Supplementary Information

Synthesis of polyhedral MoS₂@C hollow cages using a sacrificial template approach for improved reversible lithium storage

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1.Experimental

1.1. Synthesis of HP-MoS₂ and HP-MoS₂@C

All chemicals are purchased from Aladdin Industrial Corporation and used without further purification. In a typical process, 380 mg NaF, 360 mg MoO₃, 580 mg KSCN and 500 mg D-glucose powders are dispersed into 40 mL absolute ethyl alcohol and de-ionized water mixing solution (v:v=1:3) under vigorous stirring. The obtained suspension is transferred into a 50 mL Teflon-lined stainless steel autoclave, sealed and treated at 220 °C for 16 h. Upon cooling naturally to room temperature, the precipitated products are then centrifuged, ished with ethyl alcohol several times, and consequently dried at 60 °C in vacuum for 12 h. Finally, the precusor powders are calcinated at 500 °C for 2 h under Ar atmosphere to obtain the final HP-MoS₂@C product. For comparison, the bare HP-MoS₂ powders are also prepared using the same procedure without D-glucose.

1.2 Materials characterization

The crystal structures of the as-prepared powders are characterized by X-ray diffraction (XRD) using an X-ray powder diffractometer (Rigaku MinFlex II) with a Cu K α radiation source (λ =0.15406 nm). The morphology and microstructure are identified by scanning electron microscopy (SEM, SU8010) with energy dispersive spectrometer (EDS) and transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN). Thermogravimetric analysis (TGA) is conducted on a Netzsch STA449F3 Analyzer from 30 to 800 °C under air atmosphere with a heating rate of 3 °C min⁻¹. The chemical bonding states of HP-MoS₂@C are determined with an X-ray photoelectron spectroscope (ESCALAB 250Xi, Thermo Scientific) using Al Ka (1486.6 eV) excitation. The surface potentials of HP-MoS₂ and HP-MoS₂@C are measured by Kelvin probe atomic force microscopy (Bruker dimension ICON,

Germany).

1.3 Electrochemical measurements

Electrochemical performances of the as-prepared composites are evaluted using two-electrode CR2025 coin cells using lithium foil as the counter electrode and Celgard 2300 film as the separator. The slurry of anodes is mixed by 70 wt% active materials (HP-MoS₂ and HP-MoS₂@C), 10 wt% polyvinylidene fluoride (PVDF), 20 wt% Super-P (SP). The working electrodes are made by casting the slurry on the copper foil and dried at 120 °C in vacuum for 12 h. The loading density of the active materials is approximately 0.8 mg•cm⁻². Electrochemical cells are assembled in an Arfilled glove box (moisture, and oxygen level ≤ 0.1 ppm). The electrolyte is a mixture of 1M $LiPF_6$ in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume). Galvanostatic charge/discharge measurements are carried out in the voltage range of 0.01–3.0 V using a multichannel battery testing system (CT2001A, China). Electrochemical impedance spectroscopy (EIS) is recorded by electrochemical workstation (Zahner-Zennium) over a frequency range of 10 mHz to 100 KHz with AC signal amplitude of 5 mV. The cyclic voltammetry (CV) are conducted at a scan rate of 0.1 mVs⁻¹ on a CHI660C electrochemical workstation.

To evaluate the commercial application of HP-MoS₂@C anode materials, 200 mAh pouch cells using LiCoO₂ (Ningbo Jinhe New Materials Co., Ltd.) as cathodes and HP-MoS₂@C (this work) as anodes. The pouch cell contains a stack of 6 cathode and 5 anode pieces and the capacity ratio of negative to positive electrode is designed to be ~1.05:1. The weight ratio of LiCoO₂: carbon black: PVDF is 96:2:2 in the cathode, and the mass loading is 11.5 mg•cm⁻² corresponding with 1.9 mg•cm⁻² for anode electrode.

1.4 Computational method

Density functional theory calculations are carried out using the Vienna ab initio simulation package (VASP)²³ with the projector-augmented wave (PAW) potential.^{24,25} The Perdew-Burke-Ernzerhof (PBE) of generalized gradient approximation (GGA) are adoped in the exchange and correlation functions.^{26,27} The plane-wave cutoff energy is set to 500 eV. A Monkhorst-Pack of $5 \times 5 \times 4$ k-point mesh is used to sample the Brillouin zone for $3 \times 3 \times 1$ MoS₂ supercell. All atoms are relaxed until the Hellmann-Feynman force on each of them are less than 0.02 eV/Å. In the study of simulating the diffusion of Li+ ions, minimum energy pathway (MEP) and the activation energy are calculated using the climbing image nudged elastic band (CI-NEB) method,46 and calculations are performed on $3 \times 3 \times 2$ gamma-centered kmesh with force convergence thresholds of 0.05 eV/Å.



Fig. S1. TEM images of HP-MoS₂



Fig. S2. TG curve of the HP-MoS₂@C at 5 °C min⁻¹ in air.



Galvanostatic charge-discharge curves at 500 mAg⁻¹



Fig. S4. Cross-sectional SEM images of pristine (a, c) and (b, d) after rate cycling.



Fig. S5 The surface morphologies of HP-MoS₂@C after 1000 cycles at 2 A g^{-1} .



Fig. S6 (a, b) EIS profiles and (c) fitted Rtol of HP-MoS $_2@C$ and HP-MoS $_2$ electrodes for first one cycles at different potential.



Fig. S7. (a) GITT potential profiles of the two electrodes for lithiation process during the first discharge process; (d) Li-ion diffusion coefficients calculated from the GITT

potential profiles.



Fig. S8. The surface potential maps of (a) HP-MoS $_2$ and HP-MoS $_2@C$ electrodes;

(c) the surface potential map of Au as a reference sample.



Fig. S9. Schematic illustration of approaches to enhance ion diffusion and electron transport.



Fig. S10. Top and side views of the possible C-doped MoS₂ structures: (a) hollow site (H site) and (b) top site (T site). H1(T1) and H2(T2) site represents carbon located between layers and in the plane of the layer, respectively.

Table S1. The total energy for the possible sites of C-doped MoS₂.

Configuration	H1	H2	T1	T2
E _{total} (eV)	-392.63	-393.02	-392.84	-393.66

	Anode	Cathode	Electrolyte
Size	3.2*4.2 cm	3*4 cm	_
Mass loading	1.9 mg/cm ⁻²	11.5 mg/cm ⁻²	7*10 ⁻³ g/cm ⁻²
Stack	5	6	_

Tables S2. The details of pouch cell compoments, electrode loading and dimension



Fig. S11. Digital camera images of HP-MoS₂@C anode, LCO cathode, simple pack and full pouch cells.