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Supporting information

In Situ Engineered ultrafine NiS_2-ZnS Heterostructures in Micro-Mesoporous Carbon Spheres Accelerating Polysulfide Redox Kinetics for High-Performance Lithium-Sulfur Batteries

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Experimental Section

Materials

Polyacrylic acid (PAA) was purchased from Sigma-Aldrich (USA). Zinc oxide (ZnO), isopropyl alcohol (IPA), aqueous ammonia solution, nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, 99.7%), anhydrous ethanol and sulfur were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd and used without further purification. Zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$, 99.5%], nitric acid, thioacetamide (TAA), aqueous ammonia solution, anhydrous ethanol, were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Methoxy-poly(ethylene glycol)-thiol (OCH_3-PEG-SH) was obtained from Thermo Fisher Scientific. Deionized water was used in all experiments.

Characterization

Transmission electron micrographs were taken by JEOLJEM-2100F transmission electron microscope (TEM) under 200 kV accelerating voltage. Scanning electron microscopy (SEM) images were obtained by using an XL30 ESEM-FEG field emission scanning electron microscope (FEI Co.). The X-ray photoelectron spectrum (XPS) was performed with an ECSALAB 250 by using non-monochromated Al Kα radiation. N_2 adsorption-desorption measurements were measured using an intelligent gravimetric analyzer Autosorb-iQ (Quantachrome). The X-ray diffraction (XRD) patterns were obtained on a D8 Focus diffractometer with Cu Kα radiation. The thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TG-7 analyzer heated from room temperature to 700 °C at a ramp rate of 10 °C min^{-1} in air. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) was obtained on Shimadzu, ICPS-8100.

Synthesis of PAA-Zn and $Ni(OH)_2$/PAA-Zn

In a 2 L conical flask, a PAA aqueous solution (0.2 g mL^{-1}, 3 mL) and 0.12 g ZnO were added in deionized water (0.6 L) and ultrasonically dispersed for 30 min. After that, isopropyl alcohol (1.2 L) was dripped to the flask under magnetic stirring to obtain the PAA-Zn nanospheres suspension. 1 mL of $NH_3 \cdot H_2O$ (2 mol L^{-1}) solution was added into the obtained 1.8 L PAA-Zn nanospheres suspension under magnetic stirring. In succession, 2 mL of $NiCl_2 \cdot 6H_2O$ (60 mg) solution was injected dropwise into the solution at room temperature for 4 h to obtain the $Ni(OH)_2$/PAA-Zn. The obtained $Ni(OH)_2$/PAA-Zn were centrifuged and washed several times by isopropyl alcohol and finally dried at 50 °C for 24 h for further experiment.

Synthesis of $Ni_3ZnC_{0.7}$/MMC, uNiS_2-ZnS/MMC and MMC

The $Ni(OH)_2$/PAA-Zn were annealed from room temperature to 700 °C at a heating rate of 2 °C min^{-1} and then maintained at 700 °C for 4 h under a high-purity argon atmosphere to obtain the $Ni_3ZnC_{0.7}$/MMC. The as-obtained $Ni_3ZnC_{0.7}$/MMC hybrid material and sublimed sulfur (2:1, weight ratio) were well mixed and annealed under an argon flow at 300 °C for 12 h to obtain the uNiS_2-ZnS@MMC composites. After washing in HCl aqueous solution, the as-synthesized uNiS_2-ZnS/MMC NSs were converted into MMC NSs.

Synthesis of ZnS, OCH_3-ZnS@PAA-NH_4, OCH_3-ZnS@$Ni(OH)_2$/PAA-NH_4, NiS_2-ZnS

In a typical process, 0.3 g of $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in 20 mL of water in a 50 mL conical flask. Then 12.5 uL nitric acid was added under vigorous stirring. After

10 min of stirring, 0.9 g of TAA was added slowly and the mixture was refluxed at 75 °C for 2 h. After normal cooling, the precipitate washed several times with water and anhydrous ethanol to remove the unreacted reagents. The sample obtained was dried at 50 °C for 24 h for further experiment.

In a 1 L flask, PAA (1 mL, 0.2 g mL^{-1}) and 50 mg of ZnS were mixed in 200 mL of DI water with magnetic stirring for 30 min. To this mixture, 5 mL OCH_3-PEG-SH (0.5 mg mL^{-1} in DI water) were added. 30 min later, 800 mL of IPA was dripped into the suspension under magnetic stirring to form the OCH_3-ZnS@PAA-NH_4. In succession, 2 mL of $NiCl_2 \cdot 6H_2O$ (600 mg) solution was injected dropwise into the solution at room temperature for 4 h to obtain the OCH_3-ZnS@Ni$(OH)_2$/PAA-NH_4. The as-obtained OCH_3-ZnS@Ni$(OH)_2$/PAA-NH_4 and sulfur (2:1, weight ratio) were well mixed and annealed under an argon flow at 300 °C for 12 h to obtain the NiS_2-ZnS composites.

Synthesis of uNiS_2-ZnS@MMC-S, MMC-S and NiS_2-Zn-S

The prepared 30 mg uNiS_2-ZnS/MMC (or MMC) composites are mixed with 70 mg sulfur, milling for 30 min and sealed in the glass tube. Then the tube is heated at 155 °C for 12 h. All obtained products were immersed in 30 mL ethanol solution at room temperature for 15 min to eliminate the possible sulfur particles attached on the surface of the uNiS_2-ZnS/MMC-S and MMC-S composites. The NiS_2-ZnS-S was obtained by milling NiS_2-ZnS (6 mg), Super P (24 mg) and sulfur (60 mg), named as NiS_2-ZnS-S.

Adsorption simulation experiment

The Li_2S_6 solution is prepared by mixing Li_2S and sulfur at the molar ratio of 1:5 in a mixed solution of DOL and DME (1:1, volume ratio) followed by magnetic stirring for 20 h at 80 °C. Then, 20 mg Super P (MMC or uNiS_2-ZnS/MMC) power are added into as prepared Li_2S_6 (5 mL, 2 mmol L^{-1}) solution, respectively. TheNiS_2-ZnS (4 mg) and Super P (16 mg) are added into as prepared Li_2S_6.

Electrochemical Measurements

Electrochemical measurement was conducted using the 2025 foil coin cell. The sulfur composite cathodes were prepared by mixing the selected samples, acetylene black and binder (polyvinylidene fluoride, PVDF) in N-methy-pyrrolidinone (NMP) solvent with a weight ratio of 80:10:10. The mixture was stirred for 24 h, spread on an aluminum foil, and then dried in a vacuum oven at 60 °C to remove the solvent. The obtained film was punched into disks with a diameter of 12 mm. The areal mass loading of sulfur was about 1.0 mg cm^{-2}, and 30 μL of electrolyte was used in the coin cells. To construct high sulfur loading electrodes, we prepared thicker films with a sulfur areal loading of 4.0 mg cm^{-2}, and 70 μL of electrolyte was used in the coin cells. The Li-S batteries were assembled in an argon-filled glovebox with the above-prepared sulfur composite cathodes and lithium metal foil anodes. A solution of 1.0 mol L^{-1} bis (trifluoro-methane) sulfonamide lithium (LiTFSI) dissolved in a mixed solvent of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) with a 1:1 volume ratio containing $LiNO_3$ (0.1 mol L^{-1}) was used as the electrolyte. The cycling performances of Li-S cells were measured on a Neware Battery Measurement System (Neware, China) at different current densities with a potential window of 1.7-2.8 V vs

Li/Li^+. The CV curves were collected on a CHI760E electrochemical workstation at a scan rate of 0.1 mV s^{-1} between 1.7 and 2.8 V. EIS analysis was carried out in the range from 100 kHz to 0.01 Hz. For the symmetric electrochemical cell measurement, 90 wt% active material (MMC, uNiS_2-ZnS/MMC and NiS_2-ZnS/Super P) and 10 wt% PVDF binder were homogenized in NMP to form a consistent slurry, which was then uniformly coated on aluminum current collector. Each coin cell added 30 μL electrolyte (0.5 mol L^{-1} Li_2S_6 in DME electrolyte). CV curves were measured at a scan rate of 50 mV s^{-1} in a potential window of -1.0 to 1.0 V. All specific capacity values were obtained based on the mass of elemental sulfur. For the nucleation of lithium sulfide, the applied Li_2S_8 electrolyte was prepared by mixing sulfur and Li_2S with a molar ratio of 7:1 in tetraglyme with extra 1.0 mol L^{-1} LiTFSI under continuous magnetic stirring for 24.0 h. The concentration of Li_2S_8 was 2.0 mol[S] L^{-1}. 20 μL of the Li_2S_8 electrolyte was dropped onto the uNiS_2-ZnS/MMC ((MMC or NiS_2-ZnS/Super P) cathode, while 20 μL blank electrolyte without Li_2S_8 was added to the anode side. The assembled cells were first galvanostatically discharged at 0.112 mA to 2.06 V and then potentiostatically discharged at 2.05 V for nucleation of Li_2S. The potentiostatic discharge was terminated when the current was below 10^{-5} A.

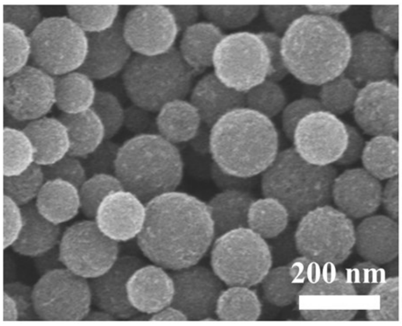

Fig. S1. SEM image of the MMC.

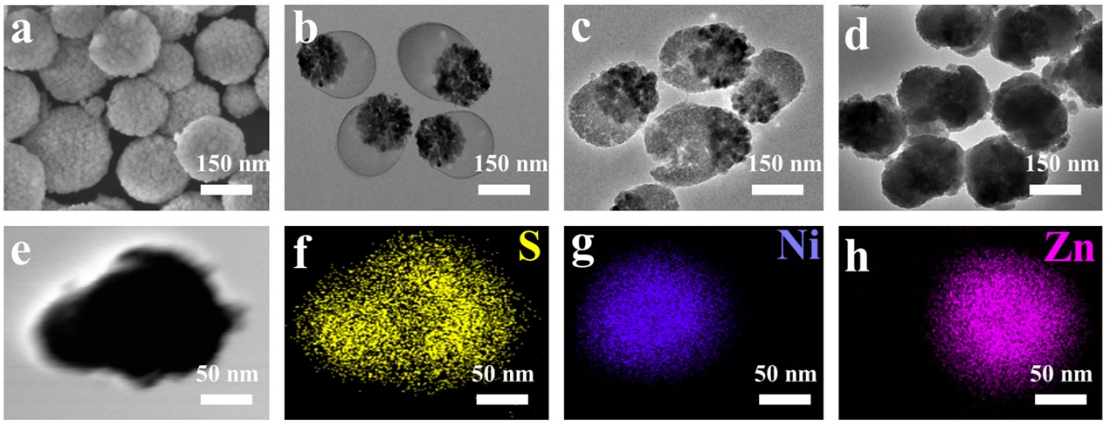

Fig. S2. SEM and TEM images of a) ZnS, b) OCH_3-ZnS@PAA-NH_4, c) OCH_3-ZnS@Ni$(OH)_2$/PAA-NH_4, d) NiS_2-ZnS. Elemental mapping images of e-h) NiS_2-ZnS.

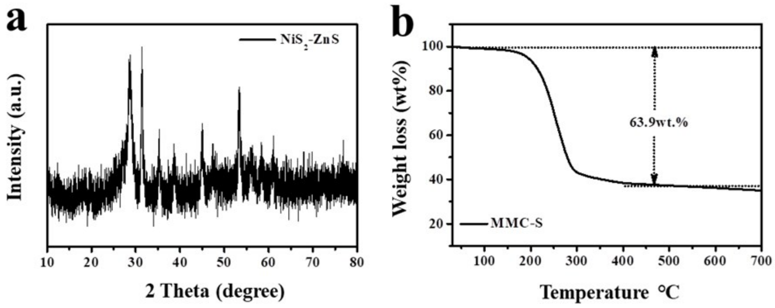

Fig. S3. XRD pattern of a) NiS_2-ZnS. TGA curves of b) MMC-S under N_2 atmosphere.

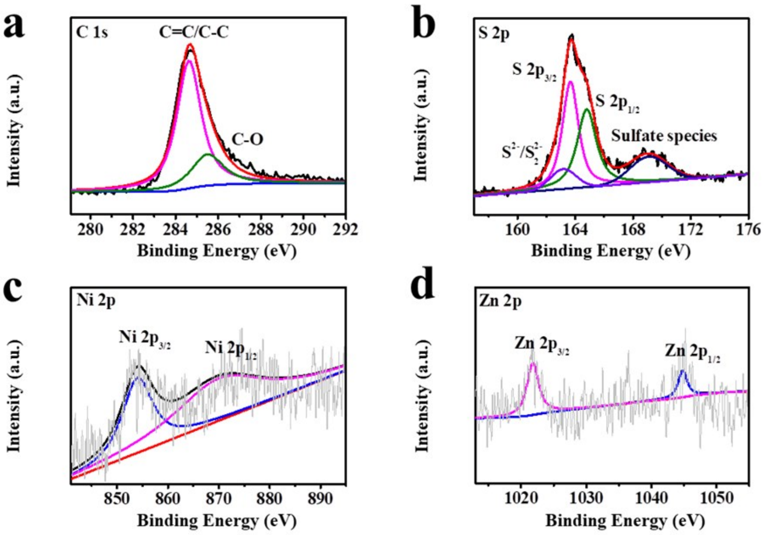

Fig. S4. High-resolution XPS spectra at a) C 1s, b) S 2p, c) Ni 2p and d) Zn 2p regions of NiS_2-ZnS/MMC-S.

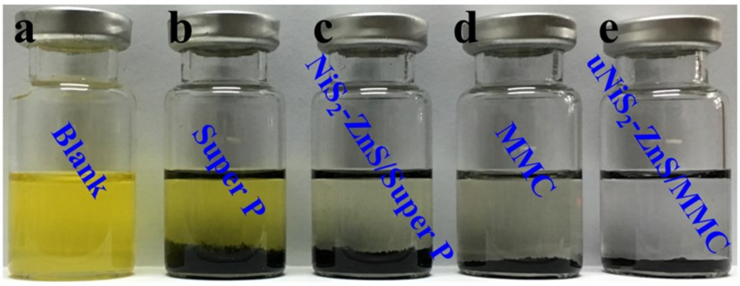

Fig. S5. Adsorption capability tests of a) blank, b) Super P, c) NiS_2-ZnS/Super P, d) MMC and e) uNiS_2-ZnS/MMC in mixed 5 mL DOL/DME solutions of 2 mmol L^{-1} Li_2S_6.

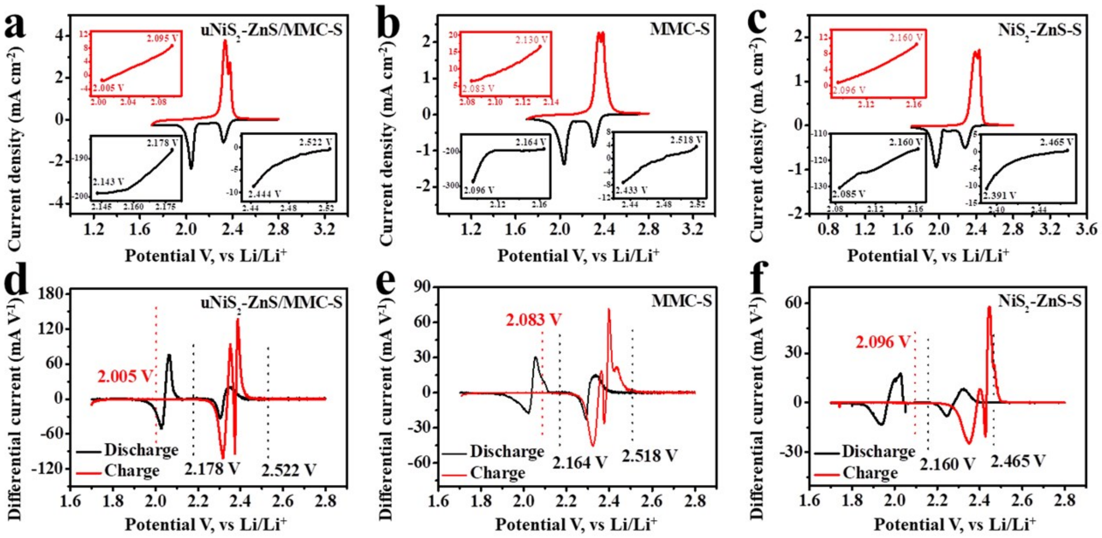

Fig. S6. CV curves and onset potentials of redox peaks of a) uNiS$_2$-ZnS/MMC-S, b) MMC-S and c) S/nNiS$_2$-ZnS/Super P cathodes, and corresponding differential CV curves of d) uNiS$_2$-ZnS/MMC-S, e) MMC-S and f) S/NiS$_2$-ZnS/Super P cathodes.

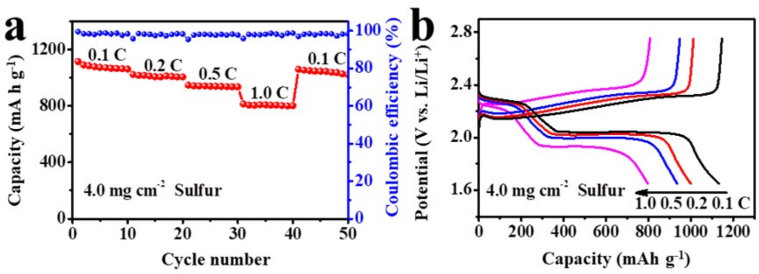

Fig. S7. a) Rate performance and b) galvanostatic discharge-charge profiles of uNiS$_2$-ZnS/MMC-S cathode with a sulfur loading of 4.0 mg cm^{-2} at different current rates.

Table S1. Performance comparison of uNiS$_2$-ZnS/MMC material with other representative heterostructured host materials.

Material	Rate	Cycles	Initial Capacity (mAh g^{-1})	Capacity retention (mAh g^{-1})	Ref.
NiO-NiCo$_2$O$_4$@C	0.5 C	500	1014	717	[1]
TiO$_2$/BaTiO$_3$	0.5 C	500	898	541	[2]
DCC/MoS$_2$/PrNP/CNTs	1.0 C	800	1046	871	[3]
MoN-VN	1.0 C	500	766	555	[4]
ZnS-FeS/NC	1.0 C	200	933	800	[5]
C/SnS$_2$/SnO$_2$	2.0 C	500	800	650	[6]
uNiS$_2$-ZnS/MMC	**0.1 C**	**100**	**1281**	**1026**	
	1.0 C	**500**	**1045**	**810**	**Our work**
		1000	**1045**	**710**	

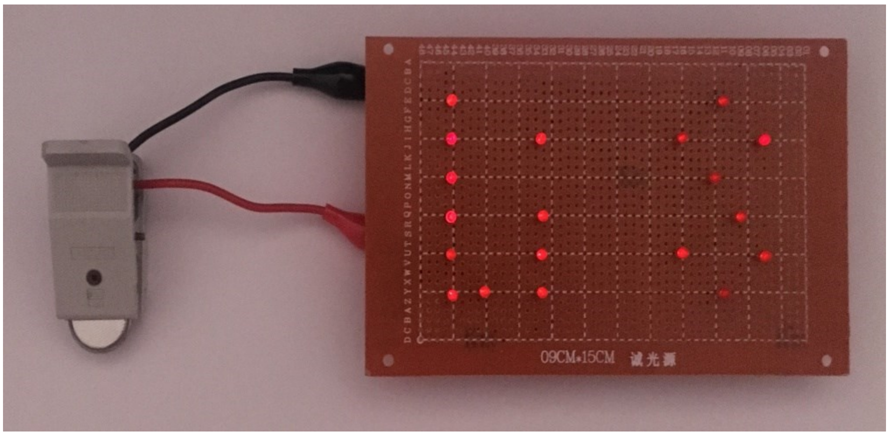

Fig. S8. The 19 light-emitting diodes lit by the uNiS$_2$-ZnS/MMC-S cell.

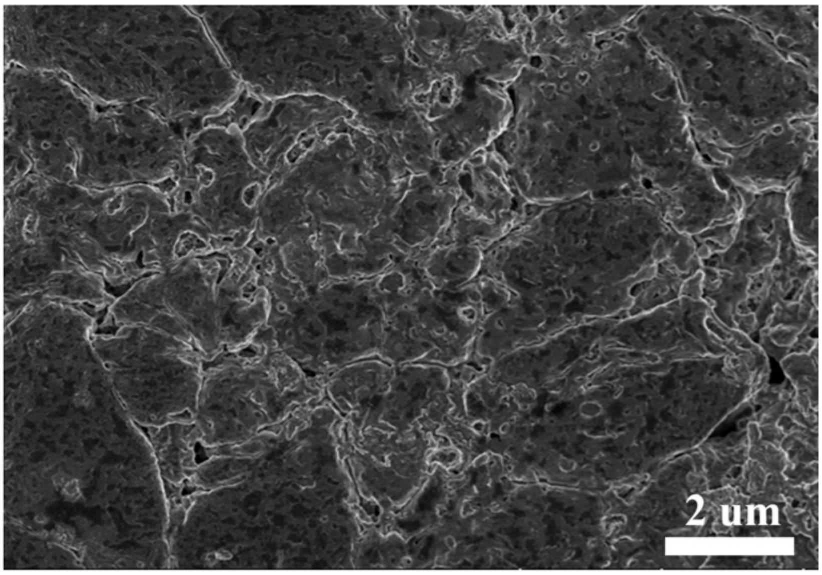

Fig. S9. After cycling at 1 C for 200 cycles, SEM image of the Li metal foil from the MMC-S coin cell after cycling.

References

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