Supporting Information

Tailoring Crystalline Phases of MoO_2 for Enhanced Lithium-Ion Storage Performance

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Experimental Section

Materials characterization

The morphologies of samples were obtained on a Hitachi S-4800 scanning electron microscope with an accelerating voltage of 15 kV, and high-resolution transmission electron microscopes (HRTEM) with an accelerating voltage of 200 kV (JEOL JEM-2010F electron microscope). The element component was measured by the energy disperse X-ray spectrum (EDS, EDAXTLS). X-ray powder diffraction (XRD) was obtained by Bruker D8 employing Cu-Kα radiation (1.54056 Å) with an operating voltage of 40 kV and a beam current of 40 mA. The structural properties of samples were recorded with Raman spectra (Bruker Senterra) at ambient temperature under an excitation of 488 nm. The surface components and valence states of samples were characterized by X-ray photoelectron spectra (XPS) (Thermo Fisher Scientific ESCALAB250Xi) employing Al Kα (1486.6 eV). The galvanostatic discharge/charge cycles were tested on battery tester (LAND CT2001A) with the voltage windows of 0.01-3.0 V. The CV curves were obtained by electrochemical workstation (CHI760E, Chenhua, Shanghai).

Electrochemistry characterization

The anode was fabricated by mixing MoO_{2-x}@C (70 wt%), acetylene black (20 wt%), and polyvinylidene fluoride (10 wt%) dissolved in N-methyl-2-pyrrolidinone, and then coated on the Cu foil and were finally dried in a vacuum oven at 110°C for 12 h. The average mass loading of the whole electrode is≈0.6-1.0 mg cm^{-2}. The CR2025 type cells were assembled in a glove box under Ar atmosphere (< 0.01 ppm of oxygen and water). For lithium-ion batteries (LIBs), it consisted of a prepared electrode, glass fibers separator (Celgard 2500), and lithium foil as the counter electrode. The electrolyte was 1 M $LiPF_6$ in ethylene carbonate (EC) dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1 by volume) with 5 vol.% fluoroethylene carbonate (FEC) additive as the electrolyte. Cyclic voltammetry (CV) was conducted on a CHI760E workstation (CHI760E, Chenhua, China) within the potential range of 0.01–3 V. Electrochemical impedance spectroscopy (EIS) was carried out by using electrochemical workstation (CHI760E, Chenhua, China) within the frequency range of 100 kHz to 0.01 Hz under open circuit voltage. The galvanostatic charge/discharge measurements were carried out with a battery testing system (Land CT2001A, Wuhan, China) in the voltage range of 0.01–3.00 V at room temperature.

Calculation of the b value and capacitive contribution

For lithium-ion battery electrode materials, the measured current-voltage (CV) curves can be categorized into two types of charge storage processes: surface capacitance-dominated processes (including surface redox pseudocapacitance and electric double-layer capacitance) and diffusion-controlled processes (involving lithium-ion intercalation/deintercalation). Generally, the charge storage kinetics can be investigated by measuring the power-law relationship between current density (*i*) and scan rate (v) using the following formula:

$$i = a\, v^{b} \qquad \text{(S1)}$$

$$\log(i) = b \log(v) + \log(a) \qquad \text{(S2)}$$

When b=0.5, it indicates that the reaction process is predominantly governed by diffusion control, whereas when b=1, it suggests that the reaction process is mainly controlled by pseudocapacitive behavior. To quantify the contribution ratios of diffusion-controlled and pseudocapacitive-controlled processes, the following formula can be employed for calculation:

$$i(v) = k_1 v + k_2 v^{1/2} \qquad \text{(S3)}$$

$$i(v)/v^{1/2} = k_1 v^{1/2} + k_2 \qquad \text{(S4)}$$

Here, $k1v$ represents the contribution ratio of pseudocapacitance-controlled processes, while $k2v^{1/2}$ denotes the contribution ratio of diffusion-controlled reactions.

The testing of electrochemical impedance spectroscopy

The assembled battery was tested using an electrochemical workstation under the following conditions: measurements were conducted at open-circuit voltage (i.e., with no current flow in the external circuit, representing the potential difference between the positive and negative electrodes) and across a frequency range spanning from 100 kHz to 0.01 kHz.

$$\omega = 2\pi f \qquad \text{(S8)}$$

$$Zre = R + \sigma\omega^{-1/2} \qquad \text{(S9)}$$

$$D_{li} = \frac{0.5R^2T^2}{A^2n^2F^2C^2\sigma^2} \qquad \text{(S10)}$$

Results and Discuss

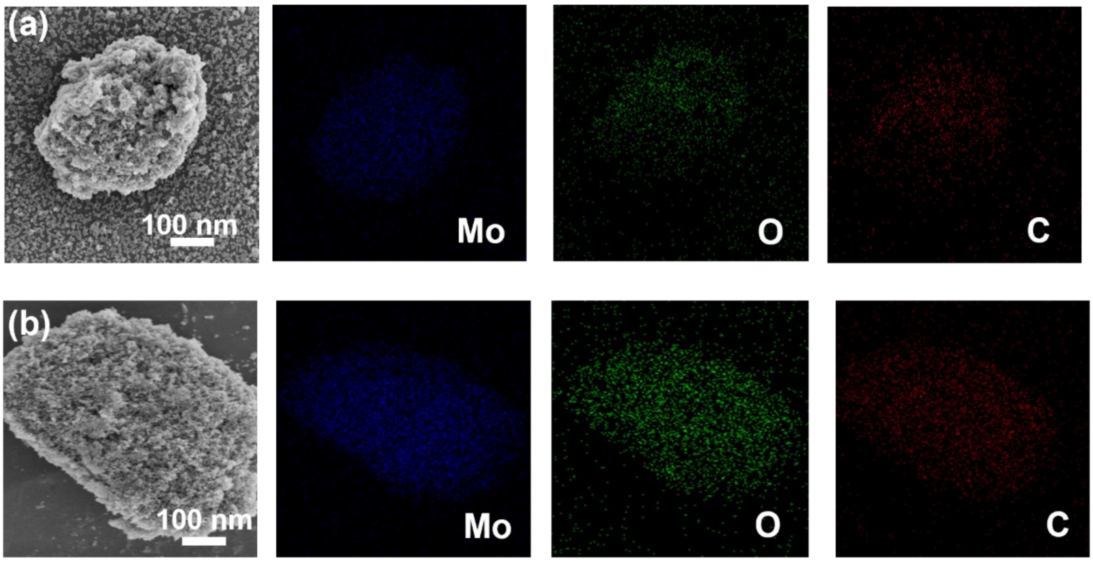

Fig. S1 STEM-EDS elemental mapping of MoO_{2-x}/C composites synthesized at (a) 350 °C and (b) 550 °C.

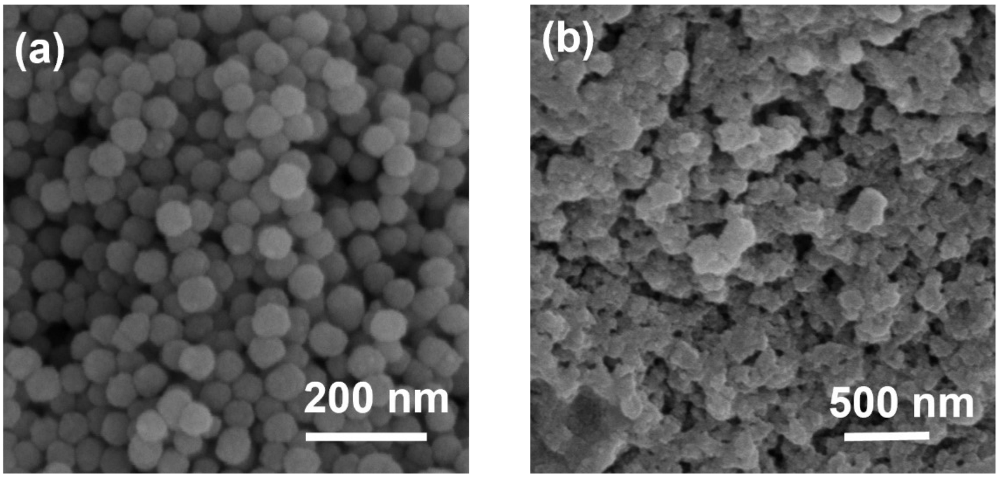

Fig. S2 SEM images of the MoO_{2-x}/C-450 electrode (a) before cycling and (b) after 500 galvanostatic charge-discharge cycles at 5.0 A g^{-1}.

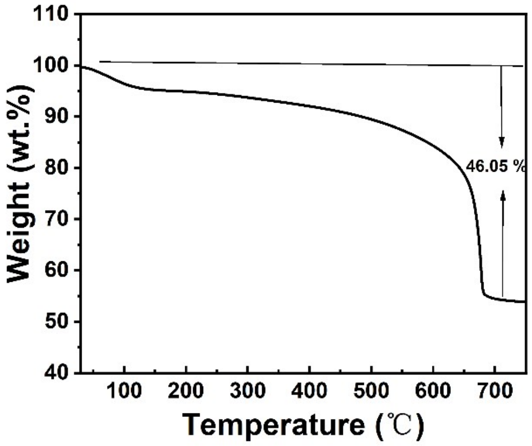

Fig. S3 In terms of the TGA curve, the residual weight of the sample after heating to 600 °C is approximately 46.05 wt.%.

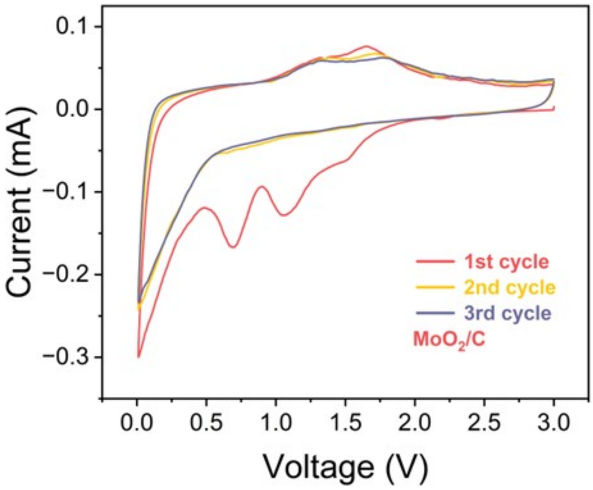

Fig. S4 CV curves of MoO_2/C.

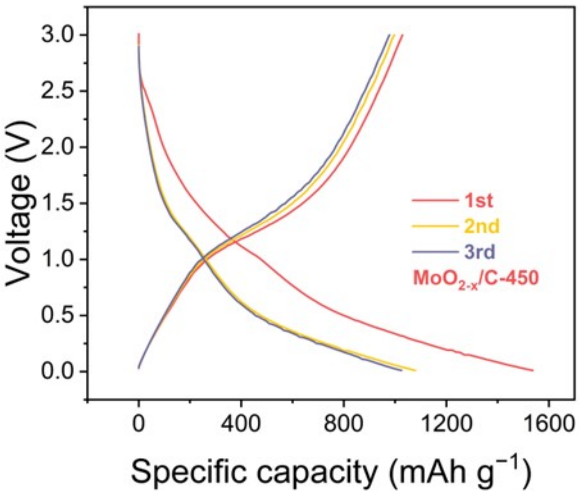

Fig. S5 GTC curves of MoO_{2-x}/C-450 at 0.1 A g^{-1}.

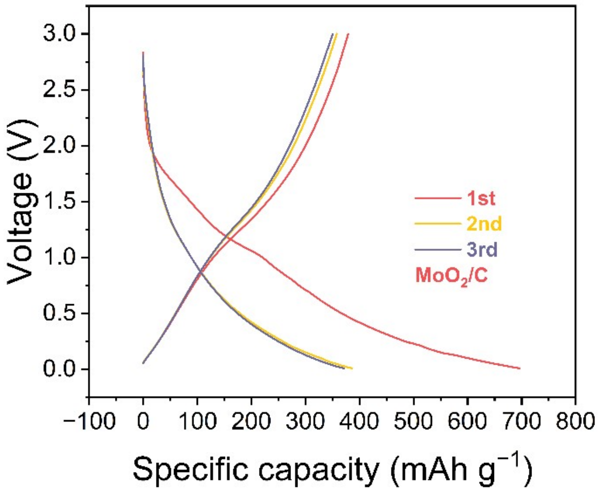

Fig.S6 GTC curves of MoO_2/C at 0.1 A g^{-1}.

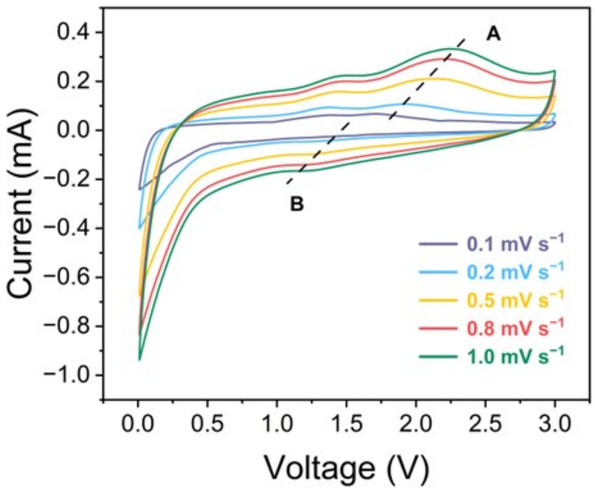

Fig. S7 CV curves of MoO_2/C.

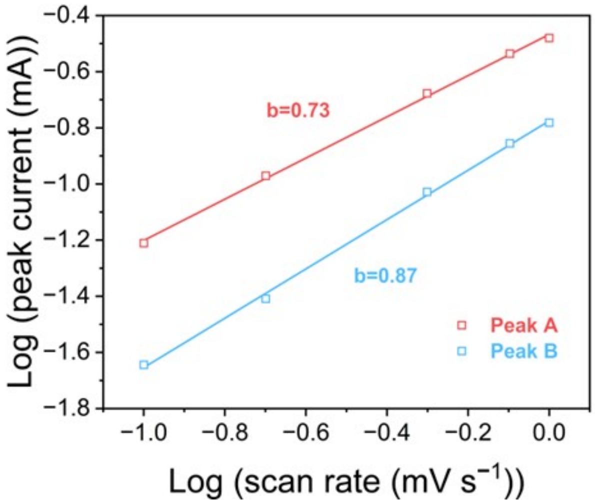

Fig. S8 b-values of MoO_2/C.

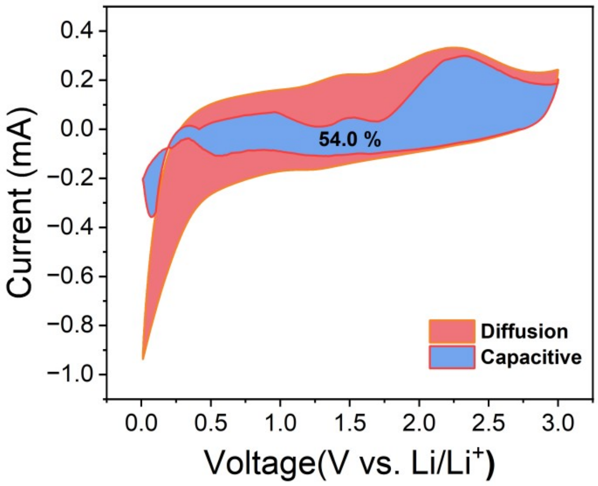

Fig. S9 Diffusion contribution and the capacitive contribution at 1.0 mVs^{-1} of MoO_2/C.

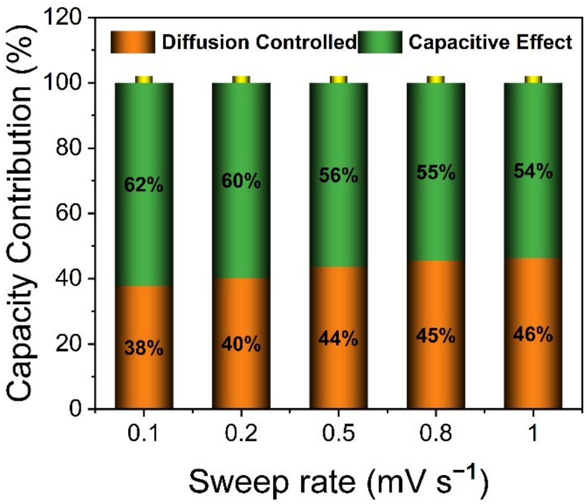

Fig. S10 Capacitance contribution of MoO_2/C.

Tab S1 Comparison of the synthesis, structure, and electrochemical performance of this work with representative MoO_2-based anodes.

Material System	**Synthesis Method**	**Structural Feature**	**Key Electrochemical Performance**	**Ref**
Amorphous MoO_{2-x}/C nanospheres	POM/Pyrrole solution 450℃	Phase-pure amorphous	436.3 mAh g^{-1} after 500 cycles at 5 A g^{-1}	This work
Core-shell MoO_2/C nanospheres	Solvothermal process followed by annealing.	Core-shell structure	500 mAh g^{-1} at 1C for 300 cycles	[1]
MoO_2@C	Rinding and annealing	Nanoflower morphology	166 mAh g^{-1} after 1000 cycles at 1.0 A g^{-1}	[2]
MoO_2@NCNTs	Low-temperature polymerization	Porous N-doped carbon nanotubes	868.3 mAh g^{-1} at 2 A g^{-1} after 100 cycles.	[3]

References

1 X. Pan, S. Li, Z. Wang, L.Y. Yang, K. Zhu, L. Ren, *Materials Letters*. 2017;**199**:139-42.

2 C. Cui, Q. Wei, L. Zhou, L. Mai, J. Ma, *Materials Research Bulletin*. 2017;**94**:122-6.

3 S. Wang, Y. Zhao, C. Li, X. Zhang, Y. Chen, *Journal of Alloys and Compounds*. 2017;**695**:1285-93.