

Electronic Supplementary Information

Graphene/MoO₂ hierarchical nanoarchitectures: an *in situ* reduction synthesis and the high rate cycling performance as lithium-ion battery anodes

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SI-1 Experimental details

Materials

All reagents were analytically pure, and purchased from Tianjin Kermel Chemical Reagent Co. Ltd. (Tianjin, China), and used without further purification.

Synthesis of graphene sheets

The graphene sheets were synthesized by a chemical method.^{S1-S2} Simply, 2 g of sodium was added into 5 mL ethanol. The mixture was then transferred into a Teflon-lined stainless steel autoclave with a capacity of 50 mL for hydrothermal treatment at 220 °C for 72 h. After the reaction, the graphene precursor (solid product) was obtained. This material was rapidly pyrolysed at 900 °C for about one minute, and the remaining black powder washed with distilled water. The suspended solid was

then vacuum filtered and dried in a vacuum oven at 80 °C for 24 h and then the graphene sheets were synthesized.

Synthesis of the hierarchical nanoarchitectures

The hierarchical nanoarchitectures constructed by MoO₂ nanocrystal-functionalized graphene were synthesized by an *in situ* reduction process. MoO₃ particles were first obtained through ammonium paramolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) annealed at 500 °C for 4 h in air.^{S2} The graphene sheets are mixed with MoO₃ powders with a mole ratios of 2:1. The mixture was ball-milled using a planetary ball mill (Fritsch Pulverisette 7) under argon atmosphere. The weight ratio of the balls to the mixture was 15:1, and the rotating speed is 600 rpm. During the process, the mixture was milled for 20 min, a time interval is 20 min, and total time is 8 h.

Electrode preparation and electrochemical measurements

The samples were mixed with acetylene black and carboxymethyl cellulose (CMC) at a weight ratio of 8: 1: 1. The mixture was painted onto a copper foil with a diameter of 15 mm. The 2016 coin-type cells were assembled in an argon-filled glove box, and pure Li foils were used as the counter electrodes. The electrolyte was made of 1 M LiPF₆ in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with the volume ratio 1:1. The cells were galvanostatically charged and discharged between 0.001 and 3.0 V versus Li⁺/Li at room temperature on a program-controlled test system.

Characterizations

The morphology and size of the obtained hierarchical nanoarchitectures were characterized by scanning electron microscope (SEM) [HITACHI S-5200] and

transmission electron microscope (TEM) [JEOL-3010F]. The operating voltage of SEM and TEM is 5 and 200 kV, respectively. The pore diameter distribution and surface area were tested by nitrogen adsorption/desorption analysis [BECKMAN COULTER SA3100]. The crystal structure of the sample was determined by X-ray diffraction (XRD) [D/max 2550 V, Cu KR radiation]. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a spectrometer with Mg Ka radiation (ESCALAB 250, Thermofisher Co.). The binding energy was calibrated with the C 1s position of contaminant carbon in the vacuum chamber of the XPS instrument (284.8 eV).

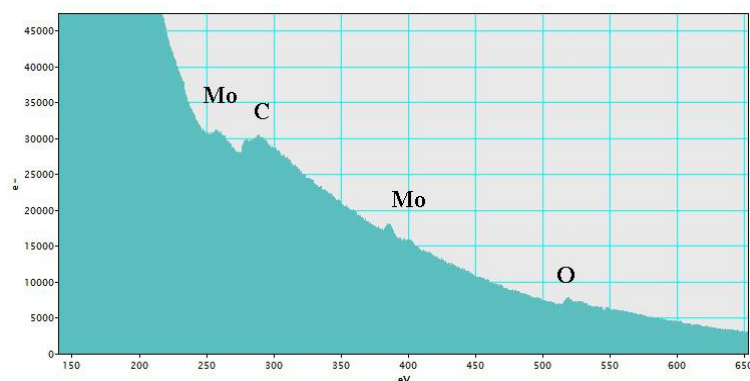


Fig. S1 EELS spectra of the hierarchical nanoartitectures

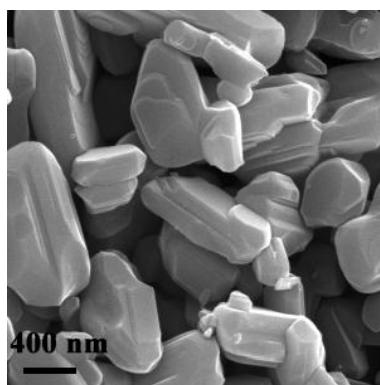


Fig. S2 SEM image of MoO₃ powder

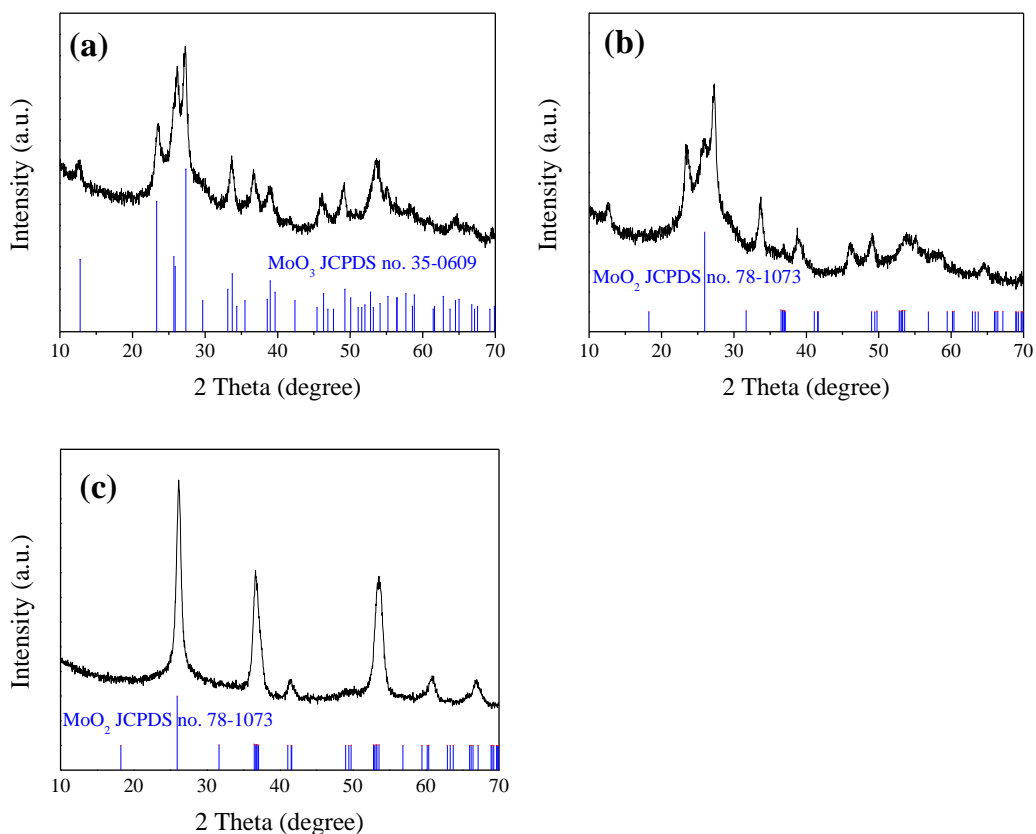


Fig. S3 XRD patterns of the products obtained at different ball milling times: (a) 2 h, (b) 4h and (c) 6h.

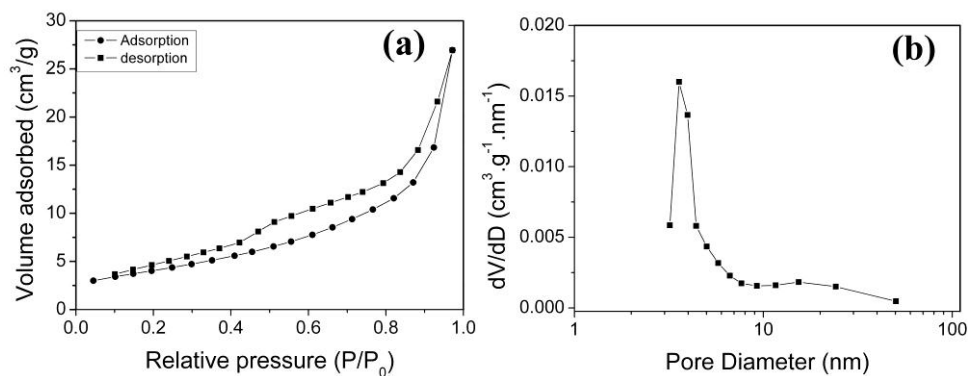


Fig. S4 (a) The nitrogen adsorption–desorption isotherm and (b) the corresponding BJH pore size distributions of the hierarchical nanoarchitectures.

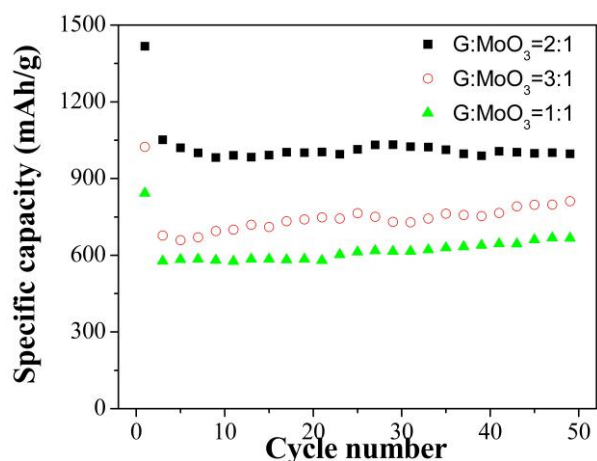


Fig. S5 Comparison of capacities of samples with different molar ratio of graphene to MoO₃ powder.

Notes and references

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