

Electronic Supplementary Information (ESI)

Bubble-supported engineering of hierarchical CuCo_2S_4 hollow spheres for enhanced electrochemical performance

Huihui You^a, Lei Zhang^{*a}, Yinzhu Jiang^b, Tianyan Shao^a, Ming Li^c, Jinlong Gong^{*ade}

^a*School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P. R. China*

^b*School of Materials Science and Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, P. R. China*

^c*Department of Mechanical, Materials and Manufacturing Engineering, University of Nottingham, Nottingham NG7 2RD, United Kingdom*

^d*Key Laboratory for Green Chemical Technology of Ministry of Education, Tianjin 300072, P. R. China*

^e*Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, P. R. China*

Experimental section

1.1 Materials

All the reagents in the experiment were analytical grade and used without any further treatment. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, sulfur powder, thiourea and thioacetamide were purchased from J&K Scientific Ltd. Ethylene glycol and isopropyl alcohol were purchased from Real&Lead Chemical Co., Ltd.

1.2 Preparation of CuCo_2S_4

Hierarchical CuCo_2S_4 hollow spheres were prepared by a solvothermal method. At first, 1 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 2 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 4 mmol of thiourea were dissolved in the mixed solution of 40 mL ethylene glycol and 40 mL isopropyl alcohol. The homogeneous pink

mixture was transferred to a 100 mL Teflon-lined autoclave and heated at 180 °C for 12 h. The precipitate was collected by centrifugation and washed with ethanol and dried at 60 °C. The precursors were calcined at 350 °C for 2 h in N₂ to obtain hierarchical CuCo₂S₄ hollow spheres. For comparison, CuCo₂S₄ with different morphologies were also prepared using sulfur powder and thioacetamide instead of thiourea by the same experimental procedure.

1.3 Material characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 (Cu K_α radiation, $\lambda=1.54056 \text{ \AA}$). The Raman spectra was recorded on a Renishaw Invia Plus laser Ramanspectrometer (Renishaw, UK), with an excitation laser wavelength of 514 nm. The morphology of samples was studied by scanning electron microscopy (SEM) (Hitachi S4800, Japan) with accelerating voltage of 5.0 kV. Transmission electron microscopy (TEM) characterization was performed on JEM 3100 (JEOL, Japan) operated at 200 kV. X-ray photoelectron spectroscopy (XPS) analyses were conducted with a Physical Electronics PHI5802 instrument using X-rays magnesium anode (monochromatic K_α X-rays at 1253.6 eV) as the source. Cycling voltammetry (CV), galvanostatic charge-discharge (CD) and electrochemical Impedance Spectroscopy (EIS) are performed with CHI660D (Shanghai Chenhua, China) electrochemical workstation.

1.4 Electrochemical measurements

The slurry of the work electrode was prepared by mixing CuCo_2S_4 , carbon black (Super P) and polytetrafluoroethylene (binder) at a mass ratio of 8:1:1. The mixed slurry was pasted onto Ni foam with 2 mg cm^{-2} followed by drying at 80°C under vacuum. Electrochemical properties were evaluated by a three-electrode system with a Pt foil as the counter electrode and a Hg/HgO (SCE) as the reference electrode in an aqueous 6 M KOH electrolyte. The CV curves was measured in a potential range of 0-0.55 V vs Hg/HgO and CD was measured at different current densities in a potential range of 0-0.48 V vs Hg/HgO. EIS measurements were carried out by applying an AC voltage with 5 mV amplitude in a frequency range of 0.1~100 kHz.

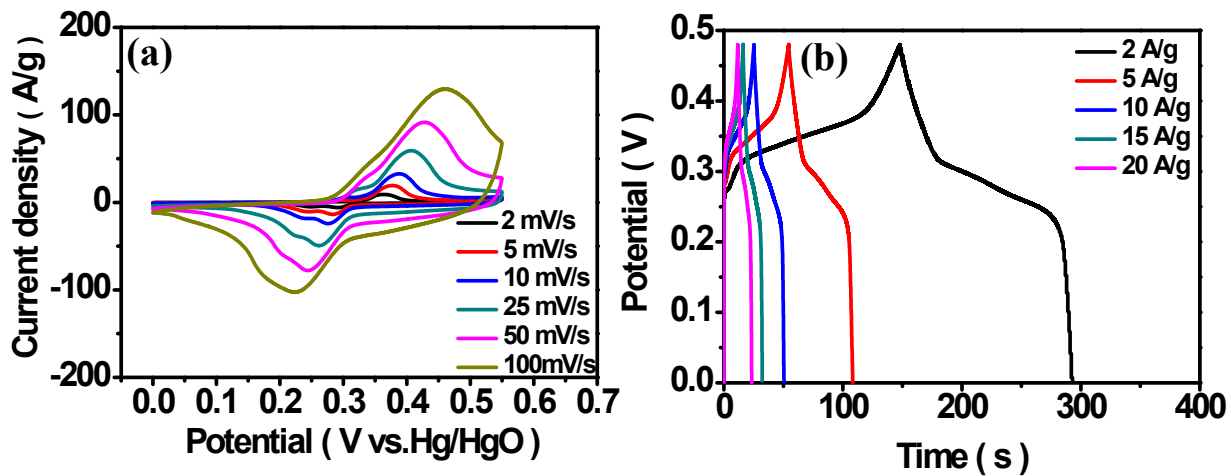


Fig. S1 (a) CV curves of the CuCo₂S₄-SP at different scan rates. (b) charge-discharge curves of CuCo₂S₄-SP at different current densities.

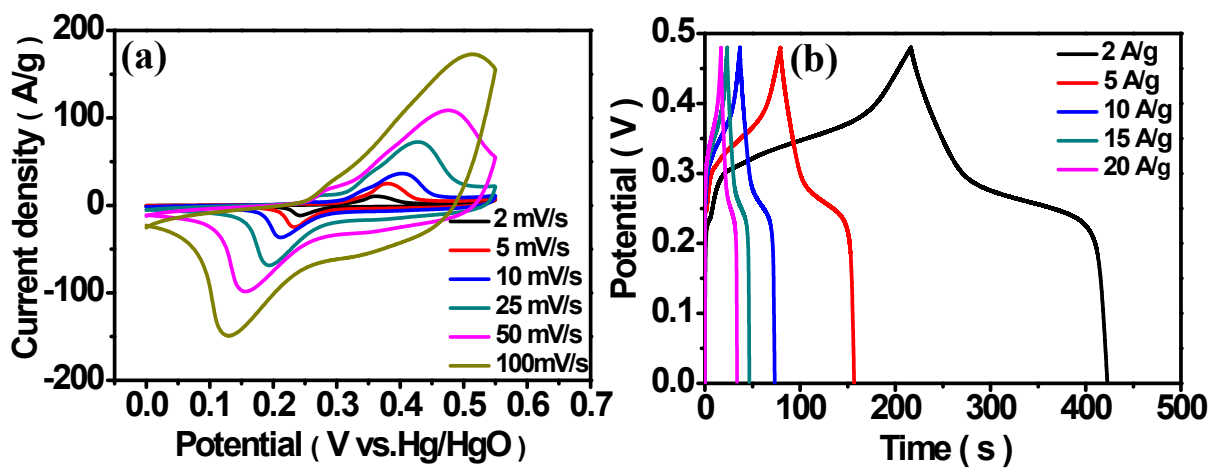


Fig. S2 (a) CV curves of the CuCo₂S₄-TAA at different scan rates. (b) charge-discharge curves of CuCo₂S₄-TAA at different current densities.

Table S1. Comparison of the specific capacitance and capacitance retention for sulfide spinels with different morphologies.

Sample	Specific capacitance	Capacitance retention	Preparation method	Reference
Mesoporous NiCo ₂ S ₄ Nanosheets	736 F g ⁻¹ at 2 A g ⁻¹	71.7 % (from 2 to 50 A g ⁻¹)	hydrothermal method	1
Mesoporous NiCo ₂ S ₄ nanoparticles	972 F g ⁻¹ at 2 A g ⁻¹	82.1 % (from 2 to 30 A g ⁻¹)	solvothermal method	2
NiCo ₂ S ₄ ball-in-ball hollow spheres	1036 F g ⁻¹ at 1 A g ⁻¹	68.1 % (from 1 to 20 A g ⁻¹)	two steps solvothermal method	3
NiCo ₂ S ₄ hollow prisms	895.2 F g ⁻¹ at 1 A g ⁻¹	65.4 % (from 1 to 20 A g ⁻¹)	sacrificial template method	4
CoNi ₂ S ₄ nanoparticles	972.2 F g ⁻¹ at 2 A g ⁻¹	60.1 % (from 1 to 5 A g ⁻¹)	solvothermal method	5
Tube-like NiCo ₂ S ₄	1048 F g ⁻¹ at 3 A g ⁻¹	50.1 % (from 3 to 10 A g ⁻¹)	hydrothermal method	6
Co ₂ CuS ₄ nanoparticle	768 F g ⁻¹ at 1 A g ⁻¹		solvothermal method	7
Mesoporous CuCo ₂ S ₄	752 F g ⁻¹ at 2 A g ⁻¹	47.9 % (from 2 to 100 A g ⁻¹)	solvothermal method	8
Hierarchical CuCo ₂ S ₄ hollow spheres	1137.5 F g ⁻¹ at 2 A g ⁻¹ , 964.2 F g ⁻¹ at 20 A g ⁻¹	84.8% (from 2 to 20 A g ⁻¹)	bubble-supported solvothermal method	This work

1. Z. Wu, X. Pu, X. Ji, Y. Zhu, M. Jing, Q. Chen and F. Jiao, *Electrochim. Acta*, 2015, **174**, 238-245.
2. Y. Zhu, Z. Wu, M. Jing, X. Yang, W. Song and X. Ji, *J. Power Sources*, 2015, **273**, 584-590.
3. L. Shen, L. Yu, H. B. Wu, X.-Y. Yu and X. Zhang, *Nat. Commun.*, 2015, **6**, 6694.
4. L. Yu, L. Zhang, H. B. Wu and X. W. Lou, *Angew. Chem.*, 2014, **126**, 3785-3788.
5. W. Du, Z. Zhu, Y. Wang, J. Liu, W. Yang, X. Qian and H. Pang, *Rsc Advances*, 2014, **4**, 6998-7002.
6. Zhang, M. Ma, J. Yang, C. Sun, H. Su, W. Huang and X. Dong, *Nanoscale*, 2014, **6**, 9824-9830.
7. M. Guo, J. Balamurugan, T. D. Thanh, N. H. Kim and J. H. Lee, *J. Mater. Chem. A*, 2016, **4**, 17560-17571.

8. Y. Zhu, X. Ji, H. Chen, L. Xi, W. Gong and Y. Liu, *RSC Advances*, 2016, **6**, 84236-84241.