Supporting Information

Synthesis of Heterostructured Dual Metal Sulfides by High-temperature Mixing Hydrothermal Method as a Ultra-high Rate Anode for Li-ion Batteries

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1. Experimental Section

1.1 Raw materials

The reagents involving Sodium molybdate dihydrate (≥99.0%, $Na_2MoO_4 \cdot 2H_2O$), Thiourea (99%, CH_4N_2S), hexadecyl trimethyl ammonium bromide (99%, CTAB), and Copper nitrate hydrate (99.99%, $Cu(NO_3)_2 \cdot xH_2O$) were directly used without further purification.

1.2 Synthesis of flower-like MoS_2 microspheres

Flower-like MoS_2 microspheres were fabricated by a conventional hydrothermal method. In brief, 0.4839 g of $Na_2MoO_4 \cdot 2H_2O$ and 0.60896 g of CH_4N_2S powders were added into 50 mL of deionized (DI) water with strong stirring. The solution was diverted into Teflon reactor and then heated at 220 °C for 24 h. After the end of the temperature preservation, the MoS_2 microspheres were acquired by washing with ethyl alcohol. Finally, the MoS_2 powders were dried at 80 °C in a vacuum oven for 12 h and then calcined at 700 °C in Ar atmosphere for 2 h.

1.3 Synthesis of CuS microspheres

CuS microspheres were fabricated by a conventional hydrothermal method. First, 0.2528 g of CTAB was added into DI water with strong stirring at 30 °C. Subsequently, 0.3751 g of $Cu(NO_3)_2 \cdot xH_2O$ and 0.4758 g of CH_4N_2S were poured into the solution with strong stirring. The miscible solution was obtained and then diverted to a 70 mL Teflon reactor and heated at 150 °C for 24 h. After the end of the temperature preservation, CuS microspheres were obtained by washing with ethyl alcohol. Finally, the MoS_2 powders were dried at 80 °C in a vacuum oven for 12 h.

1.4 Synthesis of a Cu_2S/MoS_2/rGO composite

Heterostructured Cu_2S/MoS_2/rGO microspheres were synthesized by a HTMHM with hydrothermal conditions. First, 0.1163 g of CTAB was added in 18 mL of DI water with strong stirring at 30 °C, and then 1 mmol of $Cu(NO_3)_2 \cdot xH_2O$, 3.125 mmol of CH_4N_2S, and 5 mL of graphene oxide dispersion (5 mg mL^{-1}, prepared by modified Hummers' method) were poured into the solution with strong stirring at room temperature as A solution. 0.5 mmol of $Na_2MoO_4 \cdot 2H_2O$ and 2 mmol of CH_4N_2S powders were added into 23 mL of DI water with strong stirring as B solution. Finally, A and B solutions were poured into the self-designed dual-chamber Teflon lined reactor separately. The solutions were diverted to a autoclave and heated at 150 °C for 24 h statically, whereafter, the solutions were mixed by rotating the reactor and heated at 220 °C for 24 h. A black precipitate was obtained by washing with ethyl alcohol, and then dried at 80 °C in a vacuum oven for 12 h. Then, the black precipitate was calcined at 700 °C in Ar atmosphere for 2 h to obtain Cu_2S/MoS_2/rGO. The Cu_2S/MoS_2/rGO composite denoted as MCG-2 and MCG-1 when the concentration of $Na_2MoO_4 \cdot 2H_2O$ was 0.5 mmol and 1 mmol, respectively. For comparison, the MC-2 sample was fabricated under the same conditions when the concentration of $Na_2MoO_4 \cdot 2H_2O$ was 0.5 mmol, without using the graphene oxide dispersion.

1.5 Characterization

The crystalline structure of samples was confirmed by X-ray diffraction (XRD, Panalytical) with Cu Kα radiation (λ=1.5406 Å). Field-emission scanning electron microscopy (HITACHI S-4800) and transmission electron microscopy (TEM, Tecnai G2 F30) were performed to observe the morphologies and microstructure of samples. The chemical environment and surface electronic state of samples were characterized by using X-ray photoelectron spectroscopy (Axis) and Raman spectroscopy (Horiba *Labram HR Evolution) with a 532 nm* solid−state laser. Simultaneous thermal analysis(STA449F5 Jupiter) was performed to analyze the carbon content of $Cu_2S/MoS_2/rGO$ from 30 to 800 °C with a heating rate of 10 °C min^{-1} in air. The specific surface area of samples was examined by N_2 adsorption−desorption isotherms (JW-BK200B) at 77.35 K.

1.6 Electrochemical measurement

The electrochemical performance of MCG-2, MCG-1, MC-2, and MoS_2 were tested on CR2032 coin-type half cells, which were assembled in an argon-filled glovebox. The working electrodes were fabricated by spreading the uniform slurry, which consisted of active materials (70 wt%), acetylene black (20 wt%), and polyvinylidene fluoride (10wt%) in N-methyl-2-pyrrolidon (NMP) solvent onto a Cu foil and dried at 80 °C in a vacuum oven for 12 h. The mass loading of the active materials on electrode slice was approximately 0.8−1.0 mg/cm^2. The Celgard2400 and Li foil were used as separator and counter electrode, and 1.0 M of $LiPF_6$ in ethylene carbonate/diethyl carbonate (1:1 vol/vol) was used as the electrolyte. The electrochemical workstation (CHI 660C) cyclic voltammetry was utilized to prove the cyclic voltammetry curves within the voltage window of 0.01−3 V at a scan rate of 0.1 mV/s and electrochemical impedance spectroscopy in a frequency range of 0.01 Hz to 1 MHz. Galvanostatic charge−discharge curves were obtained using a multichannel cell test system (LAND CT2001A) with a voltage window of 0.01−3 V.

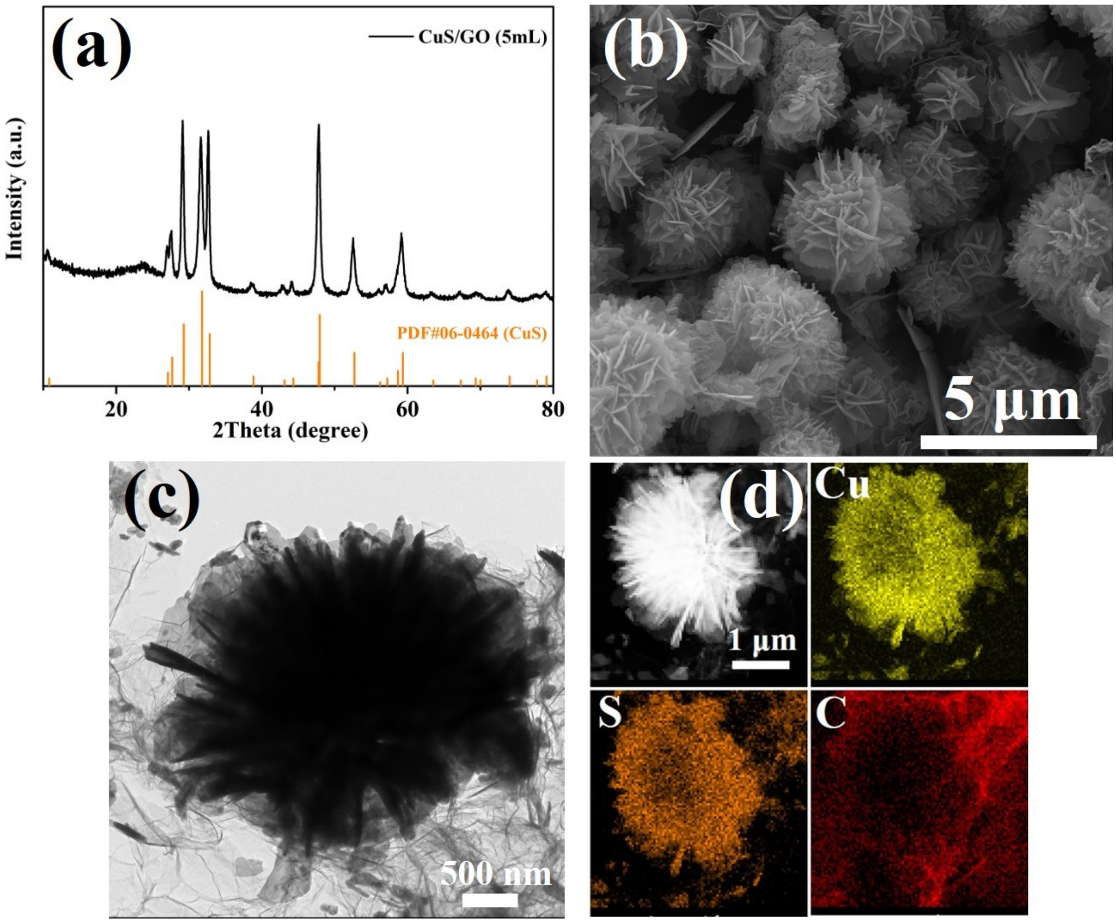

Figure S1. (a) XRD pattern, (b) SEM image, (C) TEM and (d) EDS mapping of CuS/rGO microspheres before calcination.

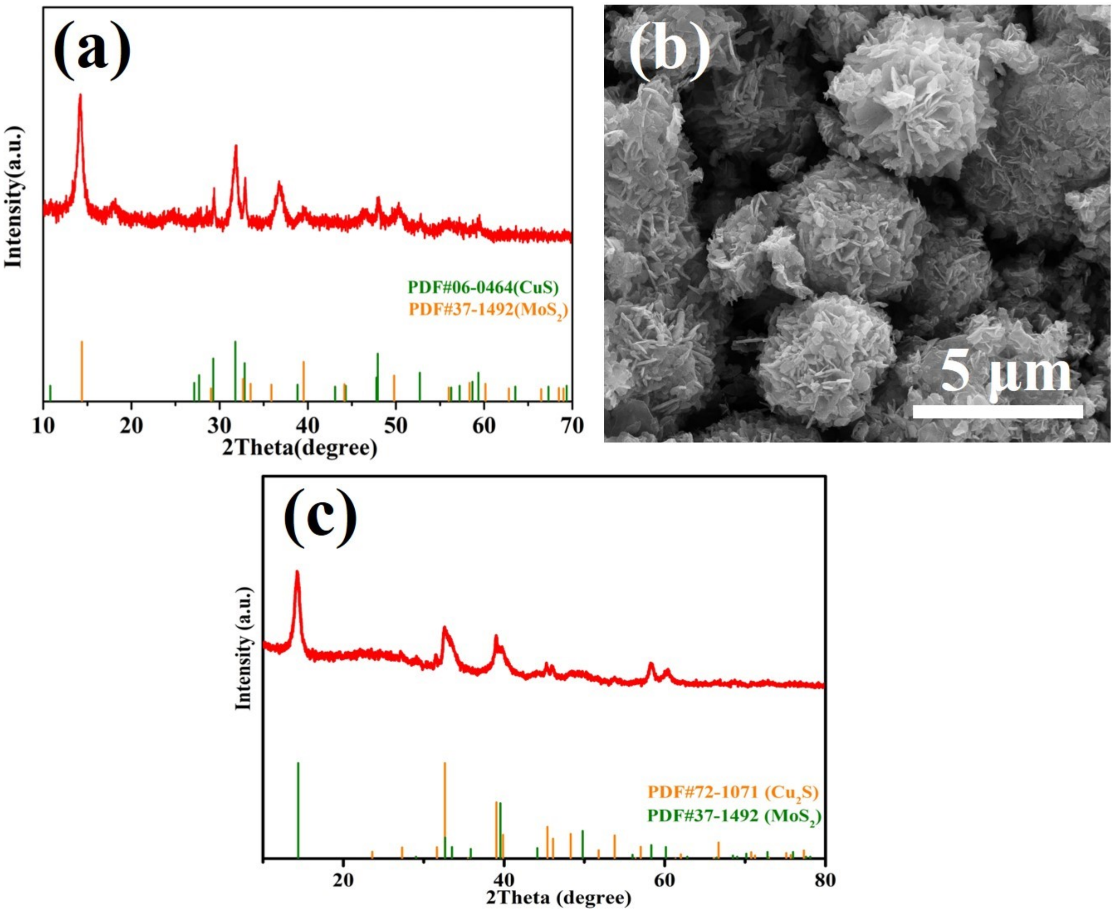

Figure S2. (a) XRD pattern and (b) SEM image of CuS/MoS_2/rGO microspheres, (c) XRD pattern of MCG-2 microspheres.

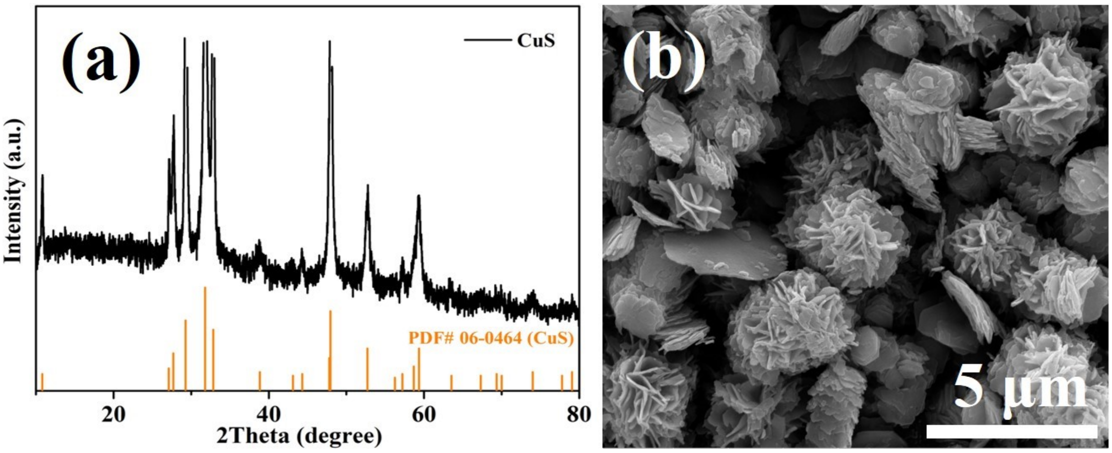

Figure S3. (a) XRD pattern and (b) SEM image of CuS nanosheets before calcination.

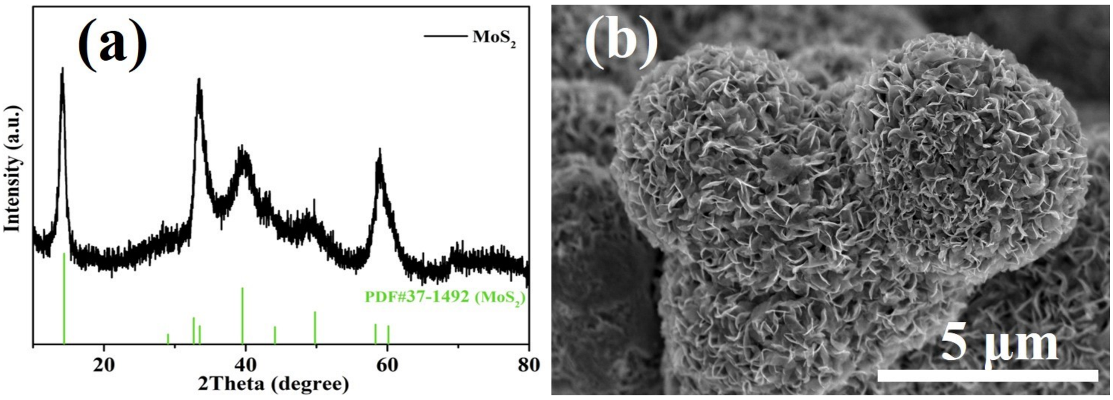

Figure S4. (a) XRD pattern and (b) SEM image of flower-like MoS_2 microspheres before calcination.

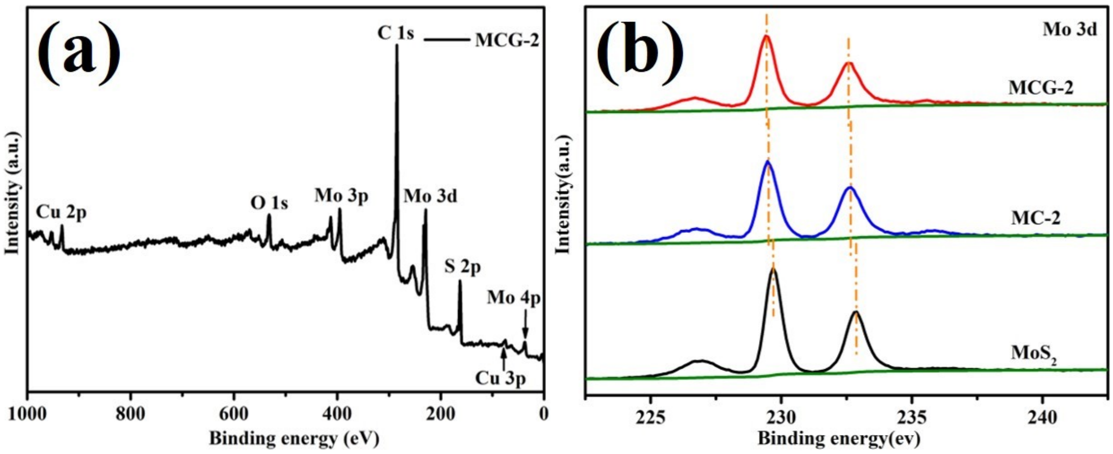

Figure S5. (a) Whole XPS spectrum of the MCG-2 composite; (b) XPS spectra of Mo 3d for MoS_2 and MCG-2 composites.

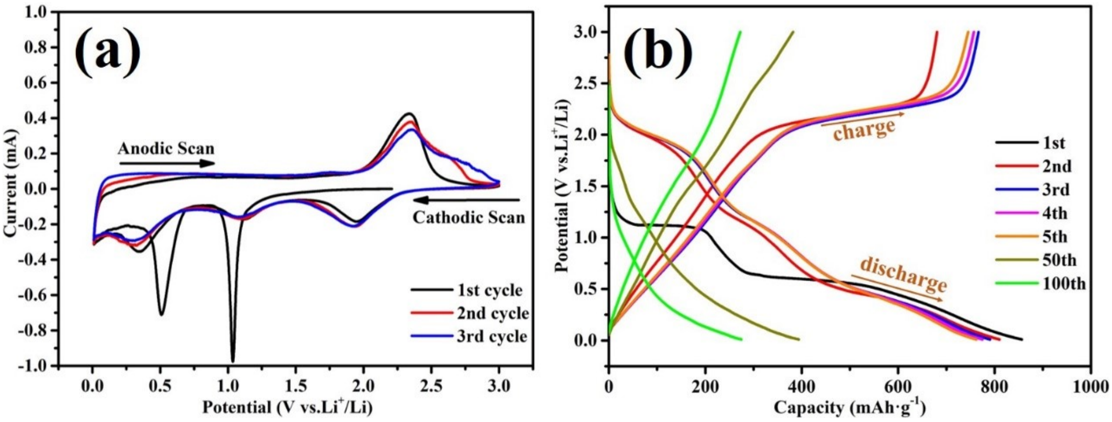

Figure S6. (a) CV curves of MoS_2 at 0.1 mV s^{-1}. and (b) GCD curves of MoS_2 at 100 mA g^{-1}.

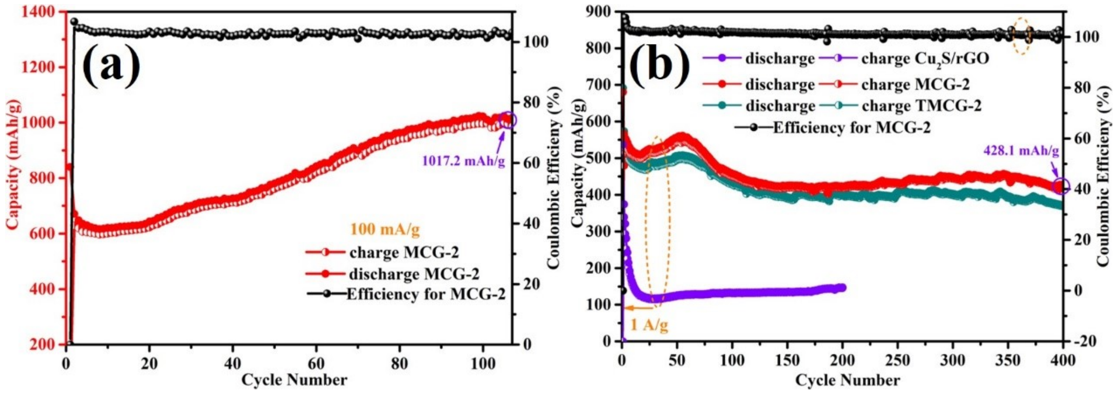

Figure S7. (a) Cycle performance of MCG-2 at 100 mA g^{-1}; (b) Cycle performance of Cu$_2$S&rGO, MCG-2 and TMCG-2 at 1 A g^{-1}

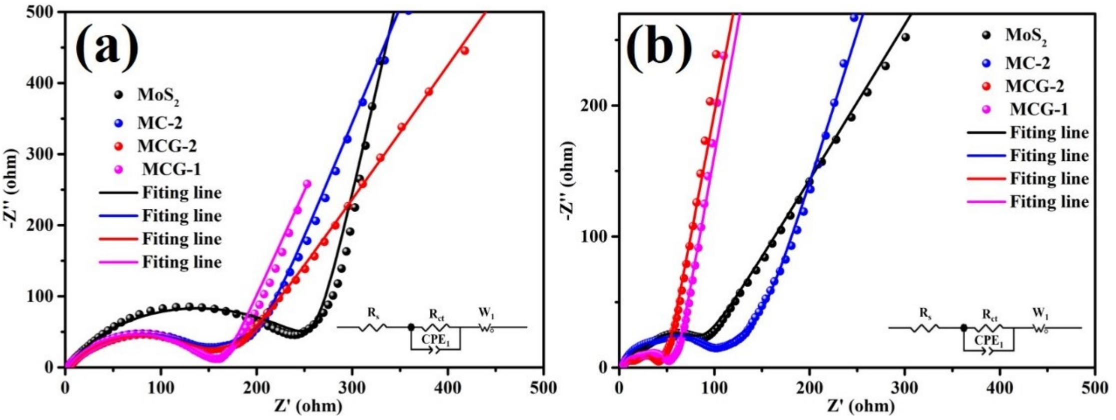

Figure S8. (a) EIS curves of MoS$_2$, MC-2, MCG-2 and MCG-1 before cycling; (b) EIS curves of MoS$_2$, MC-2, MCG-2 and MCG-1 after 100 cycles at 500 mA/g.