

Electronic Supplementary Information

Hermetical encapsulating sulfur by FePS₃ flakes for high-performance lithium sulfur batteries

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Experimental Section

Preparation of FePS₃ flakes

In a typical synthesis procedure of bulk FePS₃, 2 g of iron (99%, Alfa Aesar), phosphorus (98.9%, Alfa Aesar) and sulfur (99.95%, Aladdin) powder with a molar ratio of 1:1:3 were mixed homogeneously in an Ar-filled glovebox. Then the mixture was degassed in a vessel and heated at 700 °C for two weeks. After cooling down to room temperature, collecting, washing with N,N-Dimethylformamid (DMF) and drying at 80 °C for 12 h, the FePS₃ crystals were obtained. The exfoliated FePS₃ sheets was achieved via a DC bias (-3 V) which was supplied by an electrochemical workstation (CHI 760E, Shanghai Chenhua Instrument Factory, China) with bulk FePS₃ crystals as the working electrode and Pt wire as a counter electrode. In addition, the electrolyte solution was 60 mg tetra-n-butylammonium tetrafluoroborate in 30 mL DMF. Finally, the product was collected and washed with DMF for several times, which was ready for the follow-up application.

Synthesis of FePS₃-encapsulated hollow sulfur sphere

Hollow sulfur spheres (HSS) were synthesized with the assistance of PVP. In a typical synthesis, 100 ml of 80 mmol sodium thiosulfate (Na₂S₂O₃, Energy Chemical) solution was mixed with 100 ml 0.4 M PVP (M_w ≈ 55000, the concentration was calculated in terms of the repeating unit) drop by drop. Then the mixed solution was stirred for 15 min, and 0.8 ml of concentrated hydrochloric acid (HCl, 36.5-38.0%, Sigma-Aldrich) was added into the mixture under magnetic stirring. Then the reaction had proceeded at room temperature for 2 h. The HSS were isolated by centrifugation at 7000 rpm for 10 min. After that the product was dispersed into 0.8 M PVP aqueous solution and was collected by centrifugation at 6000 rpm for 15 min. The product was dispersed again into 50 ml distilled water for later use (~2 mg/ml). The as-synthesized exfoliated FePS₃ flakes were dispersed into 40 ml water then sonicated in a high-power sonic bath for 4 h to form a homogeneous suspension (~1 mg/ml). After that the HSS solution was dropwise mixed with FePS₃ flakes suspension solution under stirring. The mixture was stirred for 2 h at room temperature and the product was collected by centrifugation. The product was washed 3 times by water and lyophilized to collect HSS@FePS₃ product.

Material characterization

The HSS, HSS@FePS₃, FePS₃ flakes, and bulk FePS₃ were tested by field-emission scanning electron microscopy (TESCAN-MIRA3) to observe the surface morphologies and characterized by X-ray powder diffraction (XRD, Ultima IV, Rigaku) with the diffraction angle (2θ) from 5° to 80° at a scan rate of 4°/min to characterize the structure. The thermogravimetric (TG) analysis of the exfoliated FePS₃ flakes, HSS and HSS@FePS₃ are measured in nitrogen atmosphere with a heating rate of 10 °C/min in order to determine the sulfur fraction in samples (HTG-1, Beijing Hengjiu). X-ray photoelectron spectroscopy was performed by PHI 5000 VersaProbe III with a monochromatic Al K α X-ray source, with a base pressure better than 5×10^{-7} Pa for analysis. The X-ray beam size is 100 μ m and the pass energy is 55 eV. The binding energy was corrected by setting the binding energy of the hydrocarbon C 1s feature to 284.8 eV.

Electrochemical measurements

The HSS@FePS₃ active materials were mixed with Super P conduction carbon and PVDF at a weight ratio 70:20:10 in N-Methylpyrrolidone (NMP) to form electrode slurry. After stirring for 6 h, the slurry was coated on the aluminum foil current collector and dried at 60 °C overnight in a vacuum to form the working electrode. The total material loading density was around 1 mg/cm². 2032-type coin cells were assembled in an Ar-filled glovebox, using Li metal foil as anode and a Celgard 2325 membrane as the separator. The electrolyte was 1.0 M lithium bis-trifluoromethane sulfonylimide in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) mixed solution (volume ratio 1:1) with 1 wt% LiNO₃ additives. The working electrodes were cycled between 1.7 and 2.7 V vs Li/Li⁺. The charge/discharge performances were characterized by the Neware battery testing system in coin-type cells. Specific capacity values were calculated according to the mass of sulfur. Cyclic voltammetry measurements were also performed in the potential range of 1.7-2.7 V with a scan rate of 0.1 mV/s on a Ivium-n-Stat.

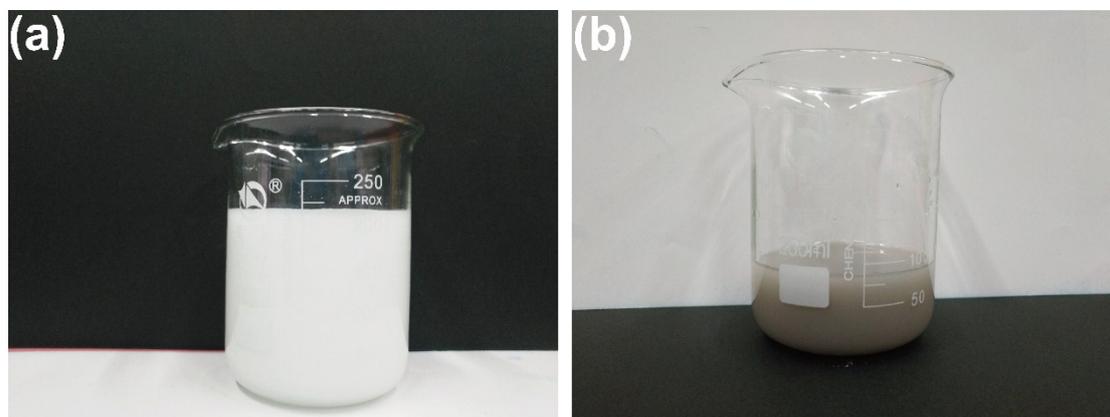


Fig. S1 The photographs of (a) HSS solution and (b) HSS@FePS₃ solution.

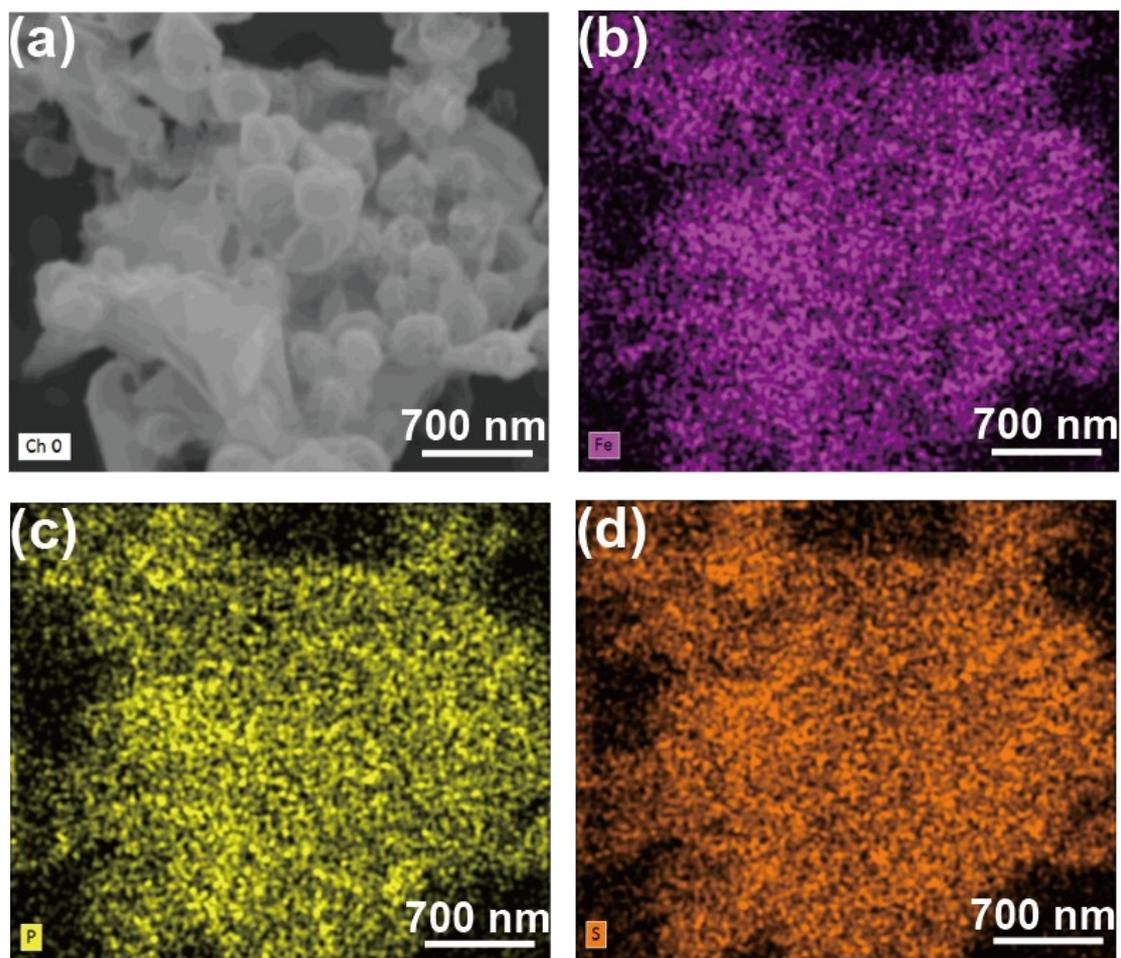


Fig. S2 (a) SEM images of HSS@FePS₃ and EDS elemental mappings of (b) Fe, (c) P, and (d) S, respectively.

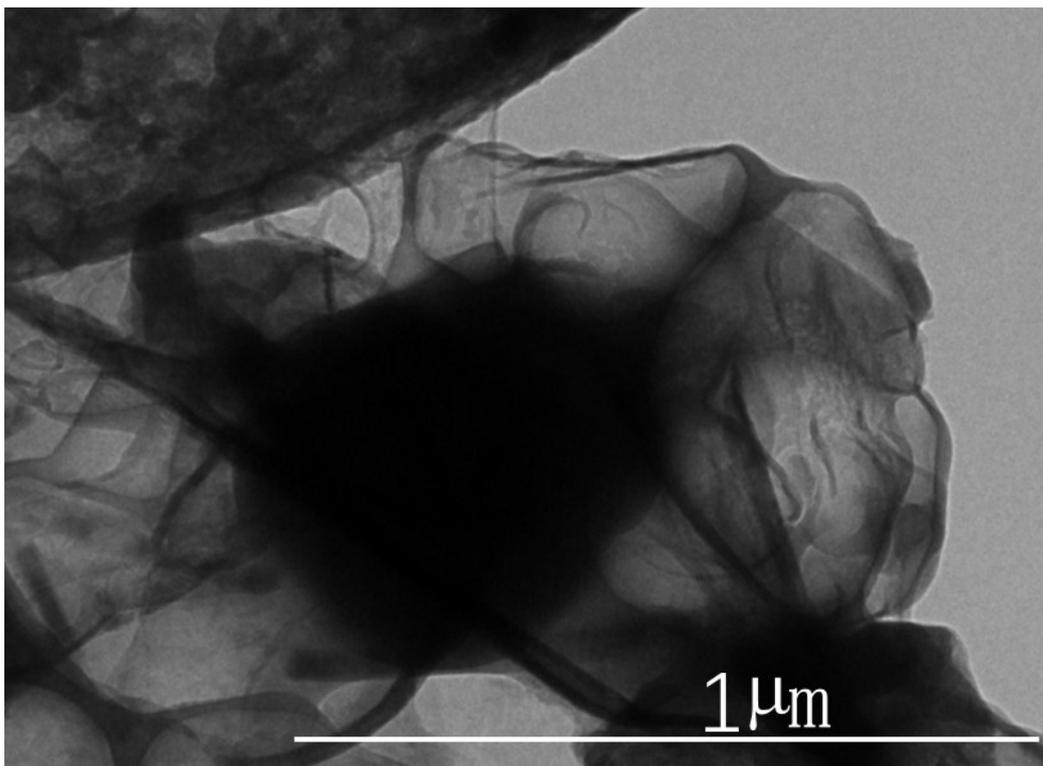


Fig. S3 TEM image of HSS@FePS₃

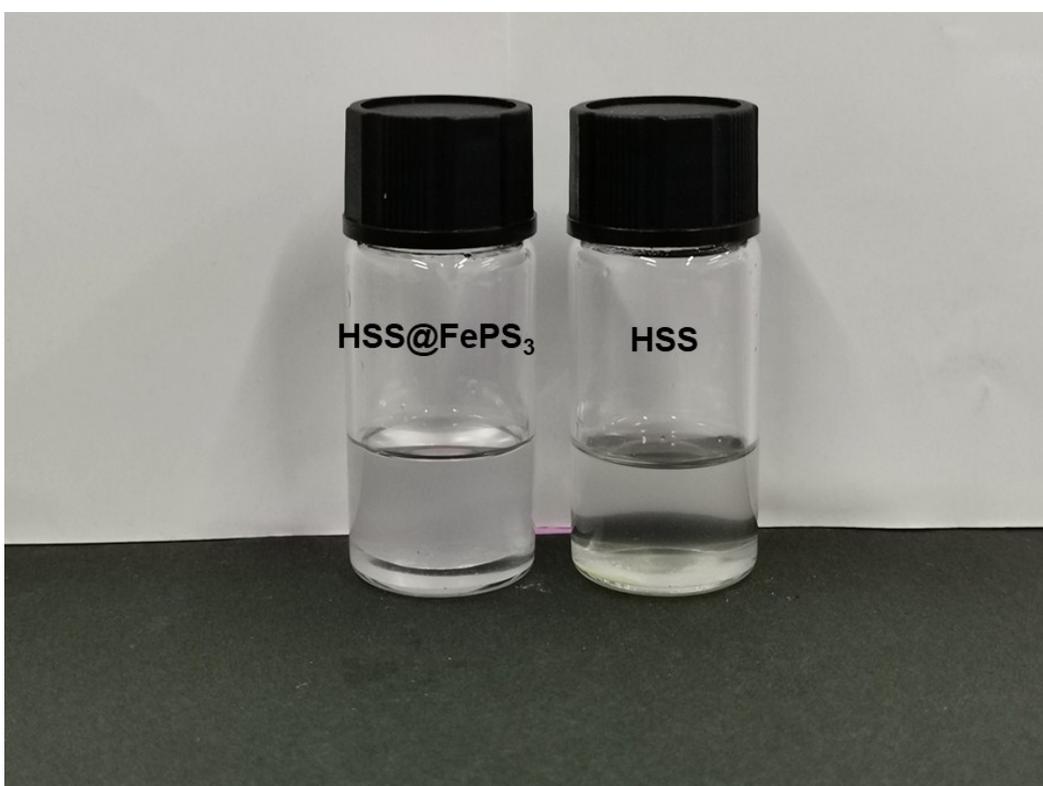


Fig. S4 The photographs of HSS@FePS₃ and HSS electrodes in the electrolyte.

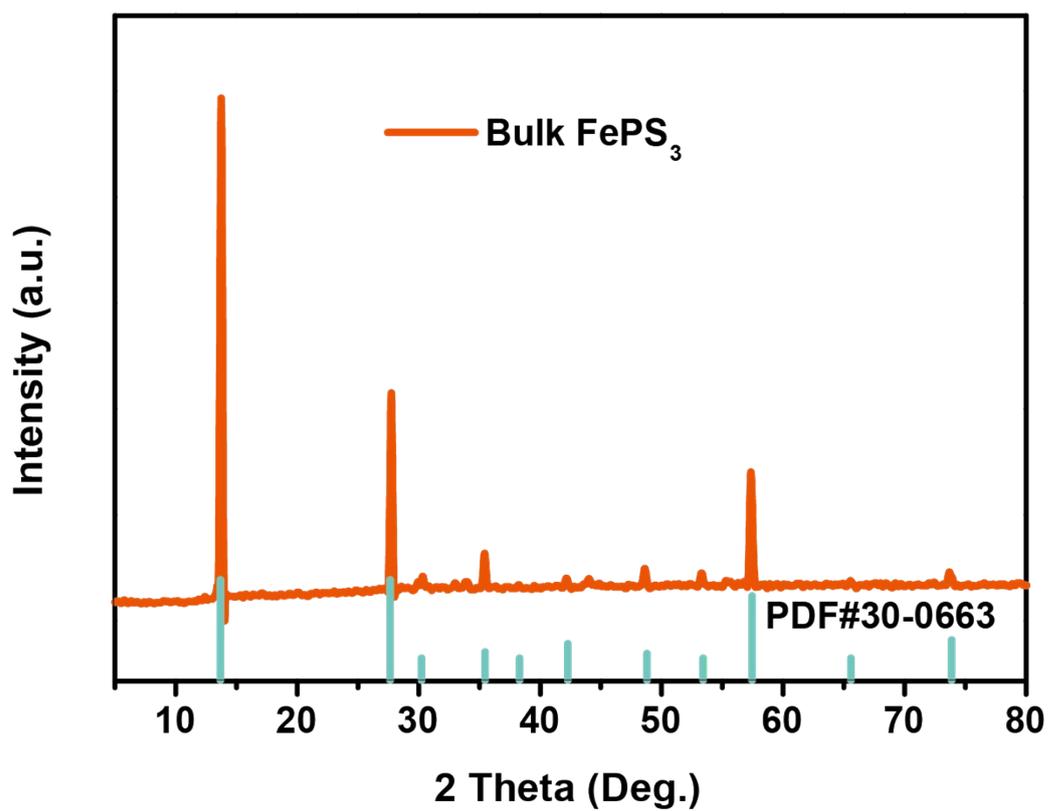


Fig. S5 XRD patterns of bulk FePS₃.

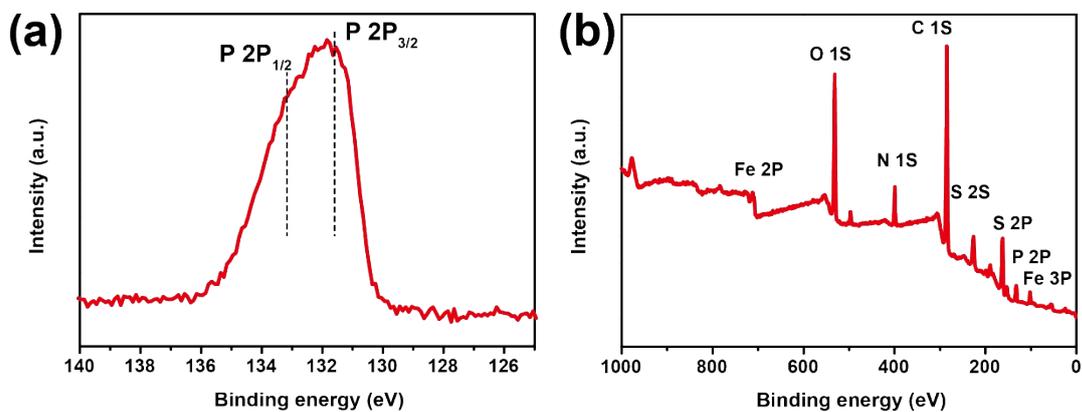


Fig. S6 High-resolution XPS of (a) P 2p, and (b) survey spectra of HSS@FePS₃.

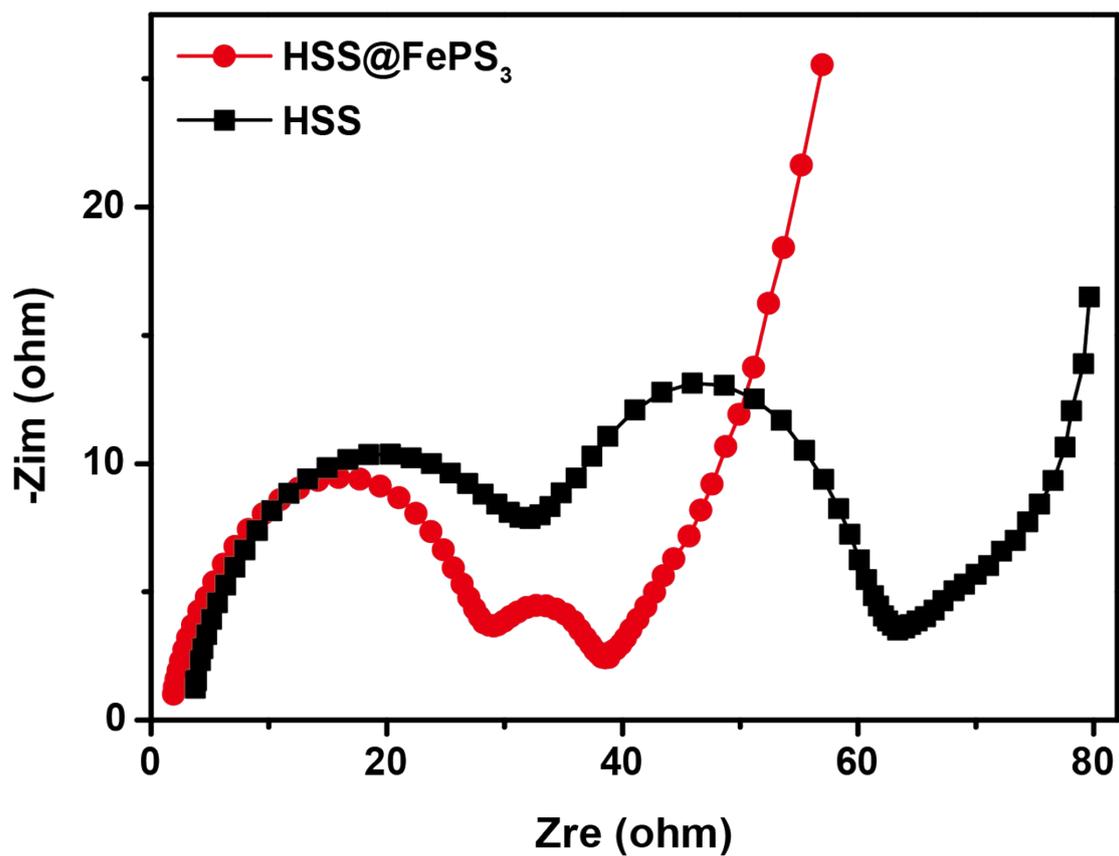


Fig. S7 EIS plots of HSS and HSS@FePS₃.

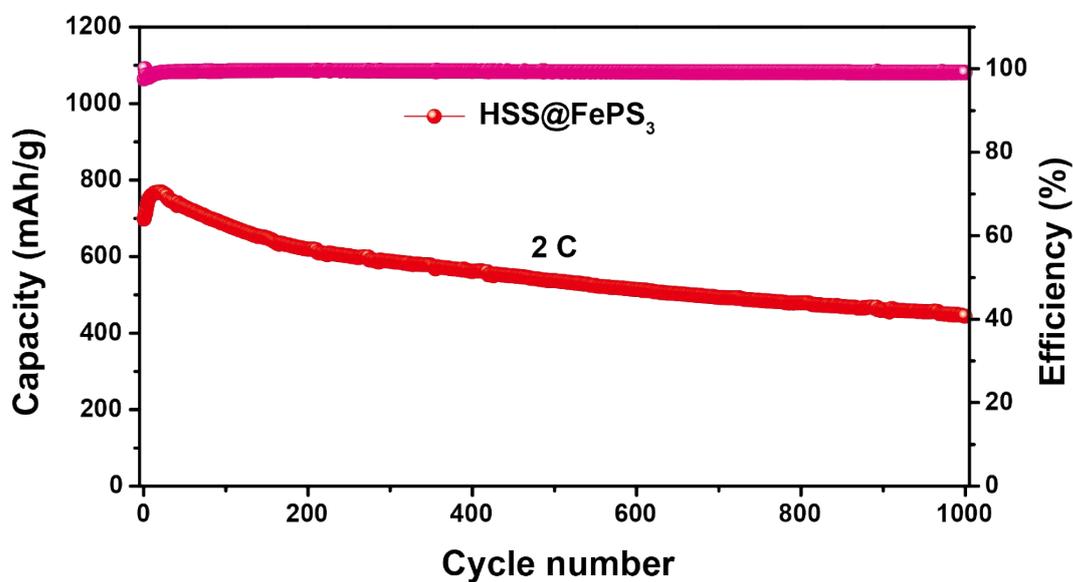


Fig. S8 Long-term cycle capability of HSS@FePS₃ at 2 C.

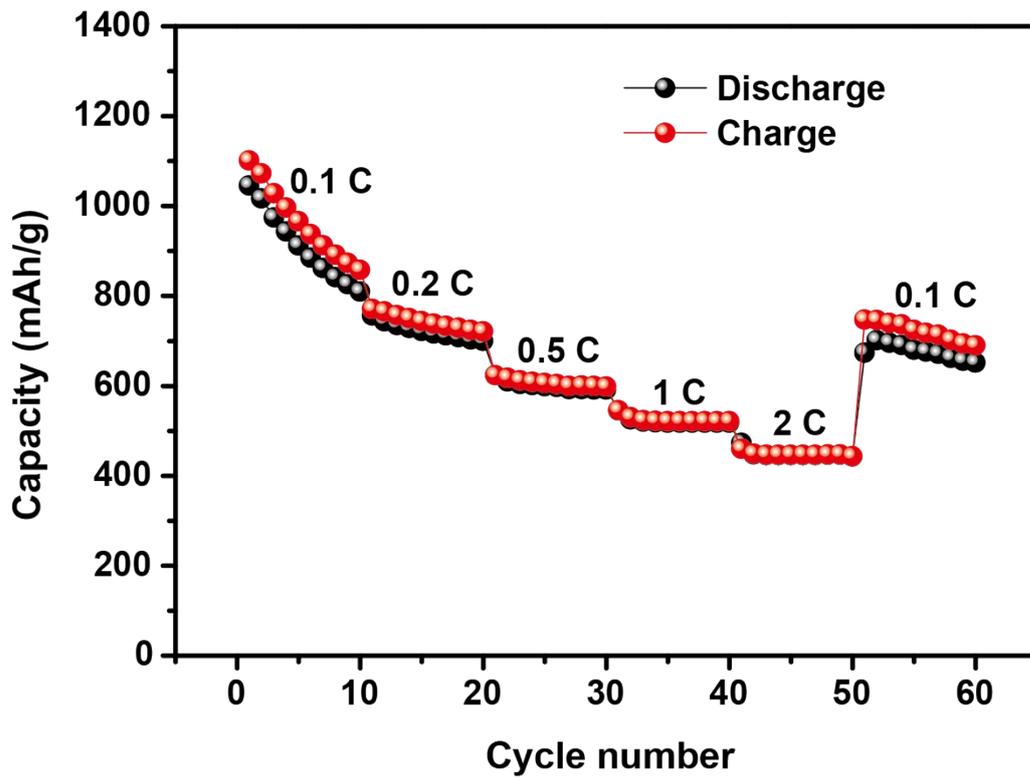


Fig. S9 Cycle capability of HSS at different rates.

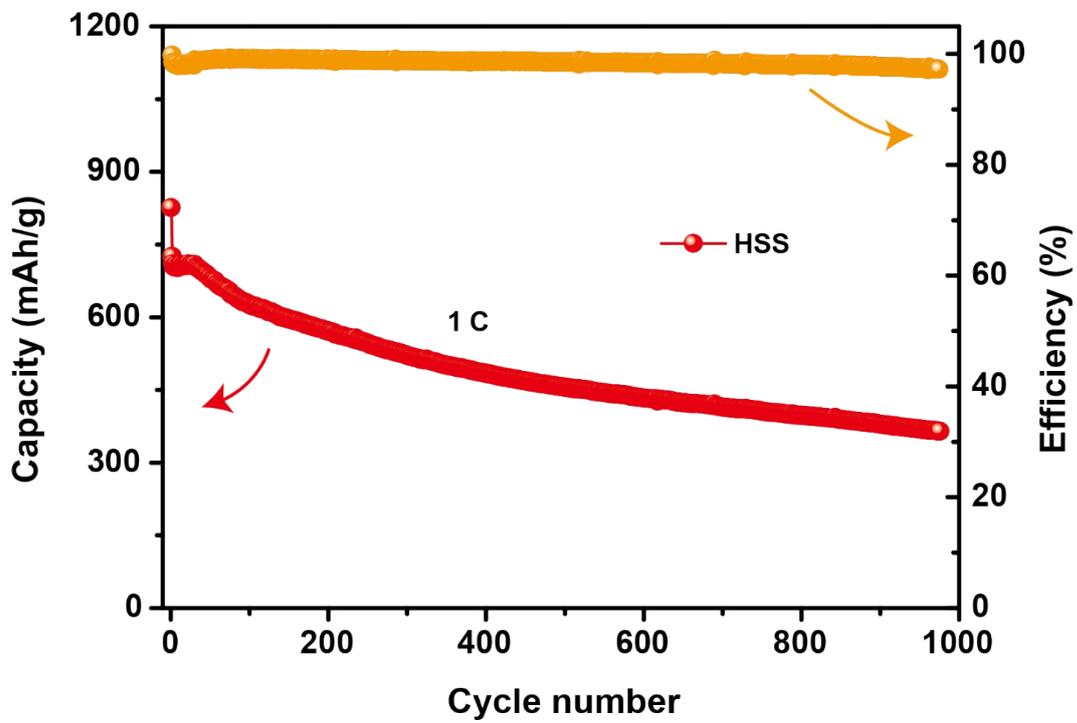


Fig. S10 Long-term cycle capability of HSS at 1 C.

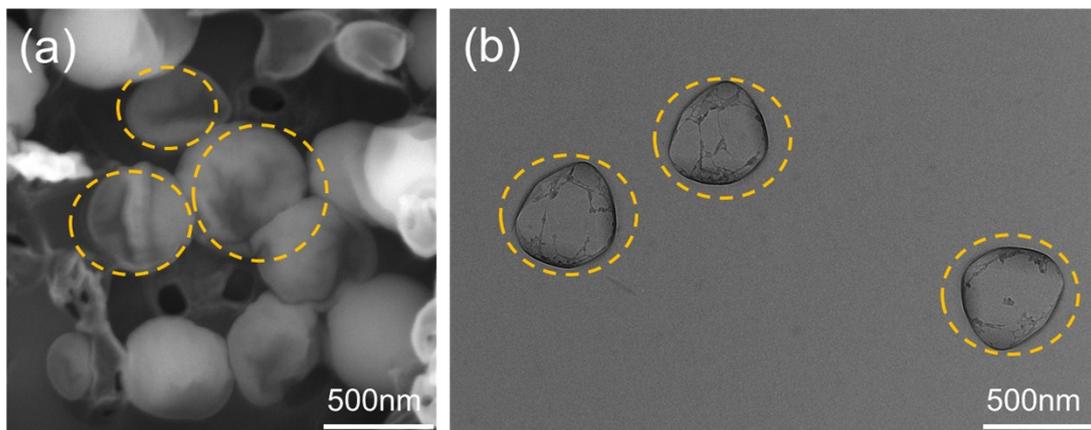


Fig. S11 (a) SEM and (b) TEM images of HSS.

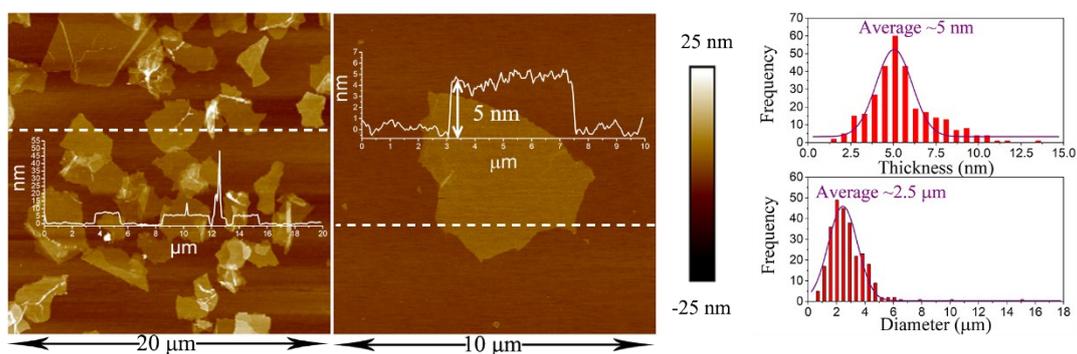


Fig. S12 The AFM images of the exfoliated FePS₃ flakes.

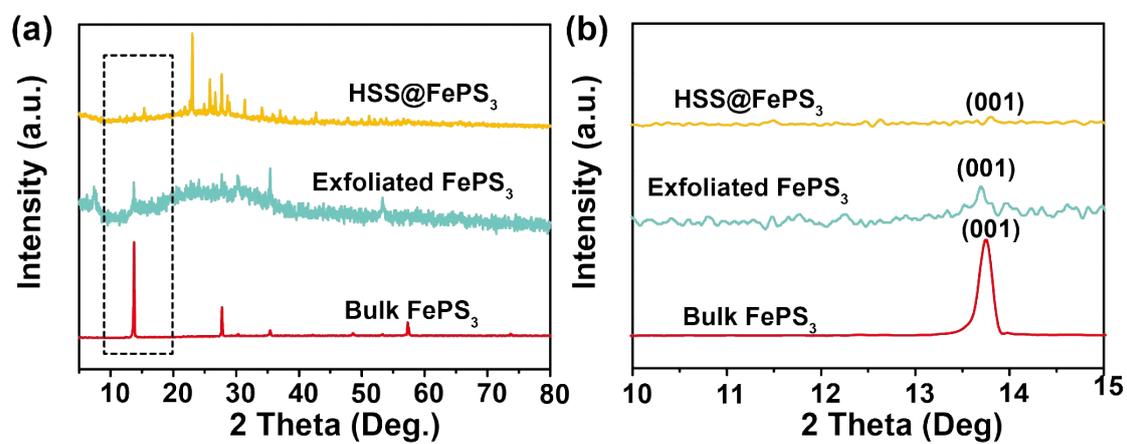


Fig. S13 XRD patterns of bulk FePS₃, exfoliated FePS₃ flakes and HSS@FePS₃.

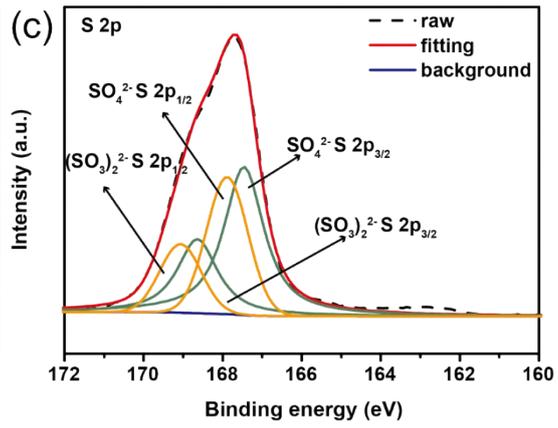
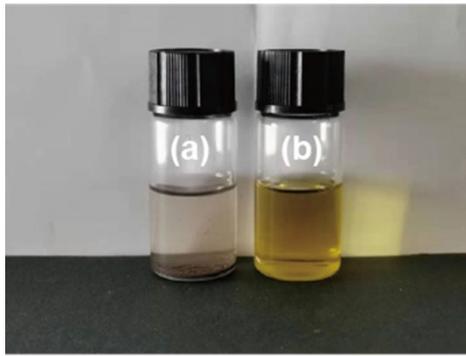


Fig. S14 (a) The FePS₃ flakes in polysulfide solution and (b) the blank polysulfide solution; (c) XPS spectra of S 2p for the FePS₃ flakes/polysulfides composite.