

Supporting Information

Reciprocal hybridization of MoO₂ nanoparticles and few-layer MoS₂ for stable lithium-ion batteries

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Experimental section

Synthesis of MoS₂ nanosheets: Typically, 0.15g of sodium molybdate (Na₂MoO₄·2H₂O) and 0.3g of thioacetamide (C₂H₅NS) were dissolved into 30 mL of deionized (DI) water with magnetic stirring, and the suspension was transferred into 50 ml Teflon-lined stainless steel autoclave and maintained at 220 °C for 24 hours. The precipitates were collected by centrifuge, washed with DI water and ethanol, and re-dispersed into 20ml aqueous solution for subsequent experiments.

Synthesis of MoO₂/MoS₂ hybrids: 0.3 g of molybdenum trioxide (MoO₃) and 10 mL of ethylene glycol were added into the MoS₂ nanosheets aqueous solution above-mentioned with magnetic stirring, and the suspension was transferred into a 50 mL Telfon-lined stainless steel

autoclave, and hydrothermally treated in an air-flow electric oven at 200 °C for 24 hours. The obtained black precipitates were collected using centrifuge, washed several times with DI water and ethanol, and freeze-dried in vacuum environment.

Synthesis of MoO₂ nanoparticles: 0.3 g of molybdenum trioxide (MoO₃) and 10 mL of ethylene glycol were added into 20 mL of DI water with magnetic stirring for 30 min, and the suspension was transferred into a 50 mL Teflon-lined stainless steel autoclave, and hydrothermally treated in an air-flow electric oven at 200 °C for 24 hours. The obtained black precipitates were collected using centrifuge, washed several times with DI water and ethanol, and freeze-dried in vacuum environment.

Characterization

XRD pattern was carried out on a X-ray diffraction (Bruker D2 Phase Table-top Diffractometer) with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 30 mV and 10 mA. Microstructural properties were determined by transmission electron microscopy (TEM, JEOL JEM-2010). Raman measurement was performed with a Renishaw 2000 system with a 514.5 nm Ar-ion laser and charge-coupled device detector. The porous properties were analyzed using nitrogen adsorption and desorption isotherms that were obtained using the surface area and a porosimetry analyzer (ASPA 2010) at 77K. The specific surface areas were calculated according to the BET theory. PSD was calculated via BJH method.

Electrochemical measurements

Electrochemical measurements were conducted by galvanostatic testing CR2016-type

coin cells assembled in an argon filled glove box (Mbraum). To prepare the working electrode, mix the active material, carbon black and polyvinyl difluoride (PVDF) in a weight ratio of 70:20:10, and then disperse the mixture in N-methyl-2-pyrrolidinone (NMP) to form uniform slurry which was cast on the Cu foil. The foil loaded with active materials was then dried at 120 °C for 12 h to remove the excess solvent. Pure lithium foil and polypropylene (Celgard 2400) were used as counter electrode and separator, respectively. The electrolyte was composed of 1.0 M LiPF_6 in a mixture of ethylene carbonate and diethyl carbonate (EC-DEC) (volume ratio = 1: 1). The galvanostatic charge-discharge cycling at different current rates was performed on an automatic battery testing system (LAND CT2001A model) in a voltage range of 0.01–3.0 V (vs. Li/Li^+) at room temperature. The cyclic voltammetry (CV) experiments were carried out on a multichannel electrochemical station (Autolab PGSTAT302N).

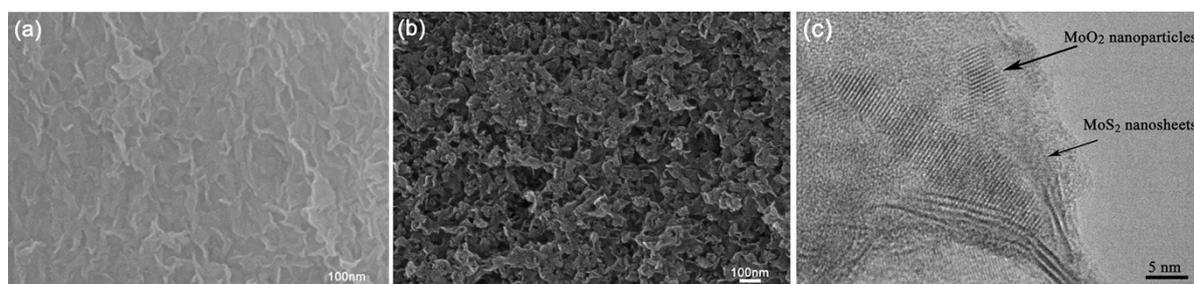


Fig. S1 (a) SEM image of MoS₂ nanosheets; (b) SEM image and (c) high-magnification TEM image of MoO₂/MoS₂ hybrids.

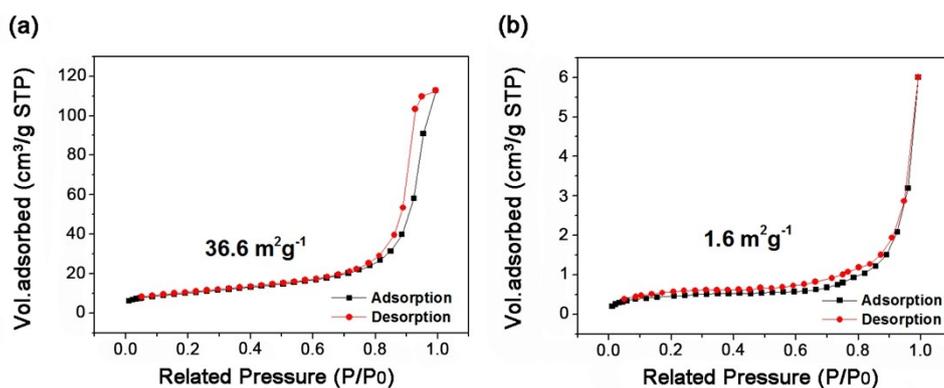


Fig. S2 N₂ adsorption-desorption isotherms of (a) MoO₂ nanoparticles; (b) MoS₂ nanosheets.

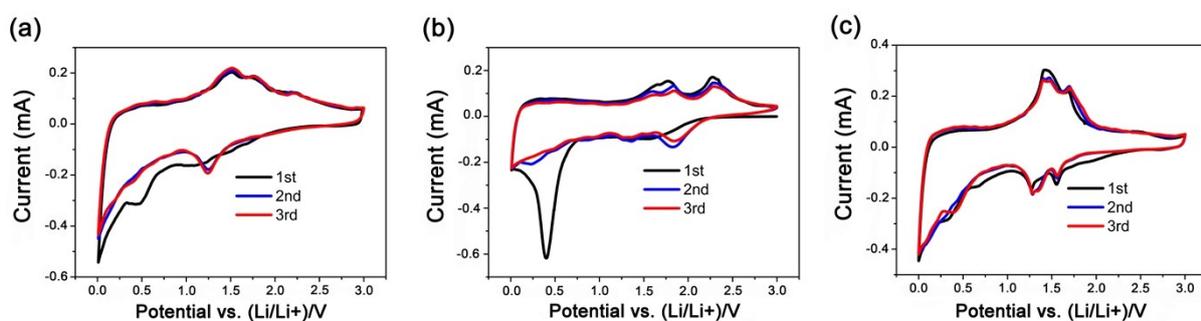


Fig. S3 CVs at a scan rate of 0.1 mV s⁻¹ for the first three cycles of (a) MoO₂/MoS₂ hybrids; (b) MoS₂ nanosheets; (c) MoO₂ nanoparticles.

The first three cyclic voltammograms (CVs) of the MoO₂/MoS₂ hybrids, the MoS₂ nanosheets and the MoO₂ nanoparticles at 0.1 mV s⁻¹ within a potential range of 0.01-3.0 V are shown in Figure S3. During the first cycle, an overlap reduction peak from 1.7 V to 1.0 V is assigned to monoclinic-orthorhombic-monoclinic phase transitions of MoO₂.¹ The reduction peak at 0.75~0.4 V corresponds to the intercalation of Li⁺ into MoS₂ lattice to form Li_xMoS₂ and the the formation of Li₂S according to Li_xMoS₂ → Mo + xLi₂S.² In the reverse anodic scan, two pronounced peaks at 1.5 V and 1.75 V can be ascribed to the phase transitions between the monoclinic phase and the orthorhombic phase in partially lithiated Li_xMoO₂,³ and the peak at 2.25 V can be attributed to the delithiation of Li₂S. In the

subsequent cycles, the oxidation-reduction peak become more obvious which is very similar to previously reported.^{4,5}

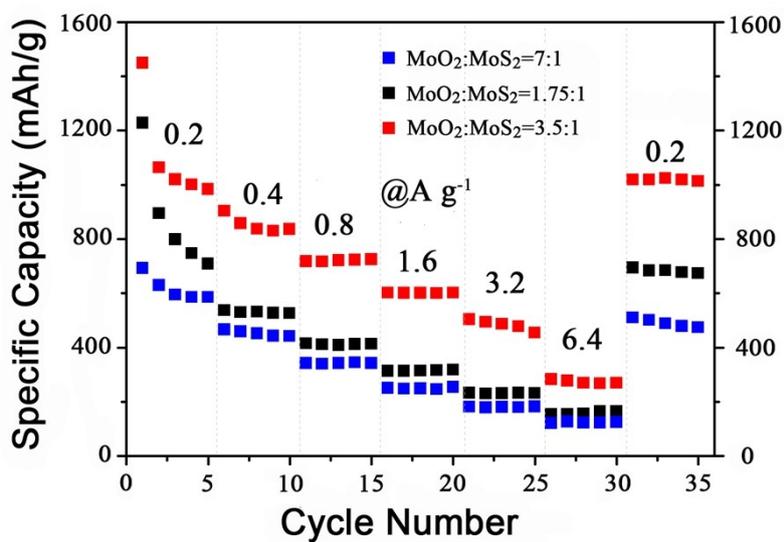


Fig. S4 The rate performances of MoO₂/MoS₂ hybrids with different component ratios.

Reference

- 1 B. K. Guo, X. P. Fang, B. Li, Y. F. Shi, C. Y. Ouyang, Y. S. Hu, Z. X. Wang, G. D. Stucky and L. Q. Chen, *Chem. Mater.*, 2012, **24**, 457-463.
- 2 H. Hwang, H. Kim and J. Cho, *Nano Lett.*, 2011, **11**, 4826-4830.
- 3 J. Liu, S. S. Tang, Y. K. Lu, G. M. Cai, S. Q. Liang, W. J. Wang and X. L. Chen, *Energy Environ. Sci.*, 2013, **6**, 2691-2697.
- 4 M. J. Hwang, K. M. Kim and K. S. Ryu, *J. Electroceram*, 2014, **33**, 239-245.
- 5 L. X. Zeng, C. Zheng, C. L. Deng, X. K. Ding and M. D. Wei, *Acs. Appl. Mater. Inter.*, 2013, **5**, 2182-2187.