Electronic Supplementary Material (ESI) for ChemComm.
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Supporting Information

Reshaping carbon-coated $Mn_2Mo_3O_8$ nanotubes and enhanced sodium storage performance

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1. Experimental Section

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1.1 Synthesis of pure $MnMoO_4$

First, 10 mmol $C_4H_6MnO_4 \cdot 4H_2O$ (Sinopharm Chemical Reagent Co., Ltd) and 10 mmol $Na_2MoO_4 \cdot 2H_2O$ (Kermel Chemical Reagent Co., Ltd) were dissolved in 50 ml distilled water respectively under magnetic stirring for 30 minutes. Then, the transparent mixed solution were quickly poured into a porcelain cup and then was placed into a microwave oven under microwave process for 30 minutes. After that, a layered yellow solution was obtained. The as-prepared yellow solution was washed with distilled water and ethanol for several times and dried at 60 ℃ for 12 h under vacuum. The achieved yellow power was placed in an alumina porcelain boat and annealed at 500 ℃ for 3 h with a heating rate of 5 ℃ min^{-1} under Ar atmosphere. The pure $MnMoO_4$ has been prepared successfully. For the convenience of comparison, the product is recorded as MMO in the manuscript.

1.2 Synthesis of $Mn_2Mo_3O_8$/C nanotubes

200 mg yellow powder (mentioned above) was poured into 100 ml Tris buffer solution under successive ultrasonication for 10 minutes. Then, 100 mg dopamine hydrochloride (Shang Hai Aladdin Biological Technology Co., Ltd) was sprinkled into the mixed solution. Interestingly, the color of above solution changes from orange to black, which indicates the gradual polymerization of dopamine monomer. After washing with distilled water and ethanol for several times, the collected black powder was dried at 60 ℃ for 12 h under vacuum and put into a mortar to ground into fine powder. The achieved fine powder was placed in an alumina porcelain boat and annealed at 500 ℃ for 3 h with a heating rate of 5 ℃ min^{-1} under Ar atmosphere. The

product is marked as MMOC-2. For comparison, products MMOC-1 and MMOC-3 were prepared by adjusting the dosage of dopamine to 50mg and 200mg, respectively.

1.3 Materials characterization

The structural and composition information were measured by X-ray diffraction (XRD, Rigaku Smart Lab 9kW, Japan) with Cu Kα radiation (λ=0.15417 nm), and external morphology of material could be observed by Scanning electron microscope (SEM, SU8100, Hitachi, Japan). Lattice fringe and element distribution could be observed by Transmission electron microscope equipped with energy-dispersive X-ray spectroscopy (TEM, FEI Tecnai F20, USA). Elemental composition and valence state were measured by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha USA). Raman spectrometer curve was recorded by using Renishaw-invia. Carbon content of the products could be measured by Thermogravimetric Analysis (TG, TGA550, USA).

1.4 Electrochemical measurements

Electrochemical measurements were tested on CR2032 coin cells assembled in Ar-filled glove box. The mixed slurry was prepared by mixing the active material, acetylene black and polyvinylidene fluoride (PVDF) with mass ratio by 8:1:1 with a proper amount of N-methyl-2-pyrrolidone (NMP), and then coated on the copper foil, next dried at 110 ℃ for 12 h under vacuum. Finally, the circular shapes with 12 mm diameter were cut as anode materials with active material loading mass of 1.3~1.5 mg. Sodium metal foil and glass fiber (Whatman GF/D) were used as counter electrode and separator. The electrolyte is 1.0 M $NaClO_4$ in a solution mixed by ethylene carbonate

(EC) and diethyl carbonate (DEC) with 1:1 vol ratio and the addition of 5 vol% fluoroethylene carbonates (FEC). Cyclic Voltammetry (CV) and electrochemical impedance spectroscopy (EIS) could be measured on electrochemical working station (CHI660E, Chenhua, Shanghai) from 0.01 V to 3.00 V (vs. Na^+/Na). Galvanostatic charge–discharge (GCD) curves, cyclic properties, and galvanostatic intermittent titration technique (GITT) measurements were studied by Neware BTS3000 battery tester using the same voltage. Sodium ion full batteries were fabricated by the similar procedure like half batteries except using $Na_3V_2(PO_4)_3$ as cathode materials and pre-sodiated $Mn_2Mo_3O_8$/C nanotubes as anode materials (N/P=1.2), respectively. The equation used for the calculation of specific capacity is as follows: $C_s = C_t/m$, C_s: specific capacity of electrode material (mAh g^{-1}); C_t: tested capacitance (mAh); m: mass of electrode material (g).

Figures

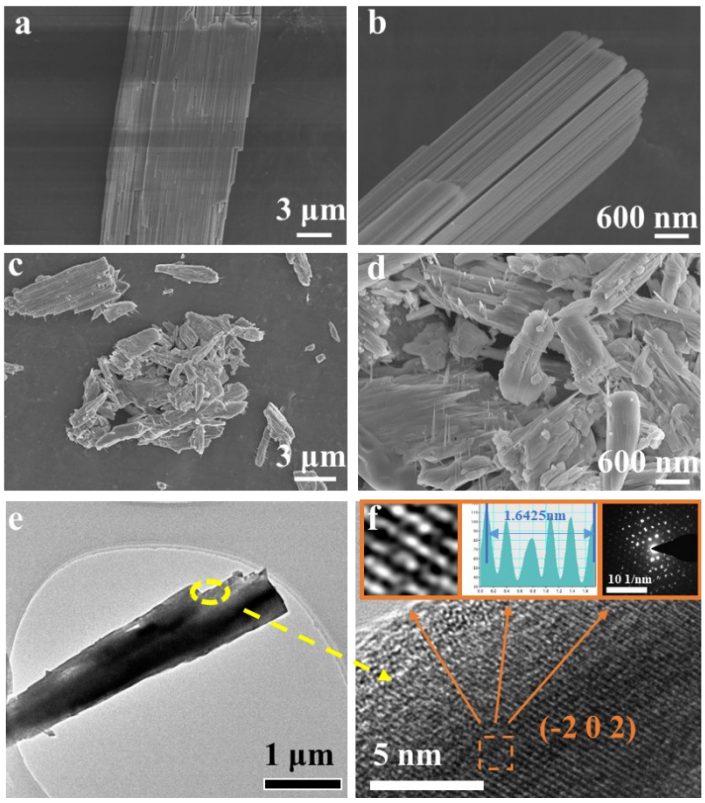

Fig. S1. SEM images of (a-b) molybdate precursors, (c-d) pure MMO. TEM images of (e-f) pure MMO.

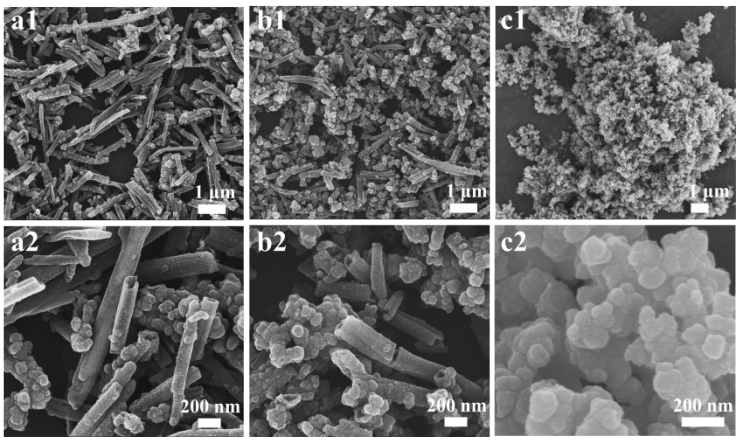

Fig. S2. SEM images of (a1-a2) MMOC-1, (b1-b2) MMOC-2, and (c1-c2) MMOC-3.

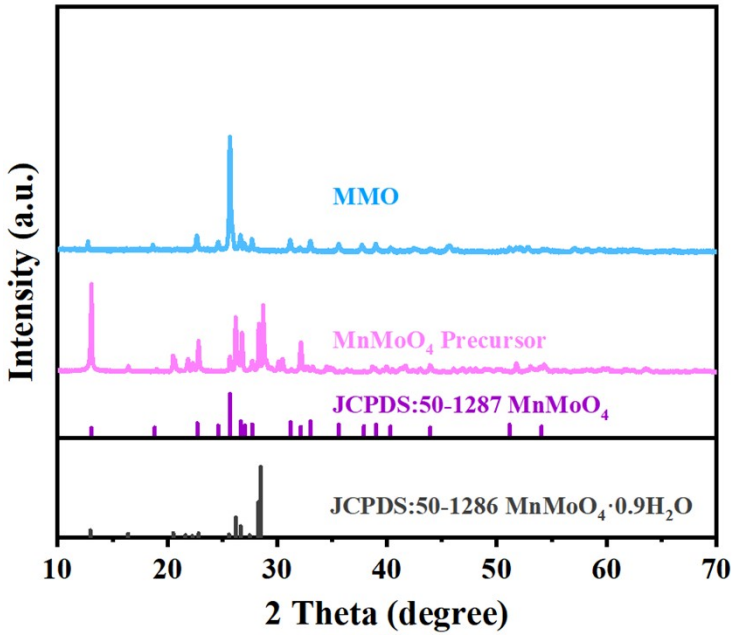

Fig. S3. XRD patterns of MMO and $MnMoO_4$ precursor.

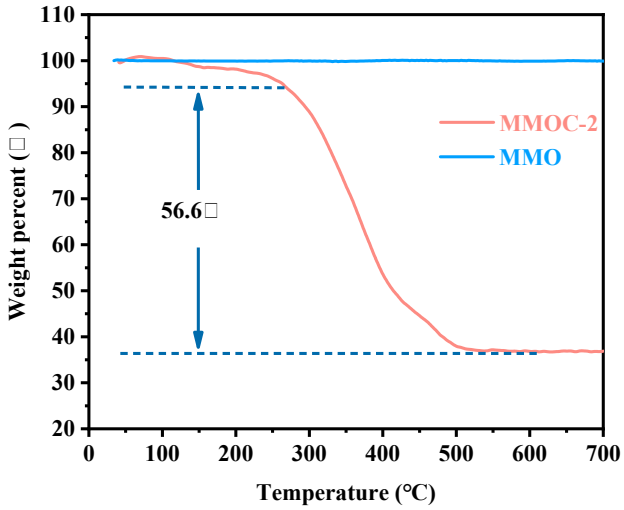

Fig. S4. TG curves of products.

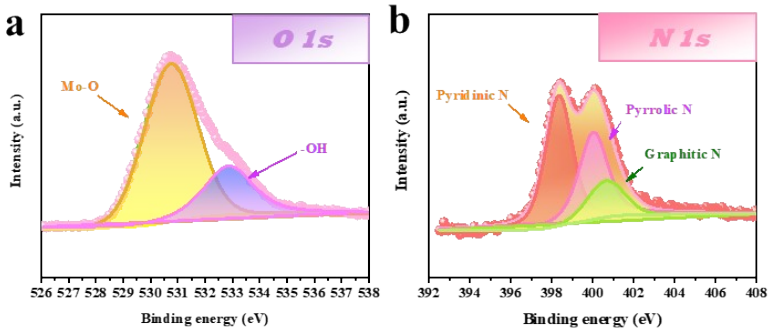

Fig. S5. The corresponding XPS spectra of (a) O 1s and (b) N 1s.

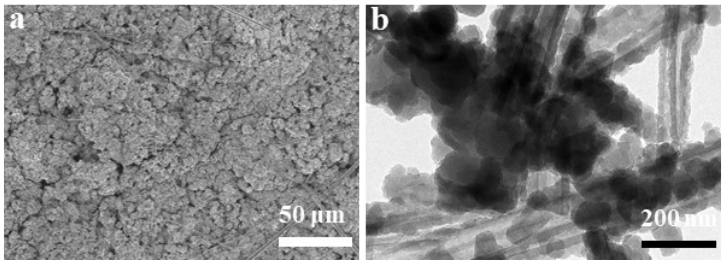

Fig. S6. SEM and TEM images of MMOC-2 after cycling test.

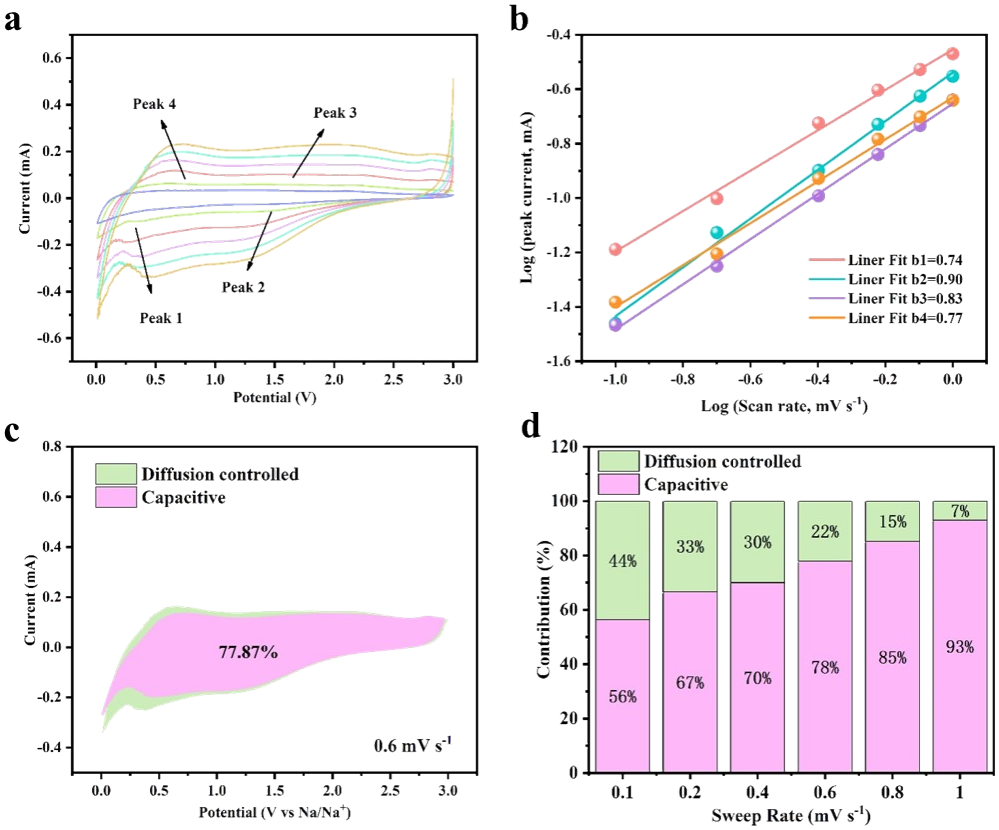

Fig. S7. (a) Multi-sweep CV curves. (b) Plots of log (i) vs. log (v). (c) The capacity contribution ratios at 0.6 mV s^{-1} and (d) capacity contribution ratios at different scan rates.

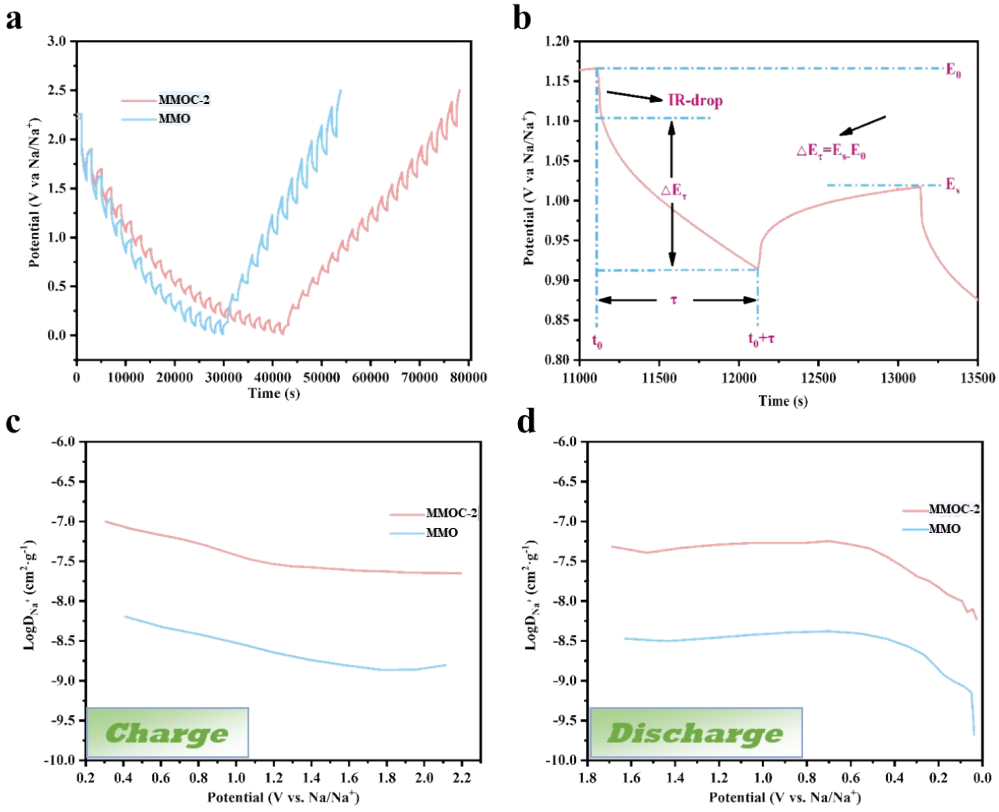

Fig. S8. (a) The GITT curves and (b) detailed voltage response. The Log D_{Na}^{+} curves of (c) charge and (d) discharge processes.

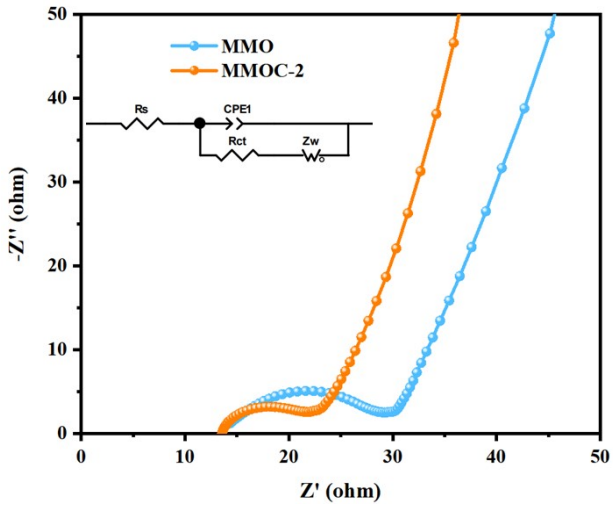

Fig. S9. The impedance diagrams of MMOC-2 and MMO.

Table S1. A electrochemical performance comparison with previous literature

Sample	Current Density	Cycles	Capacity *Vs*. Na^+ (mAh g^{-1})	Ref.
$CoMoO_4$ nanorod	0.05 A g^{-1}	100	197	[1]
$NiMoO_4$/NiO	0.1 A g^{-1}	100	154	[2]
$BaMoO_4$	0.05 A g^{-1}	100	50	[3]
$MnMoO_4$/C microrod	0.1 A g^{-1}	100	199	[4]
$FeMoO_4$/Graphene	0.1 A g^{-1}	500	204	[5]
$ZnMoO_4$ nanotube	0.1 A g^{-1}	500	190	[6]
MMOC-2	**0.1 A g^{-1}**	**500**	**216**	**This work**

References

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