Electronic Supplementary Information (ESI)

A novel caterpillar-with-eggs mesostructured iron sulfide as Li-ion battery anode displaying stable electrochemical performance

Ting Zhou[a], Yan Wang[a], Yajun Zhu[a], Tianli Han[a,*], Huigang Zhang [b,c,*], Jinyun Liu[a,*]

Experimental section

Chemical materials

The $FeCl_3 \cdot 6H_2O$, urea, sulfur powder, trisodium citrate dehydrate were obtained from Aladdin. Tetraethyl silicate (TEOS) and iron acetylacetonate were purchased from Macklin. The $NH_3 \cdot H_2O$, glycerol, $FeSO_4 \cdot 7H_2O$, Sodium acetate, ethylene glycol, and anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used directly without further processing.

Synthesis of 1D Fe_3O_4@SiO_2

The Fe_3O_4 nanospheres were prepared by dispersing evenly $FeCl_3 \cdot 6H_2O$ (4.3 g), NaAc (4.0 g), and trisodium citrate dehydrate (1.0 g) in 70 ml of ethylene glycol. Then, a transparent solution was transferred into a Teflon-lined stainless steel autoclave and kept in an oven at 200 ℃ for 10 h. 0.05 g of Fe_3O_4 nanoparticles were ultrasonically dispersed in 240 mL of anhydrous ethanol, and 30 mL of ammonia was added under a strong mechanical rate (800 rpm)

for 10 min. Subsequently, 2 mL of TEOS was slowly added under a low agitation (350 rpm). After stirring for 15 min, the solution was held under an external magnetic field for 100 s. Finally, after standing for 12 h, the 1D Fe_3O_4@SiO_2 was synthesized by washing with deionized water and ethanol, and drying at 60 °C for 12 h.

Preparation of 1D yolk-shell Fe_3O_4@void@FeOOH nanoneedles

0.1 g of Fe_3O_4@SiO_2 was ultrasonically dispersed in a mixture of 30 mL H_2O and 10 mL glycerin. Then, 0.7 g of $FeSO_4 \cdot 7H_2O$ was added to the above solution and ultrasonically dispersed for 30 min, which was placed in an autoclave and kept in an oven at 120 °C for 24 h. At last, the Fe_3O_4@SiO_2@FeOOH was obtained by washing several times with deionized water. Then, the sample was ultrasonically dispersed in 10 mL ammonia and 25 mL deionized water, and placed in an 50 mL-autoclave at 150 °C for 8 h to obtain the Fe_3O_4@void@FeOOH.

Preparation of the 1D yolk-shell CWE FeS_2

The sample was prepared by separately placing the above Fe_3O_4@void@FeOOH and sulfur powder on either side of a tube furnace, which was calcined at 400 °C for 1 h under an Ar gas at a rate of 2 °C min^{-1}.

Characterization

The structure and phase of the sample were characterized by a field emission scanning electron microscopy (SEM, Hitachi S-8100), a transmission electron microscopy (TEM, HT-7700), and a X-ray diffractomerter (XRD, Bruker D8 Advance). Elemental mappings were

presented on an energy dispersive X-ray spectrometer. An energy dispersive X-ray spectroscopy (EDS) tester was used to preform the composition of sample. The components and valence states of the product were analyzed by using X-ray photoelectron spectroscopy (XPS, ESCALAB 250). The BET surface area and pore-size distribution were measured using a Micrometritics ASAP 2460 analyzer.

Electrochemical measurements

The electrochemical properties of 1D yolk-shell CWE FeS_2 were evaluated by using CR2032 coin cell system, which was assembled in an argon-filled glove box (H_2O and O_2 < 0.01 ppm). The homogeneous slurry of the sample (70 w%), conductive carbon black (20 w%) and poly-vinylidene fluoride (PVDF, 10 w%) in N-methyl-pyrrolidinone (NMP) was evenly coated on a copper foil, which was dried in a vacuum oven at 80 °C for 24 h, then was cut into a 12 mm-diameter discs. The electrolyte was prepared with 1 M of $LiPF_6$ in ethylene carbonate (EC) and ethyl methyl carbonate (EMC, volume ratio=1:1). Li metal was used as the counter electrode. The electrochemical performance of fresh cells was measured on a CT-4008 system (Shenzhen Neware Technology Co., Ltd). An electrochemical workstation (CHI-660D) was used to measure cyclic voltammetry (CV) in the potential range of 0.01-3 V and electrochemical impedance spectra (EIS) at a frequency of 0.01 to 100 kHz.

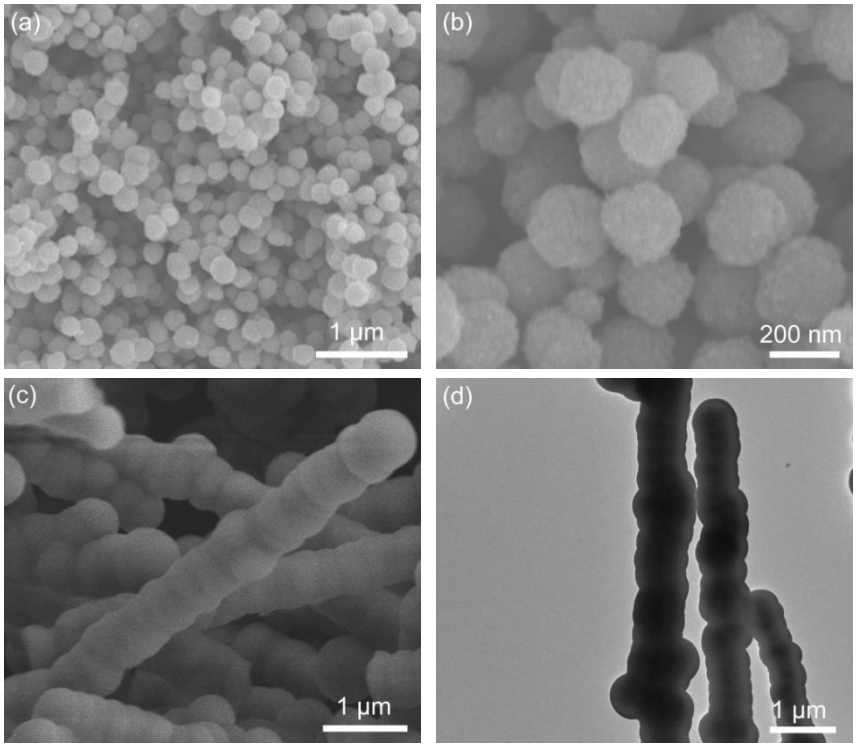

Fig. S1 SEM images of the (a,b) Fe_3O_4 nanospheres, (c) Fe_3O_4@SiO_2. (d) TEM images of Fe_3O_4@SiO_2.

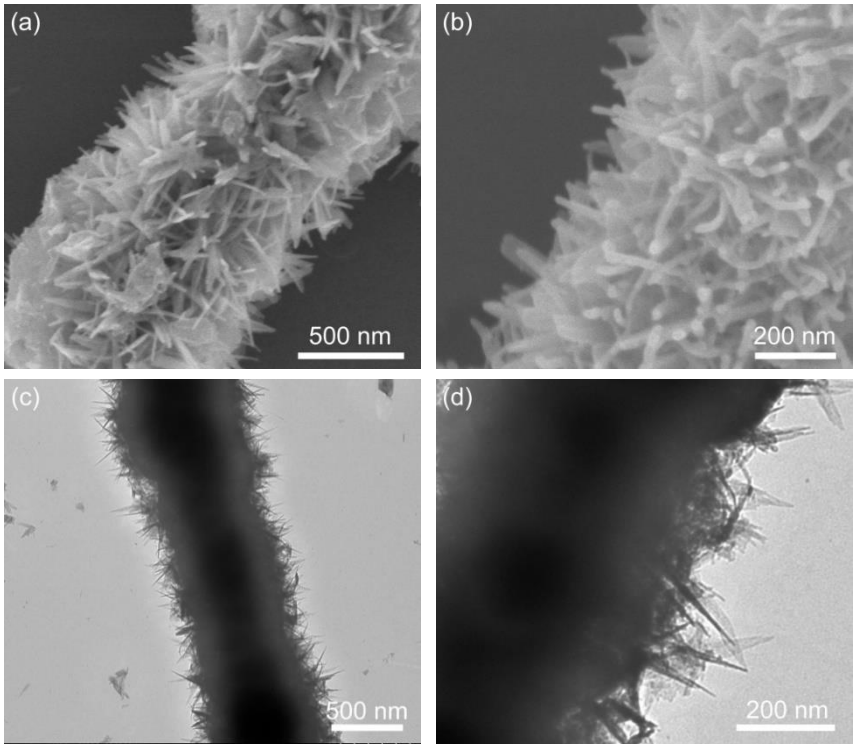

Fig. S2 (a,b) SEM images of the Fe_3O_4@SiO_2@FeOOH. (c,d) TEM images of the Fe_3O_4@SiO_2@FeOOH.

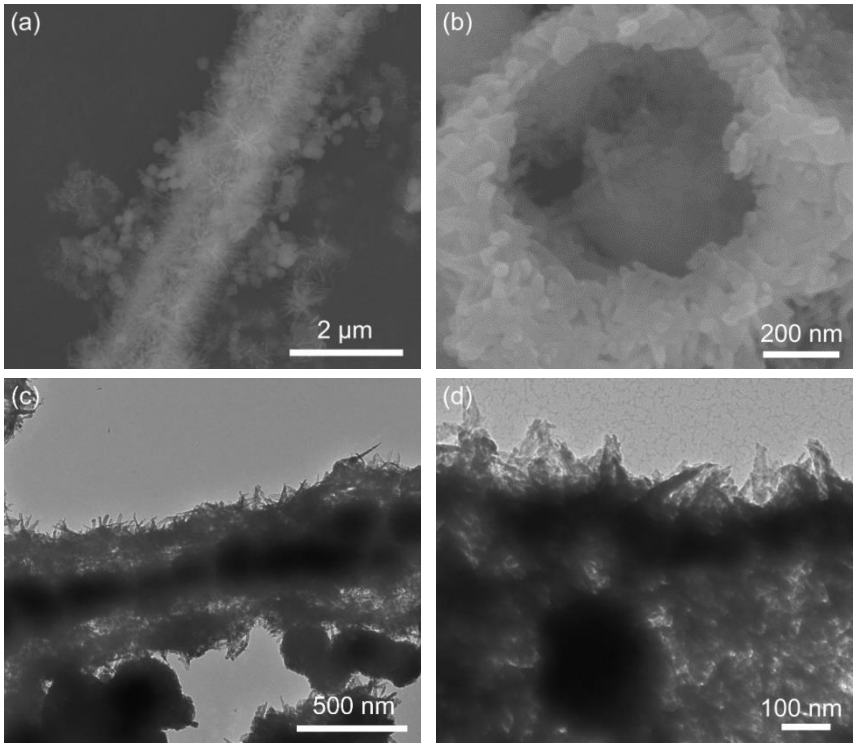

Fig. S3 (a,b) SEM and (c,d) TEM images of CWE FeS_2.

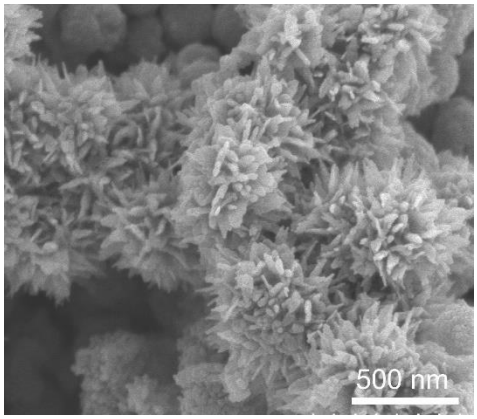

Fig. S4 SEM image of the yolk-shell FeS_2 nanospheres.

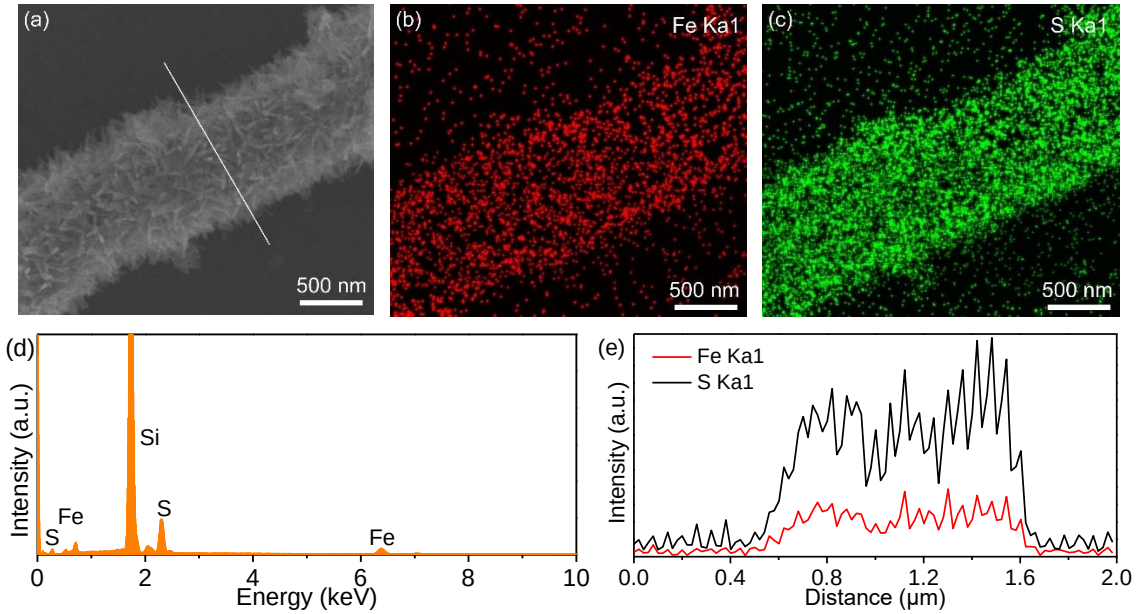

Fig. S5 (a) SEM and (b,c) elemental mapping images of the CWE FeS_2. (d) EDS spectrum. (e) The line-scanning profiles.

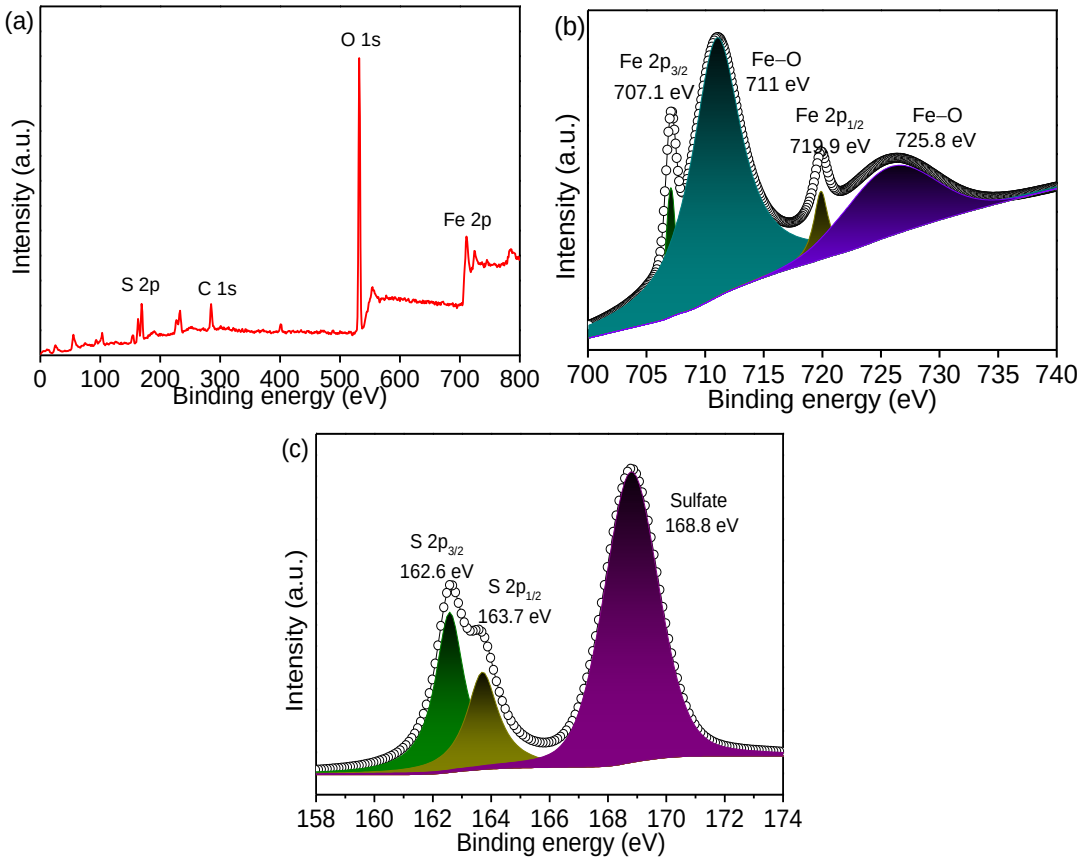

Fig. S6 (a) XPS survey spectrum. High-resolution spectra of (b) Fe 2p and (c) S 2p of FeS_2.

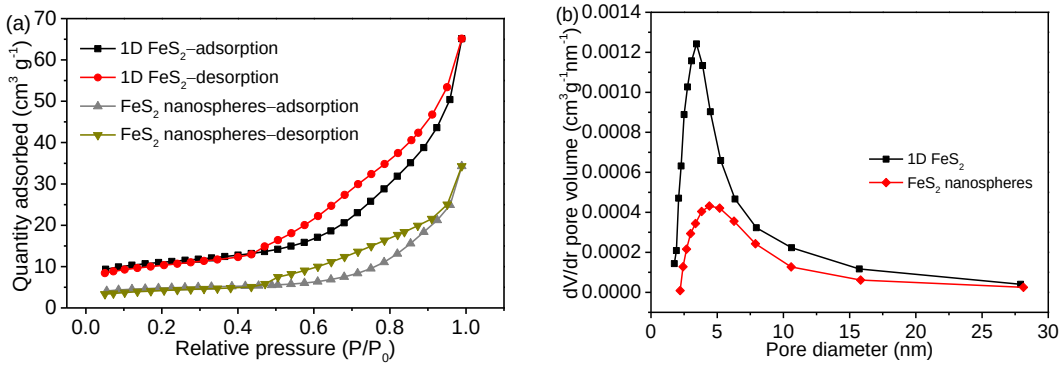

Fig. S7 (a) The N_2 adsorption-desorption isotherms. (b) The pore-size distributions.

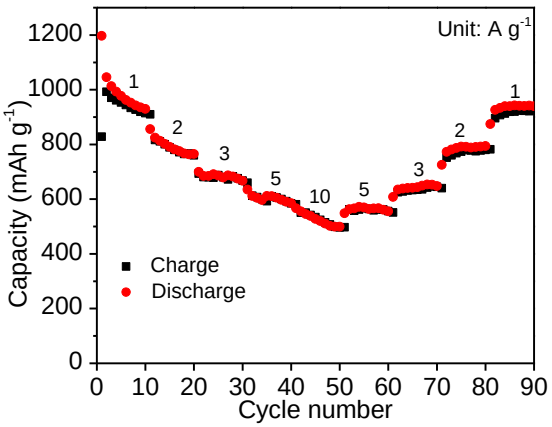

Fig. S8 Rate-performance of the CWE FeS_2.

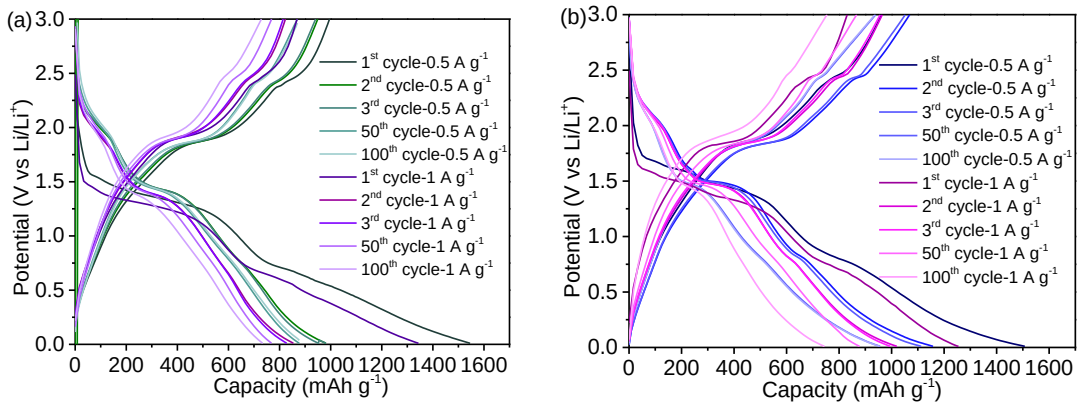

Fig. S9 Charge-discharge curves of the CWE FeS_2 at rates of 0.5 and 1 A g^{-1} under different temperatures: (a) –10 °C and (b) 45 °C.

Table S1. Comparison on the electrochemical performance of some other FeS_2-based anodes.

Anode	Preparation method	Cycling rate ($A\ g^{-1}$)	Cycle number	Capacity ($mAh\ g^{-1}$)	Ref.
FeS_2/carbon nanotubes hybrids	Solvothermal method	0.2	200	800	1
FeS_2@sulfur-doped carbon	A sulfuration process	1	300	849	2
Yolk-shell FeS_2@carbon spheres	Calcination process	0.1	100	560	3
Core-shell FeS_2@N-graphene	Hydrothermal route	0.5	400	402	4
FeS_2@bifunctional carbon nanotubes	Solvothermal method	1	500	698	5
FeS_2 microspheres	Solvothermal method	1	100	540	6
Yolk-shell CWE FeS_2	Template method	1	100	887	This study
		2	500	805	

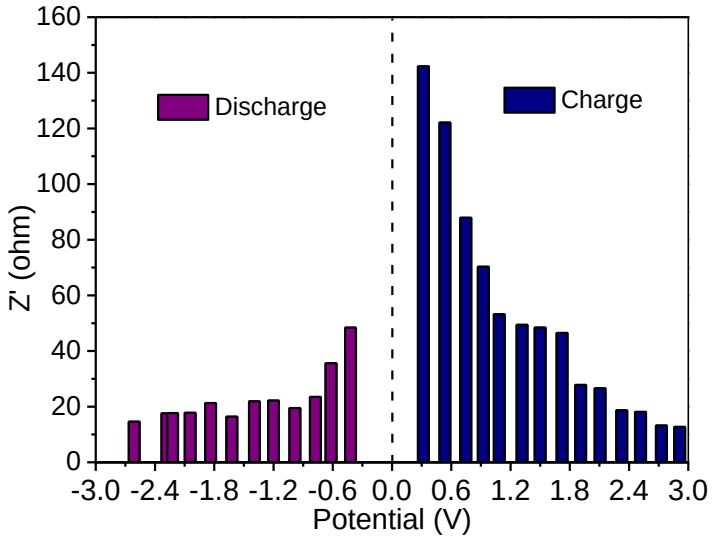

Fig. S10 The charge transfer resistance within one charge-discharge cycle.

Table S2. Charge transfer resistance of the CWE FeS_2-based anode within one charge-discharge cycle.

Discharging potential (V)	Charge transfer resistance (Ω)	Charging potential (V)	Charge transfer resistance (Ω)
2.556	14.6	0.263	142.3
2.225	17.6	0.481	122.1
2.167	17.7	0.692	87.9
1.989	17.8	0.87	70.3
1.782	21.3	1.031	53.2
1.567	16.4	1.262	49.4
1.338	21.9	1.445	48.4
1.145	22.2	1.667	46.5
0.929	19.5	1.855	27.8
0.721	23.5	2.052	26.6
0.563	35.6	2.271	18.7
0.365	48.4	2.461	18.1
-	-	2.673	13.2
-	-	2.858	12.7

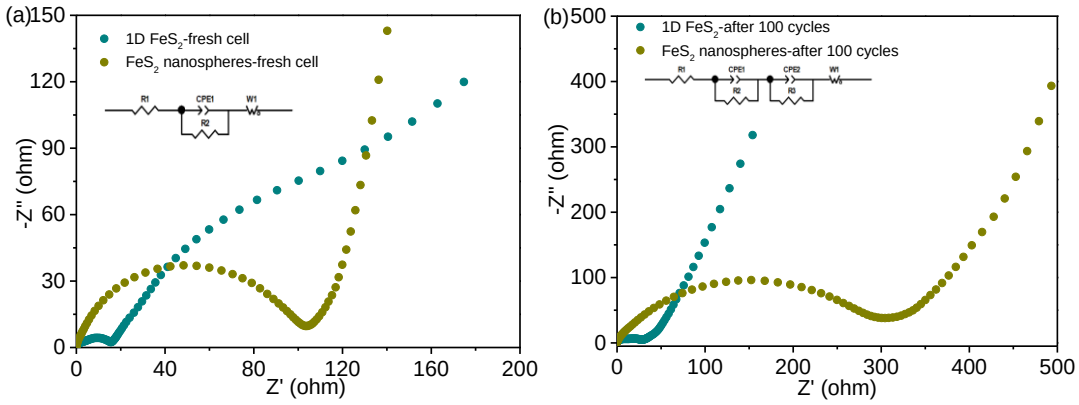

Fig. S11 EIS spectra of CWE FeS_2 and the FeS_2 nanospheres (a) before and (b) after cycling 100 times at 1 A g^{-1}. The inserts display the equivalent circuit models.

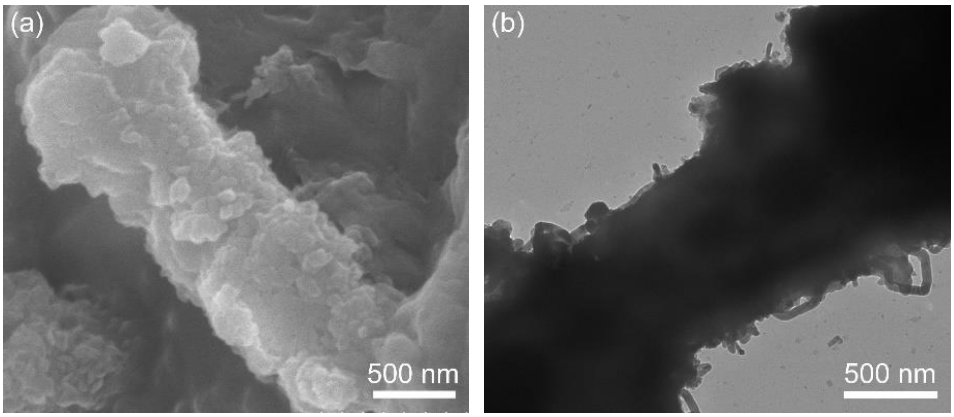

Fig. S12 (a) SEM and (b) TEM images of the CWE FeS_2 after 100 cycles at 1 A g^{-1}.

References

1 L. Xu, Y. J. Hu, H. X. Zhang, H. J and C. Z. Li, *ACS Sustainable Chem. Eng.,* 2016, **4**, 4251−4255.

2 W. Chen, Q. Z. Li, H. X. Zhang, X. H. Wu, W. W. Wu and M. Xu, *Energy Fuels,* 2021, **35**, 12599−12609.

3 Y. J. Liu, W. Q. Wang, Q. D. Chen, C. Xu, D. P. Cai and H. b, Zhan, *Inorg. Chem.,* 2019, **58**, 1330−1338.

4 R. Tan, J. L. Yang, J. T. Hu, K. Wang, Y. Zhao and F. Pan, *Chem. Commun.,* 2016, **52**, 986−989.

5 J. H. Lu, F. L, L. L. Guan, Y. X. Zhang and F. Ding, *J. Mater. Chem. A,* 2019, **7**, 991−997.

6 Z. Hu, K. Zhang, Z. Q. Zhu, Z. L. Tao and J. Chen, *J. Mater. Chem. A,* 2015, **3**, 12898−12904.