Supporting Information

Confining Ultrafine MoO_2 in Carbon Matrix Enables Hybrid Li-ion and Li-metal Storage

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Experimental Section

Materials synthesis: Experiment: α-MoO_3 nanobelts were prepared through a reported hydrothermal method. Firstly, 0.96 g of molybdenum powder was added in a mixture of 20 mL hydrogen peroxide (30 %) and 20 mL deionized water. Then, the solution was stirred for 12 h under 25 ^oC. After that, the mixture was sealed in a Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h. Subsequently, a white suspension (α-MoO_3 nanobelts) was obtained.

For the synthesis of MoO_2/C, 0.1214 g Tris was dispersed in 100 ml deionized water. Then, 2 mL α-MoO_3 nanobelt suspension was added dropwise into the buffer solution. Subsequently, 0.3 g dopamine hydrochloride was added in the solution under stirring at 25 ^oC for 4 h. After that, the solution was washed with deionized water and alcohol for several times and dried. Finally, the MoO_2/C was obtained after annealing at 800 °C for 2 h under Ar atmosphere. MoO_2 nanobelts were prepared through thermal treatment with Ar at 350 °C for 1 h followed by H2/Ar at 700°C for 2h.

Characterization: Field-emission scanning electron microscopy (JEOL JSM-7100 F) was used to study the morphology of the as-prepared products at an acceleration voltage of 20 kV. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and scanning transmission electron microscopy (STEM) were investigated by a Titan Themis G2 60-300. X-ray energy-dispersive spectra (EDS) were recorded using an Oxford IE250 system. Rigaku D/MAX-III diffractometer with monochromatized Cu Kα radiation was used to record the X-ray diffraction (XRD) patterns of the products. Raman spectra were measured using a Renishaw IN VIA micro-Raman spectroscopy system. Thermogravimetric analysis (TGA) curves were collected by NETZSCH STA 449F5. Brunauer-Emmett-Teller (BET) surface areas were obtained by N_2 adsorption isotherms, which are taken on a Tristar II 3020 instrument at 77 K. Fourier Transform Infrared Spectrometer (FTIR) spectra were taken on the FTIR spectrometer (Nicolet, Magna IR 560). X-ray photoelectron spectroscopy (XPS) spectra were collected on the ESCALAB 250 system with a monochromatic Al Kα source (1,486.6eV).

***In-situ* TEM characterization**:*In-situ* TEM tests were carried out through operating transmission electron microscope (Titan Themis G2 60-300) and *in-situ* sample holder (Zep tools Co. Ltd., China). The MoO_2/C that is attached to a copper mesh was used as the working electrodes. The metallic lithium (Li) loaded onto the tungsten tip was used as the counter and reference electrode. The thin lithium oxide (L_2O) on the Li surface was used as the solid electrolyte. Both the copper mesh and the tungsten tip with metal lithium were assembled onto the TEM sample holder under protection in Ar atmosphere, and then the holder was inserted into the specimen chamber. Once the Li_2O-covered Li electrode that was manipulated by a micro motor contacted the free end of the selected nanocomposite, a constant voltage between –5 and 5 V was applied across the sample to induce lithium of the MoO_2/C.

Electrochemical measurements: Electrochemical properties measurements were taken in 2016 type coin cells assembled in an argon-filled glovebox. The lithium metal acted as the counter and reference electrodes. The active materials, conductive carbon black (acetylene black) and carboxymethylellulose (CMC) binder were mixed by H_2O with a mass ratio of 7:2:1. Then the slurry was coated on a Cu foil to make electrodes. The electrolyte used was a solution of 1 M LiPF6 in ethylene carbonate, dimethyl carbonate, ethyl methyl carbonate (1:1:1 by volume). The *in-situ* batteries were assembled in anargon-filled glove box using special battery molds with Be window allowing the penetrating of X-ray. Galvanostaticdischarge/charge experiments were performed in the potential range of 0.01 – 3 V with a battery testing system (LAND CT 2001A) at room temperature. Cyclicvoltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted using an Autolab PGSTAT302N electrochemical workstation.

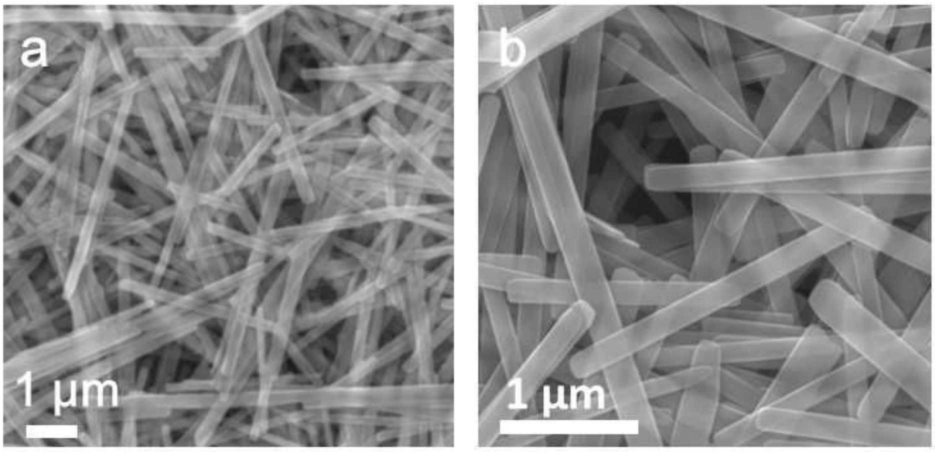

Figure S1. (a, b) SEM images of α-MoO_3 nanobelts.

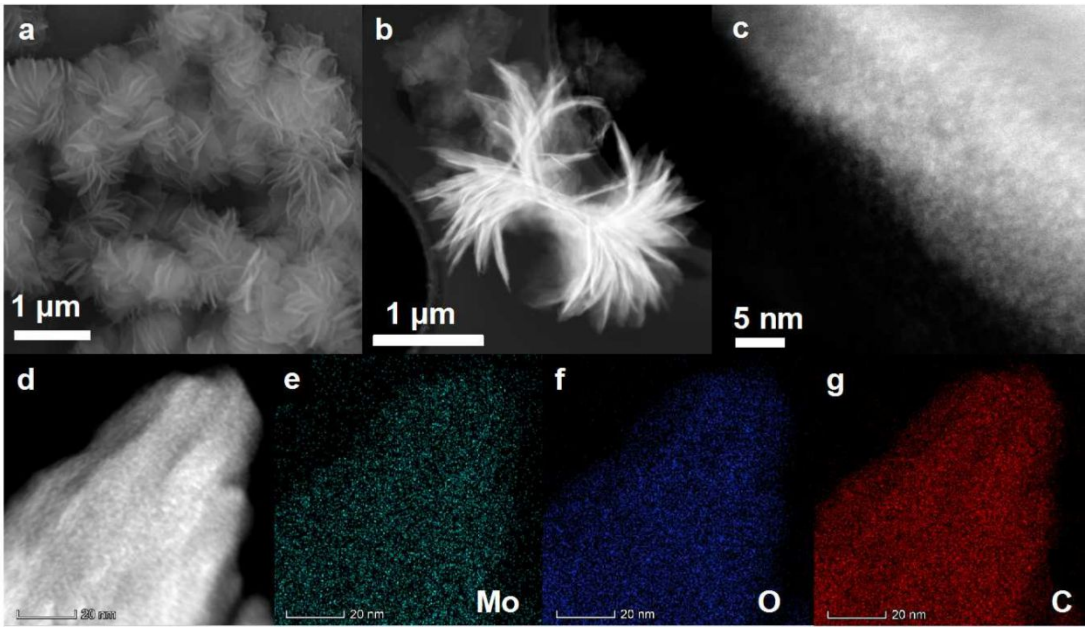

Figure S2. (a) SEM image, (b, c, d) STEM images, (e–g) EDS elemental mappings of flower-like Mo-PDA hybrid composites.

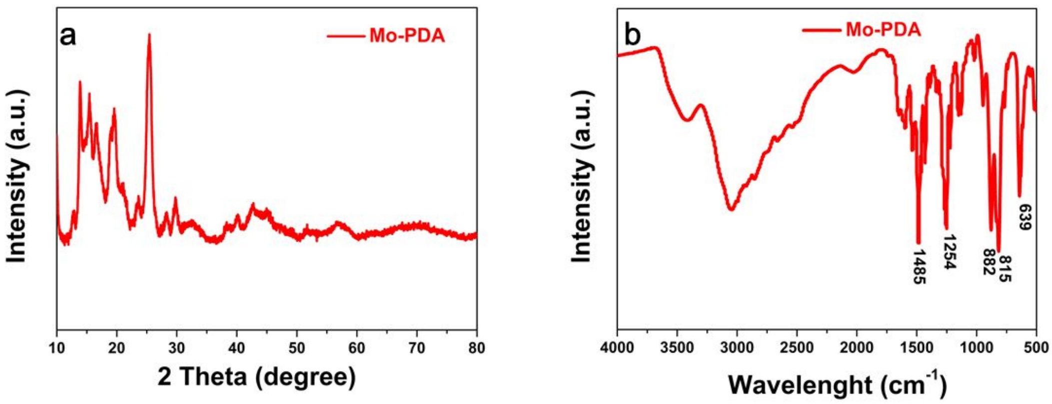

Figure S3. (a) XRD pattern, (b) FTIR spectrum of flower-like Mo-PDA composites.

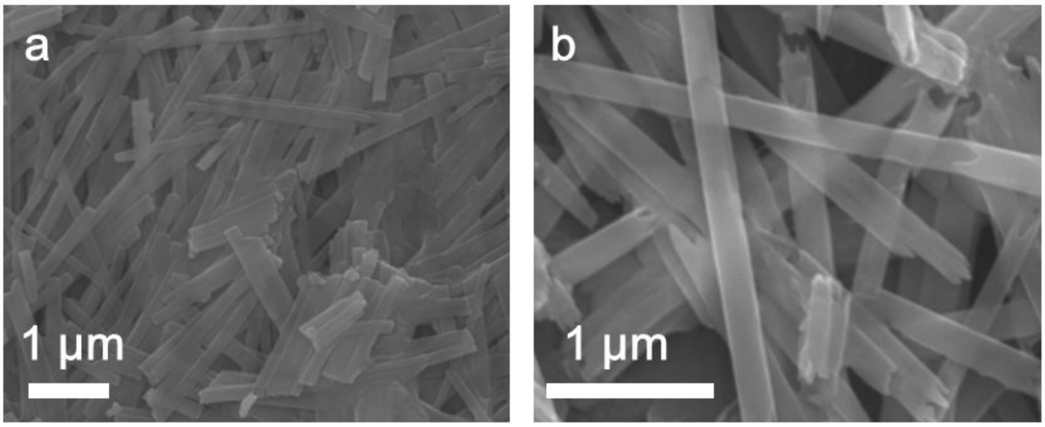

Figure S4. SEM images of MoO_2 nanobelts.

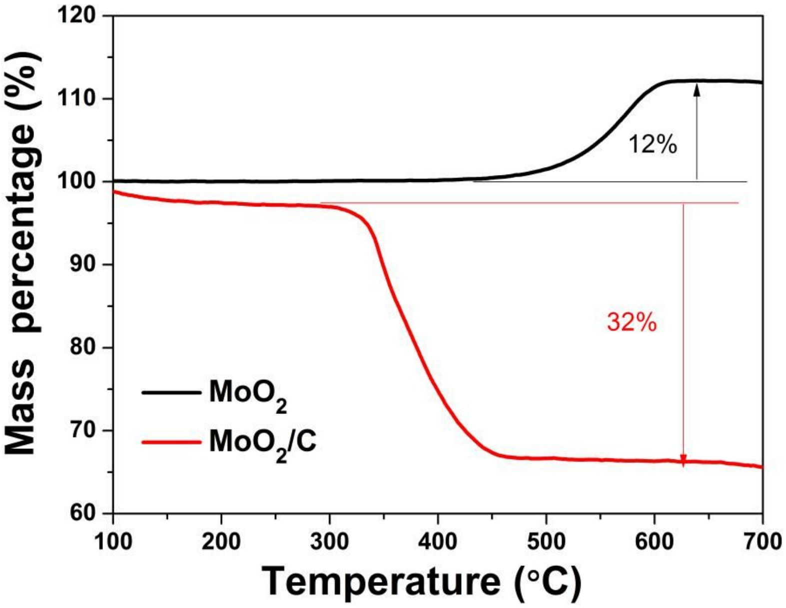

Figure S5. TGA curves of the MoO_2/C and MoO_2 nanobelts.

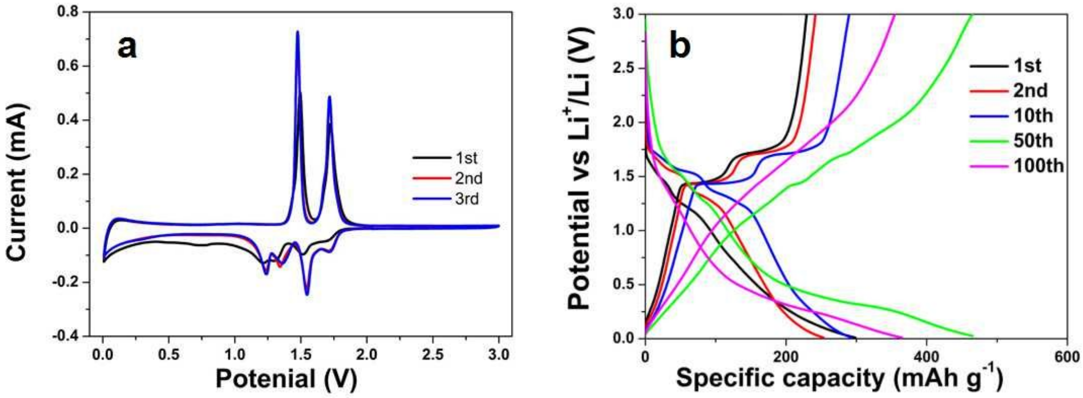

Figure S6. CV curves of the MoO_2 nanobelts at a sweep rate of 0.2 mV s^{-1} in the potential range of 0.001 – 3.0 V *vs.* Li/Li^+ (a); galvanostatic discharge-charge profiles of MoO_2 nanobelts at 200 mA g^{-1} (b).

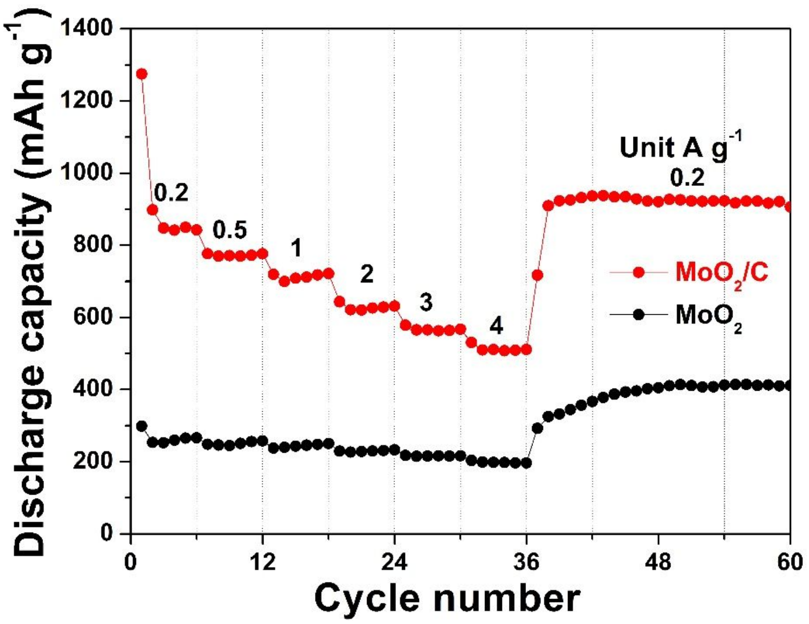

Figure S7. Rate performance of the MoO_2/C and MoO_2 nanobelts.

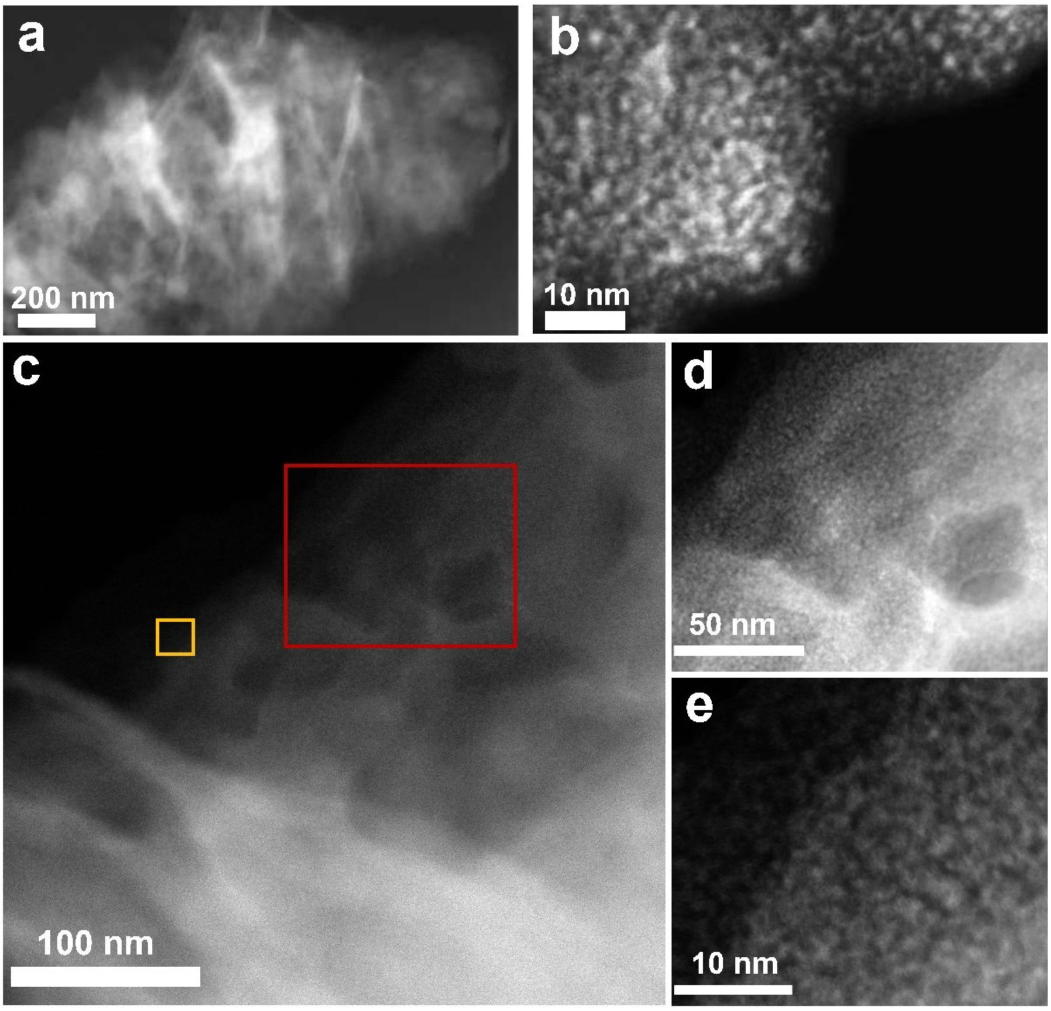

Figure S8. *Ex-situ* STEM and *in-situ* STEM of the MoO_2/C after lithiation. (a, b) *ex-situ* STEM images after second lithiation, (c, d, e) *in-situ* TEM images of lithiated MoO_2/C (Figure S8d is from the red labeled area in Figure S8c, Figure S8e is from the orange labeled area in Figure S8c,).