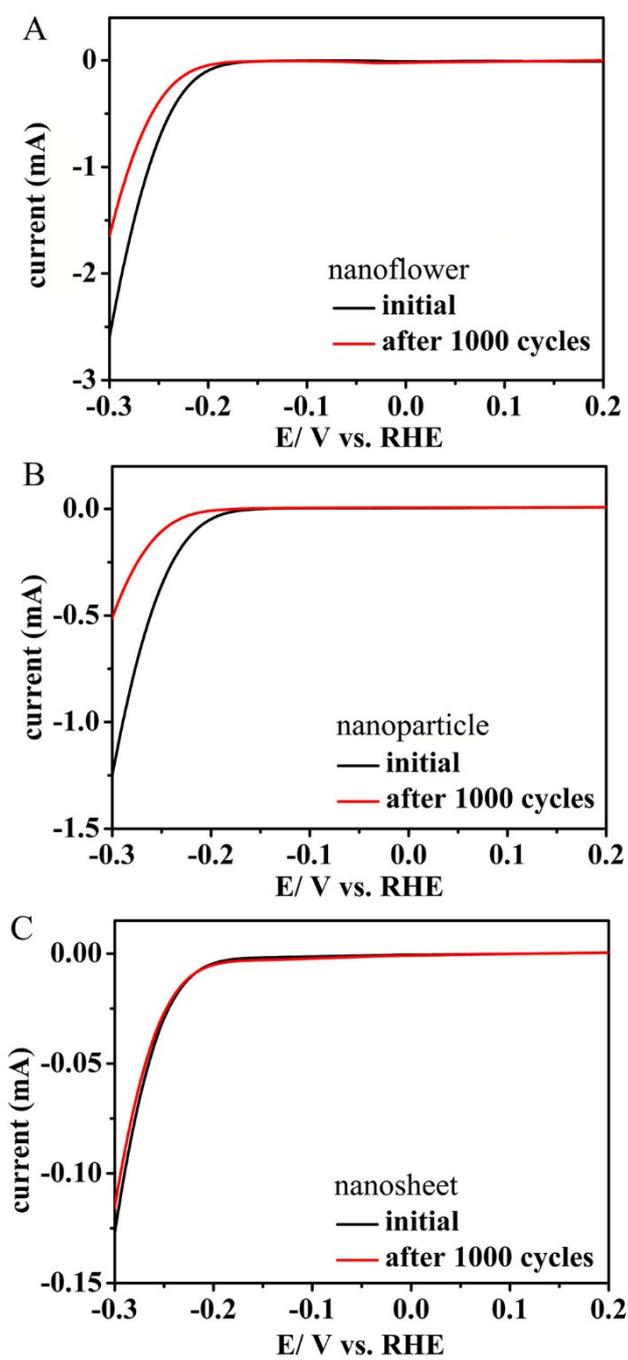


Fig. S4. durability test of nanoflower (A), nanoparticle (B) and nanosheet (C).

References

- 1 D. F. Zhang, H. Zhang, L. Guo, K. Zheng, X. D. Han and Z. Zhang, *J. Mater. Chem. A* 2009, **19**, 5220-5225.