

Supplementary Information

TiO₂-coated MoP/Phosphorus Doped Carbon Nanorods for
Ultralong-Life Sodium Ion Batteries with High Capacity

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Experimental section:

Preparation of materials

Preparation of Mo-MOF nanorods ^[1]: $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (0.240 g, 1.0 mmol) was mixed with p-Xylylenediphosphonate acid (H_4xdp) (0.140 g, 0.5 mmol) in 16 ml deionized water. The pH of the solution was adjusted to 1.0 by adding concentrated hydrochloric acid droplet by droplet. And then above solution was placed in a pressure tube of 25 cm³ and heated at 120 °C for 15 h. Washed the white crystallized material thoroughly with deionized water several times and dry at room temperature.

Preparation of Mo-MOF@TiO₂ nanorods: Typically, 200 mg Mo-MOF was dissolved in a mixture of anhydrous ethanol and concentrated ammonia, and 0.1037 ml ml tetraisopropyl titanate were added by continuous stirring at 45 °C. After filtrated, the white powder was harvested.

Preparation of MoP@TiO₂/P-C: Above white powder was heated at 900 °C and kept for 2 h. As the temperature cooling down to room temperature, the final sample was collected and named as MoP@TiO₂/P-C. On this basis, the amount of tetraisopropyl titanate of 0.0518 ml, 0.2334 ml, 0.3113 ml were used and corresponding products were denoted as MoP@TiO₂/P-C-1, MoP@TiO₂/P-C-2 and MoP@TiO₂/P-C-3.

MoP/P-C nanorod was also prepared using the similar method except the addition of tetraisopropyl titanate for reference.

Material characterization:

The material phase composition of the sample was determined by X-ray diffractometer (D8). The specific content of the elements in the sample was done by Inductive Coupled Plasma Emission Spectrometer testing (ICP). The morphology and microstructure were further observed by SEM/EDS, SU-8010 and TEM, Tacnai F20. Carbon content of MoP/P-C and MoP@TiO₂/P-C was determined at 25-900 °C by thermogravimetric instrument (TGA, TA-Q50). The surface elemental valence components of samples were recorded by X-ray photoelectron spectroscopy (XPS). Raman spectra were obtained using the Nd line as a laser source ($\lambda = 514 \text{ nm}$).

Electrochemical measurements

Electrochemical performance was tested by CR-2032 coin cells assembled from working electrodes, reference electrodes, separator and electrolytes. The working electrode was prepared by grinding the electrode material (70w%), Super P (20wt%), and polyvinylidene fluoride binder (PVDF, 10wt%) in a moderate amount of N-methyl-2-pyrrolidone (NMP) to form a uniform, smooth slurry, which was then coated with copper foil collector fluid. After 12 h drying in a vacuum oven at 120 ° C, the working electrode is then pressurized under 10 MPa and then cut into 10 mm diameter poles with a load mass of 1-2 mg cm⁻² of active material. Sodium foil with 14 mm diameter was used as reference electrodes. Fiberglass produced by Whatman, GF/D was used as a separator. Sodium electrolyte was 1 M NaPF₆ dissolved in ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl carbonate (EMC) (volume ratio 1: 1), and 5 wt% fluoroethylene carbonate (FEC) as additives.

Charge/discharge testing was performed on a cell tester (Novavax, China) with a voltage range of 0.01-3.0 V (vs. Na/Na⁺) at 30 °C. CT2001A cell equipment (Wuhan LAND) was used for GITT testing at 0.1 A g⁻¹ current density. The cyclic voltammetry (CV) test and electrochemical impedance spectroscopy (EIS) test were performed using CHI 600E electrochemical workstations with voltage ranges of 0.01-3.0 V and scanning rates of 0.1-1.0 mV s⁻¹. The EIS profile was measured at frequencies ranging from 0.01 Hz to 100 KHz.

Reference

- 1 A. A. Ayi, A. D. Burrows, M. F. Mahon, V. M. Sebestyen, *CrystEngComm* 2013, **15**, 930

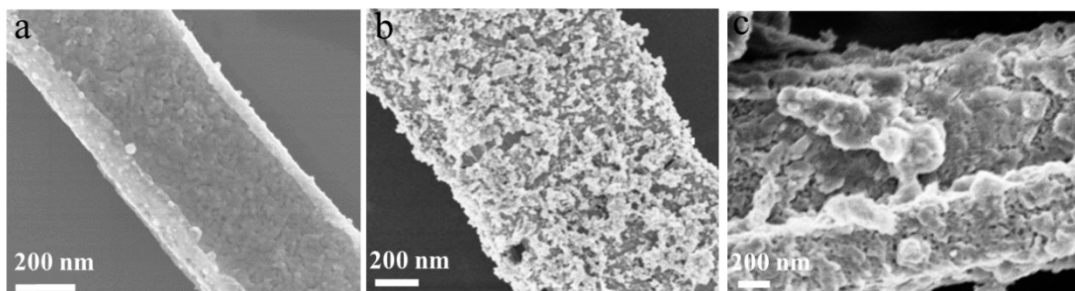


Figure S1. SEM images of (a,b,c) MoP@TiO₂/P-C -1, MoP@TiO₂/P-C-2 and MoP@TiO₂/P-C-3.

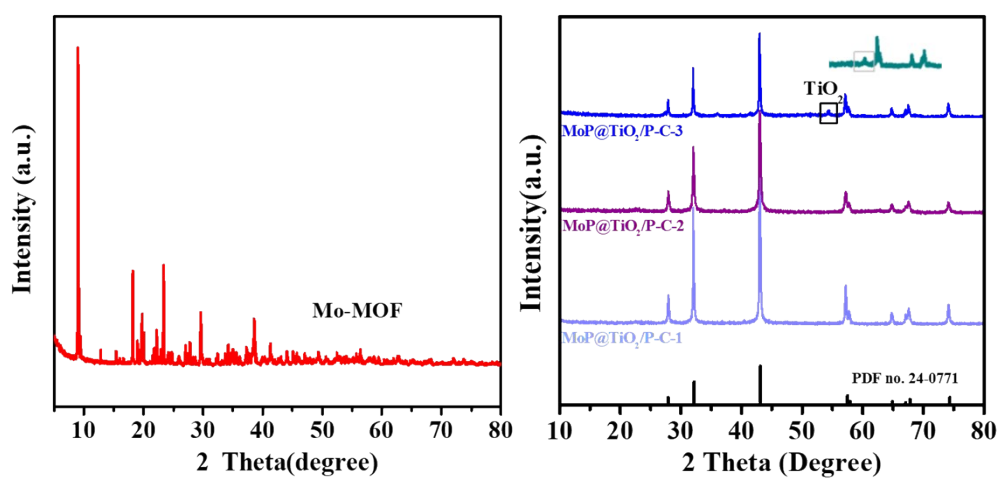


Figure S2. XRD patterns of samples: (a) Mo-MOF, (b) MoP@TiO₂/P-C-1, MoP@TiO₂/P-C-2 and MoP@TiO₂/P-C-3.

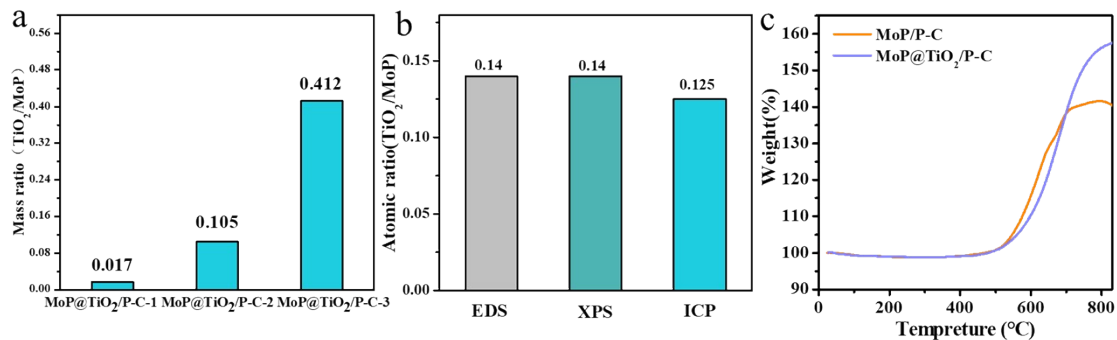


Figure S3. (a) Mass ratios of TiO_2 and MoP for different ratios of TiO_2 samples in ICP testing (b) Mass ratios of TiO_2 and MoP of MoP@ TiO_2 /P-C in EDS, XPS and ICP (c) The TG of MoP/P-C and MoP@ TiO_2 /P-C.

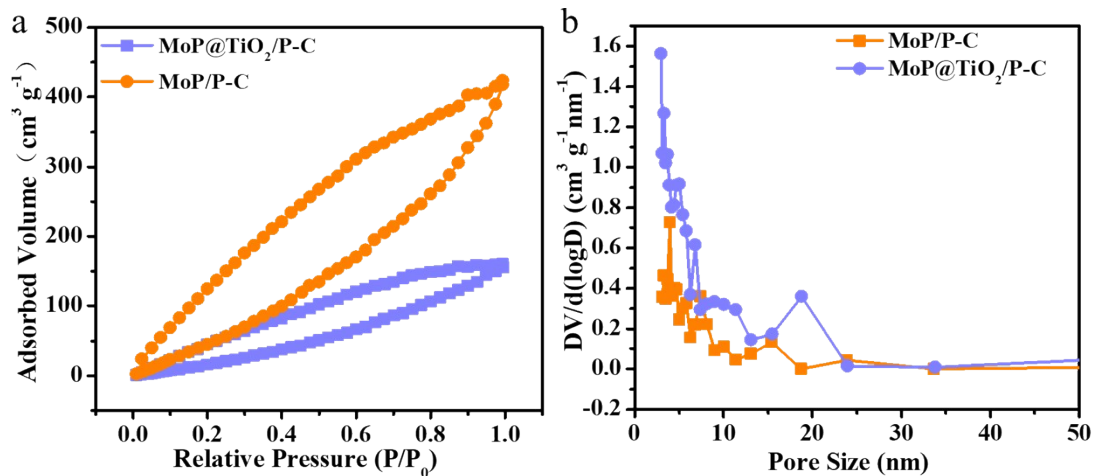


Figure S4. (a) Nitrogen adsorption and desorption curves of MoP/P-C and MoP@ TiO_2 /P-C, (b) the pore size distribution of MoP/P-C and MoP@ TiO_2 /P-C.

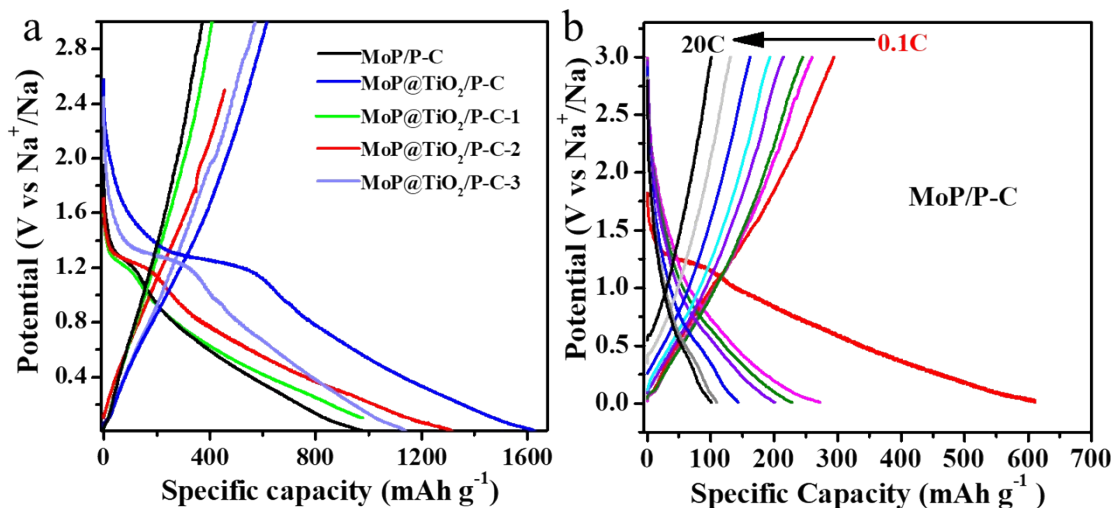


Figure S5. (a) Initial three galvanostatic charging/discharging curves of all samples (b) Charge-discharge curves of MoP/P-C (0.05 A g^{-1} - 10 A g^{-1}).

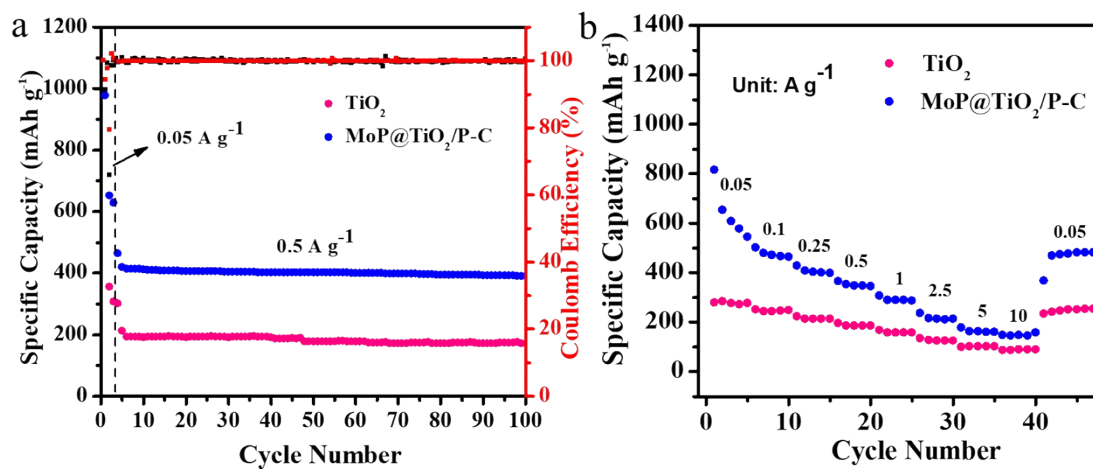


Figure S6. Cycle and rate performance comparison between MoP@TiO₂/P-C and MoP/P-C.

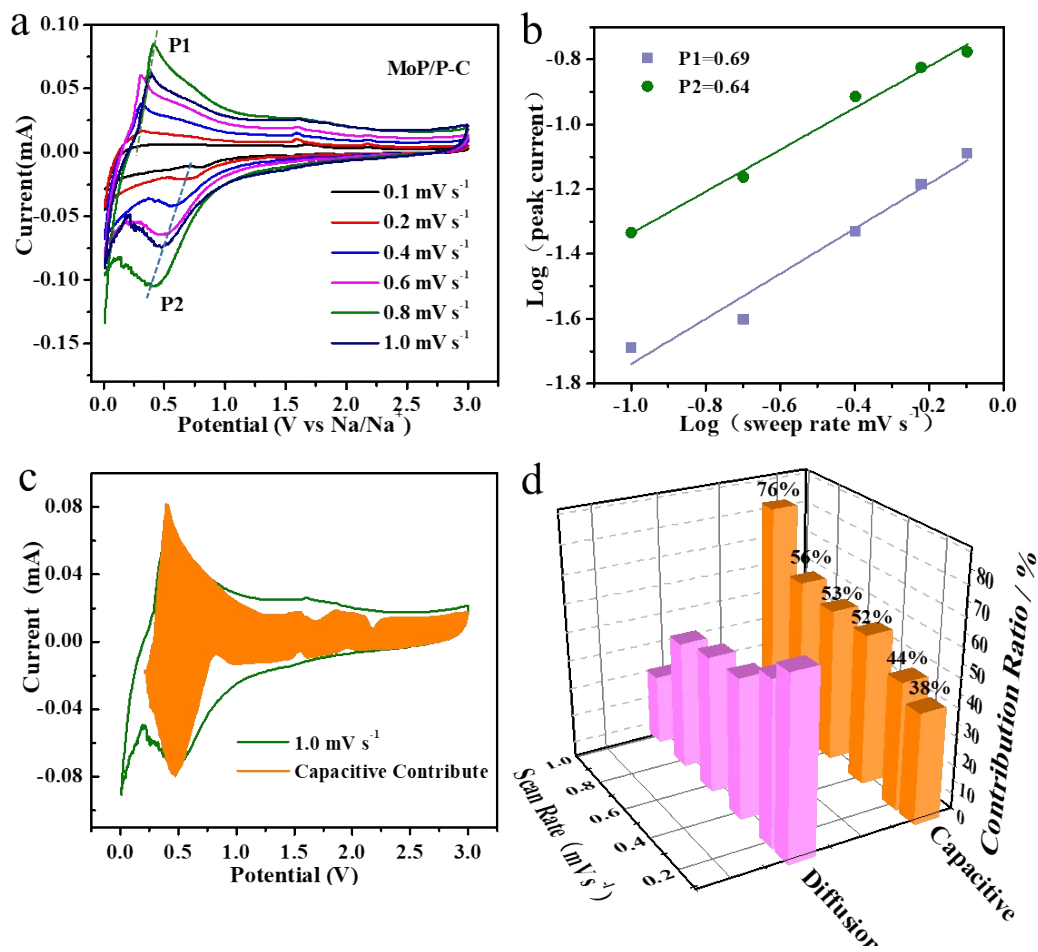


Figure S7. (a) CV curves of MoP/P-C at different scan rates, (b) fitted b-values of the corresponding peaks, (c) capacitance contribution in the CV curve at 1 mV s^{-1} , and (d) capacitance contribution at different scan rates.

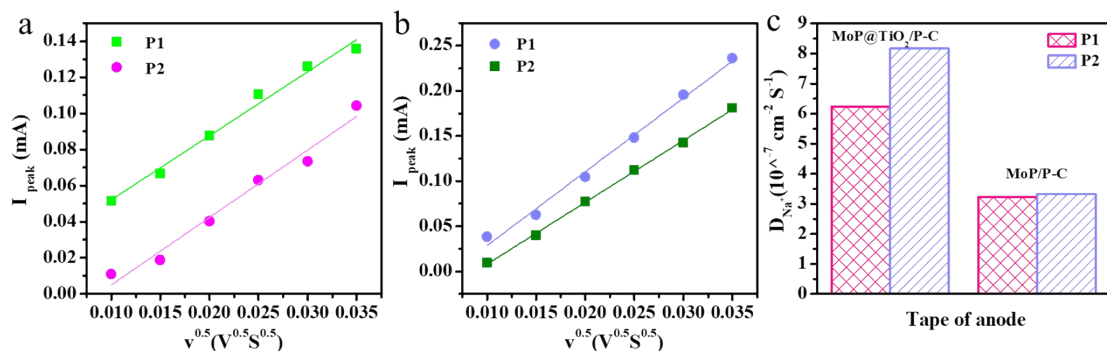


Figure S8. $I_{\text{peak}}-v^{0.5}$ curves of (a) MoP/P-C and (b) MoP@TiO₂/P-C, (c) The D_{Na^+} of MoP@TiO₂/P-C and MoP/P-C.

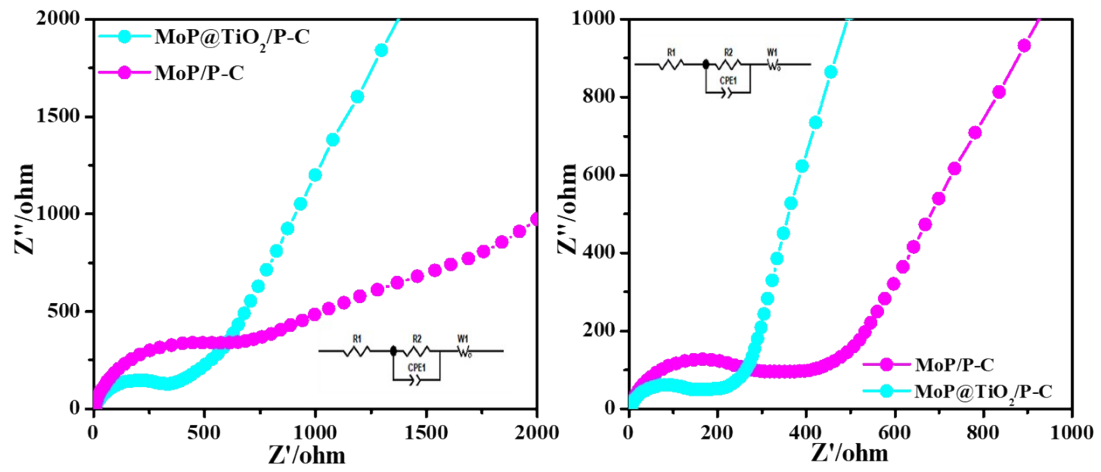


Figure S9. EIS spectra of MoP/P-C and MoP@TiO₂/P-C before (a) and after (b) 100 cycles.