

## Supporting Information

### **Novel Hollow MoS<sub>2</sub>@C@Cu<sub>2</sub>S Heterostructures for High Zinc Storage**

#### **Performance**

Yujin Li<sup>a,c</sup>, Jing Xu<sup>a\*</sup>, Xinqi Luo<sup>a</sup>, Futing Wang<sup>c</sup>, Zhong Dong<sup>a</sup>, Ke-Jing Huang<sup>b\*</sup>,  
Chengjie Hu<sup>a</sup>, Mengyi Hou<sup>a</sup>, Ren Cai<sup>c\*</sup>

(a) College of Chemistry and Chemical Engineering, Xinyang Normal University,  
Xinyang 464000, China.

(b) Education Department of Guangxi Zhuang Autonomous Region, Key Laboratory  
of Applied Analytical Chemistry, Guangxi Collaborative Innovation Center for  
Chemistry and Engineering of Forest Products, Guangxi Key Laboratory of  
Chemistry and Engineering of Forest Products, Key Laboratory of Chemistry and  
Engineering of Forest Products, State Ethnic Affairs Commission, School of  
Chemistry and Chemical Engineering, Guangxi Minzu University, Nanning  
530006, China.

(c) Molecular Science and Biomedicine Laboratory, State Key Laboratory for  
Chemo/Bio-Sensing and Chemometrics, College of Material Science and  
Engineering, College of Chemistry and Chemical Engineering, College of Biology,  
Hunan University, Changsha, 410082, China.

E-mail address: [xujing@xynu.edu.cn](mailto:xujing@xynu.edu.cn) (J. Xu), [kejinghuang@163.com](mailto:kejinghuang@163.com) (K.-J. Huang)  
[cairen@hnu.edu.cn](mailto:cairen@hnu.edu.cn) (R. Cai).

## Materials and methods

**Synthesis of Cu<sub>2</sub>O nanocubes:** First, CuSO<sub>4</sub>·5H<sub>2</sub>O (1.99 mmol) and sodium citrate (2.00 mmol) are dissolved in DI-water by stirring for 30 min. Then, 80 mL NaOH (1.25 M) and ascorbic acid (6.00 mmol) are slowly added to the above mixture. The above solution is allowed to rest for 1 h. Finally, the precipitates are collected by centrifugation, washed several times with DI-water and ethanol, and dried for 12 h at room temperature in a vacuum.

**Synthesis of hollow CuS nanocubes:** First, Cu<sub>2</sub>O nanocubes (3.49 mmol) and Na<sub>2</sub>S·9H<sub>2</sub>O (1.37 mmol) are dispersed in DI-water. The mixture is aged for 1 h at room temperature. The as-prepared products are centrifuged in DI-water and ethanol several times, and dried for 12 h in a vacuum. As-obtained nanocubes are dispersed into 100 mL ethanol by sonification. Then, 160 mL Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution (1.0 M) is added to the above mixture under agitation, and the mixture is aged for 1 h at room temperature. The precipitate is collected by centrifugation, washed with DI-water and ethanol several times, and dried for 12 h in a vacuum to obtain hollow CuS nanocubes.

**Synthesis of hollow C@Cu<sub>2</sub>S nanocubes:** CuS hollow nanocubes (0.37 mmol), 0.1817 g Tirs-HCl, and 0.03 g dopamine hydrochloride (PDA) are mixed in 75 mL DI-water and stirred for 3 h. Then, the as-obtained PDA@CuS nanocubes are collected by centrifugation. Finally, C@Cu<sub>2</sub>S nanocubes are obtained by annealing PDA@CuS nanocubes at 550 °C at 5 °C/min for 3 h in a tubular furnace under N<sub>2</sub>.

**Preparation of hollow MoS<sub>2</sub>@C@Cu<sub>2</sub>S nanocubes:** A 0.08 g sample of as-prepared hollow C@Cu<sub>2</sub>S nanocubes, 0.06 g (0.05 mmol) ammonium molybdate tetrahydrate, and 6 g (49.52 mmol) L-cysteine are dispersed in 75 mL DI-water under strong stirring for 30 min. Later, the above solution is transferred to a 100 mL Teflon autoclave and maintained at 220°C for 24 h. After cooling, the final products are

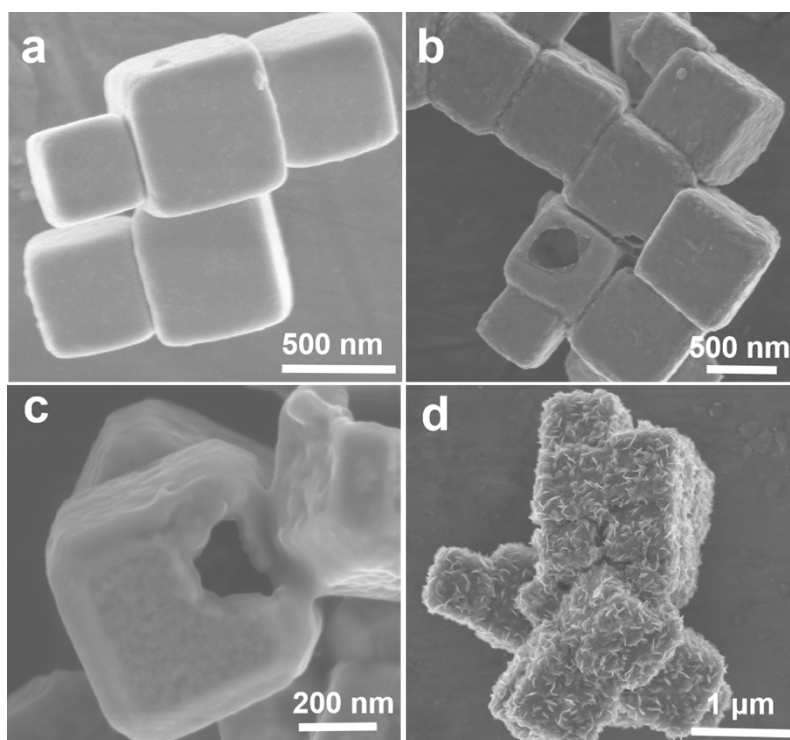
washed with ethanol and DI-water alternately several times.

### **Characterization and electrochemical testing**

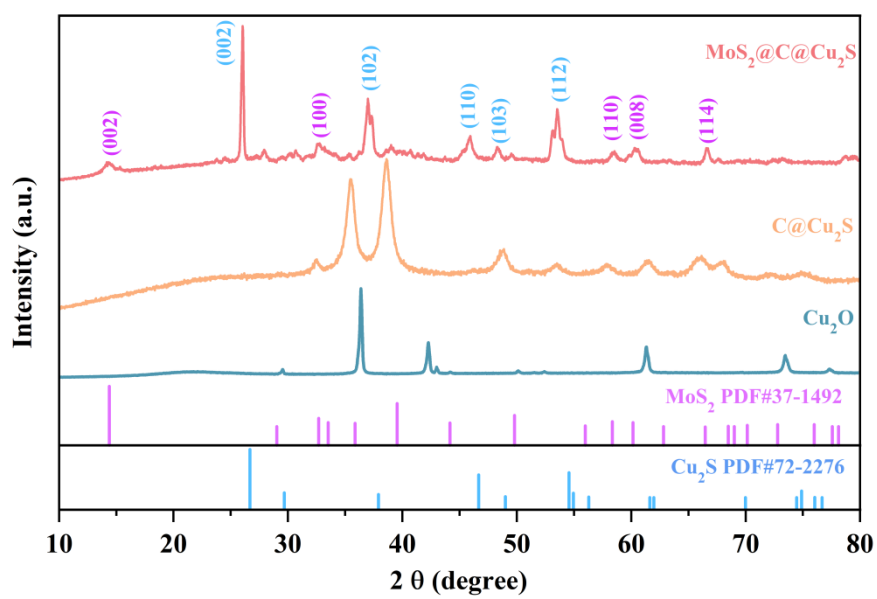
Structural information was obtained by scanning electron microscopy (S 4800), transmission electron microscopy (TEM, Tecnai G2F20), Raman spectroscopy (LabRAM HR 800), X-ray powder diffractometry (XRD, Smartlab9), and X-ray photoelectron spectroscopy (XPS, K-Alpha<sup>+</sup>, Thermo Scientific). The CV curves at different scan rates were conducted in a VMP3 electrochemical workstation (Biologic SAS). The EIS spectra were collected on VMP3, and the galvanostatic charge-discharge test and constant current cycling were conducted on the LAND CT2001.

### **Battery testing**

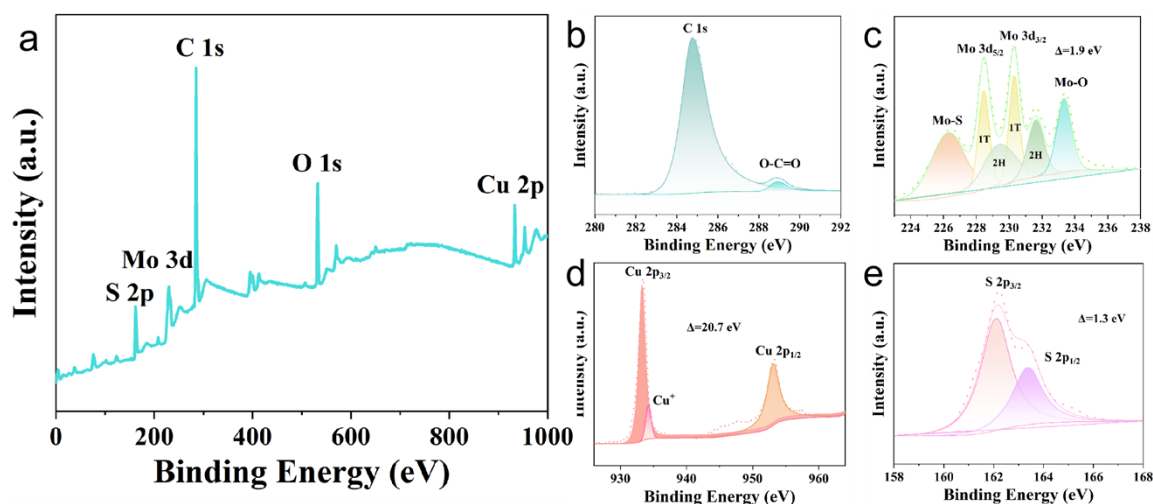
For the working electrode, a homogeneous slurry was coated on copper foil by first mixing a 70 wt% hollow MoS<sub>2</sub>@C@Cu<sub>2</sub>S heterostructures with 20 wt% carbon black (ketjen black) and 10 wt% adhesive (carboxymethyl cellulose) using DI-water as the solvent. The specific mass load of the three electrodes was about 1.0 mg cm<sup>-2</sup>. The CR 2016 button battery was assembled with a circular copper foil as cathode electrode, zinc sheet as anode electrode, glass fiber filter paper as diaphragm, and the 1.0 M ZnSO<sub>4</sub> solution as electrolyte.



**Figure S1.** The SEM images: (a)  $\text{Cu}_2\text{O}$  nanocubes; (b) hollow  $\text{CuS}$  nanocubes; (c) hollow  $\text{C@Cu}_2\text{S}$  nanocubes; (d) hollow  $\text{MoS}_2\text{@C@Cu}_2\text{S}$  heterostructures.

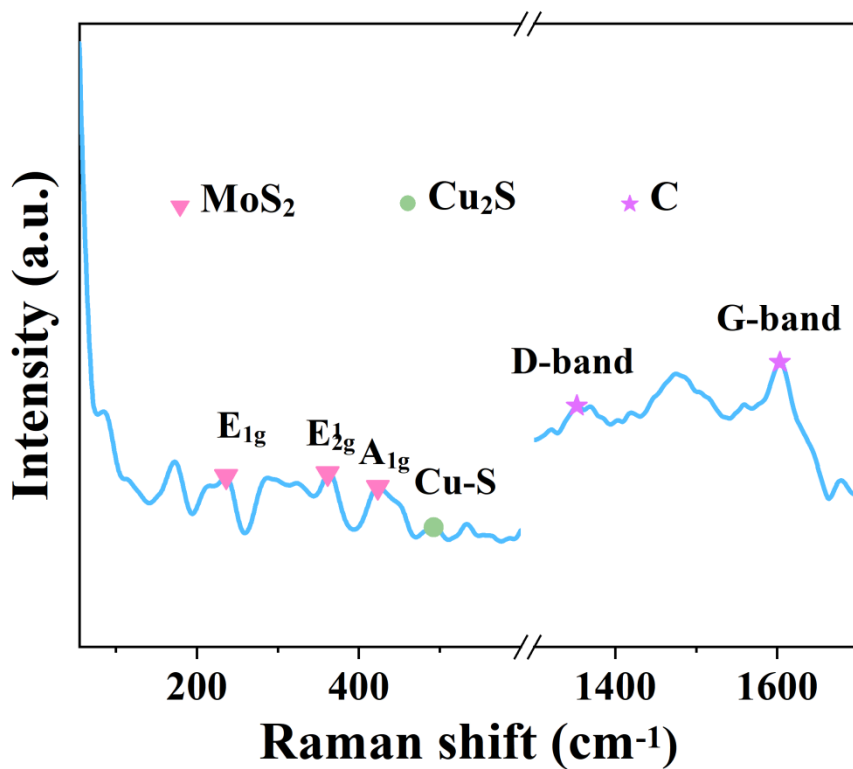


**Figure S2.** XRD patterns of  $\text{Cu}_2\text{O}$  nanocubes, hollow  $\text{C}@\text{Cu}_2\text{S}$  nanocubes and hollow  $\text{MoS}_2@\text{C}@\text{Cu}_2\text{S}$  heterostructures.



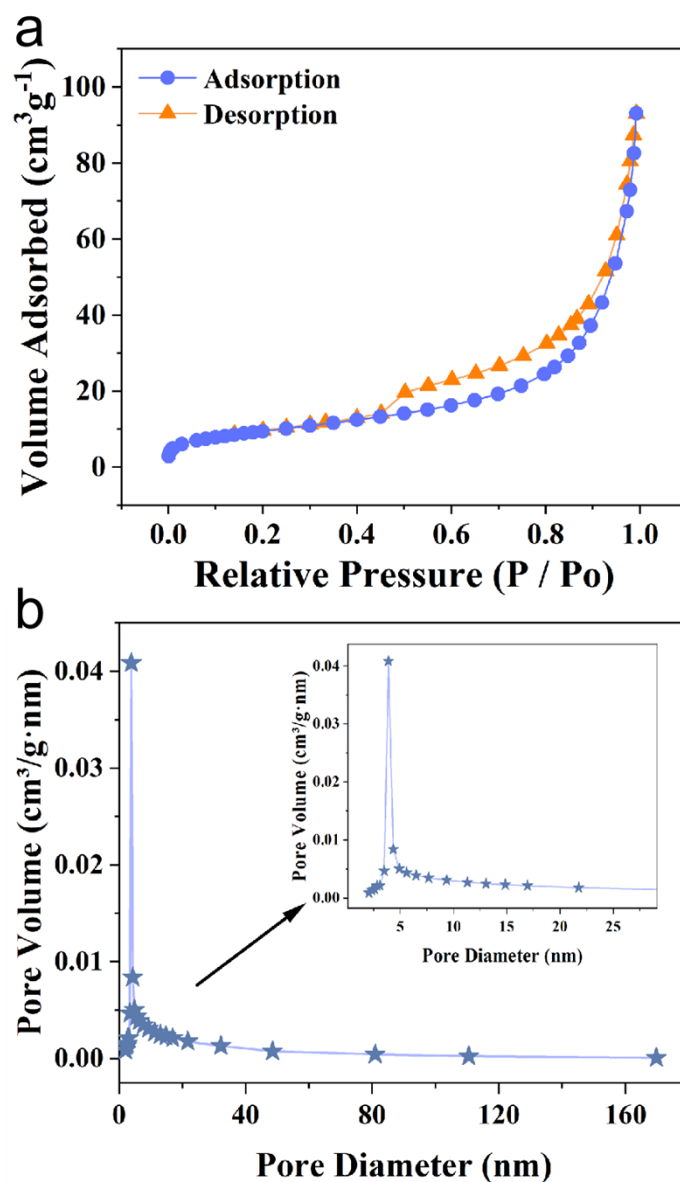
**Figure S3.** (a) Survey XPS spectrum of MoS<sub>2</sub>@C@Cu<sub>2</sub>S heterostructures, (b-d) high resolution XPS spectra in the region of: (b) C 1s, (c) Mo 3d, (c) Cu 2p, (d) S 2p.

Note: The carbon spectrum peak is corrected in **Figure S3b**, and the binding energy position of C-C single bond is at 284.4 eV. Clearly, **Figure S3c** shows the characteristic peaks located at 228.6 and 230.6 eV in the spectrum of the Mo 3d orbital, which represents the binding energy of the 3d<sub>5/2</sub> and 3d<sub>3/2</sub> orbitals of Mo<sup>4+</sup> in 1T-MoS<sub>2</sub>. The peaks at 229.4 and 231.8 eV correspond to 2H-MoS<sub>2</sub><sup>[2]</sup>. The peak at 233.7 eV can be attributed to the 3d<sub>3/2</sub> orbital of Mo (VI), corresponding to the Mo-O bond, caused by a small amount of oxidation on the MoS<sub>2</sub>@C@Cu<sub>2</sub>S heterostructure surface. A weak peak at 226.1 eV is attributed to Mo-S. **Figure S3d** shows the spectra of Cu element. Two characteristic peaks located at the 933.0 and 953.7 eV are related to the Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub>, respectively, and the weak peak at 934.4 eV is attributed to Cu<sup>+</sup>. As shown in **Figure S3e**, the binding energies of S 2p<sub>3/2</sub> and 2p<sub>1/2</sub> are at 162.1 and 163.4 eV, respectively, indicating the successful preparation of the MoS<sub>2</sub> nanosheets.



**Figure S4.** The Raman spectrum of MoS<sub>2</sub>@C@Cu<sub>2</sub>S heterostructures.

Note: For MoS<sub>2</sub> nanosheets, two significant peaks at 378 cm<sup>-1</sup> and 404 cm<sup>-1</sup> correspond to be the E<sub>12g</sub><sup>1</sup> and A<sub>1g</sub> modes.<sup>[3]</sup> The peak at 474 cm<sup>-1</sup> belongs to the lattice vibration of Cu<sub>2</sub>S. The spectrum displays a D-band at 1350 cm<sup>-1</sup> and a G-band at 1580 cm<sup>-1</sup>. Moreover, the G-band is stronger than the D-band, which means that the carbon layer was well graphitized<sup>[4]</sup>.



**Figure S5.** (a) Nitrogen adsorption-desorption isotherms and (b) BJH pore size distribution curves of MoS<sub>2</sub>@C@Cu<sub>2</sub>S, respectively.

Note: Adsorption average pore diameter (4V/A by BET) is of ~ 5 nm and the BET Surface Area is 34.10 m<sup>2</sup> g<sup>-1</sup>.



## References

- [1] Y. J. Fang, D. Y. Luan, Y. Chen, S. Y. Gao and X. W. Lou, Rationally designed three-layered  $\text{Cu}_2\text{S}@Carbon@MoS_2$  hierarchical nanoboxes for efficient sodium storage, *Angew. Chem. Int. Ed.*, 2020, **59**, 7178-7183.
- [2] D. Z. Wang, Y. Y. Xiao, X. N. Luo, Z. Z. Wu, Y. J. Wang and B. Z. Fang, Swollen ammoniated  $\text{MoS}_2$  with 1T/2H hybrid phases for high-rate electrochemical energy storage, *ACS Sustain. Chem. Eng.*, 2017, **5**, 2509–2515.
- [3] Z. Dong, X. Wu, M. Y. Chen, H. X. Chen, K. J. Huang, L. L. Wang and J. Xu, Self-supporting 1T- $\text{MoS}_2@WS_2@CC$  composite materials for potential high-capacity sodium storage system, *J. Colloid Interface Sci.*, 2023, **630**, 426–435.
- [4] S. B. Wang, B. Y. Guan, L. Yu and X. W. Lou, Rational design of three-layered  $\text{TiO}_2@Carbon@MoS_2$  hierarchical nanotubes for enhanced lithium storage, *Adv. Mater.*, 2017, **29**, 1702724.