Supplementary Material

Enhanced pseudocapacitive energy storage properties of budding-branch like MoO_2@C/CNT nanorods

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Experimental and Method

For the synthesis of MoO_2@C/CNT composite, ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}$, AR, 99+%), aniline(C_6H_7N, AR, 99+%) and hydrochloric acid (HCl, AR, 36~38%) were purchased from Sinopharm Chemical Reagent Co., Ltd. The carbon nanotubes (CNT, >95%, 10~30 μm) were purchased from XFNANO. All the chemical reagents were of analytical grade and directly used after purchase without further purification.

Materials synthesis.

Synthesis of the Mo-O-C precursor ($Mo_3O_{10}(C_6H_8N)_2\cdot 2H_2O$) : The Mo-O-C precursor was synthesized by process as follows: 2.5 g (0.002 mol) ammonium molybdate tetrahydrate were dissolved in 40 mL DI water and 3 g (0.033 mol) aniline was added. Then 1 M HCl aqueous was added dropwise with magnetic stirring at room temperature until white precipitate appeared. After magnetic stirring at 50 °C for 2 h, the white product was filtered and thoroughly washed with ethanol and dried at 60 °C for 24 h.

Synthesis of the MoO_2@C composite : The MoO_2@C composite was prepared by calcining the prepared Mo-O-C precursor loaded on a quartz boat at 700 °C for 2 h under N_2 atmosphere. According to the theoretical carbon ratio, this composite was labeled as MoO_2@C-0.1. For comparison, a series of samples were prepared under the same conditions but with different carbon ratio of 7.5% and 12.5% by changing the dosage of aniline during the synthesis of Mo-O-C precursor, which were labeled as MoO_2@C-0.075 and MoO_2@C-0.125, respectively.

Synthesis of the MoO_2@C/CNT composite : The MoO_2@C/CNT-10% was synthesized by process as follows: 10 mg CNT was dispersed into 50 mL ethanol by ultrasonicating for 15 min, and then 90 mg prepared MoO_2@C composite was added and ultrasonicated for another 15 min. The resultant mixture was magnetic stirred for 6h, and the product was collected by filtration, followed by freeze-drying for 24h. A series of samples were prepared under the same conditions but with different CNT contents of 5 % (MoO_2@C/CNT-5%) and 15% (MoO_2@C/CNT-15%) for comparison.

Materials Characterizations

X-ray Diffraction (XRD, Rigaku-D/max 2500 V) equipped with Cu Kα radiation (λ= 1.5418 Å) was carried out to confirm the crystalline structures. Microstructure was investigated by Scanning Electron Microscope (SEM, FEI, Sirion 200) and Transmission Electron Microscope (TEM, Tecnai G2F20, FEI). The Thermogravimetric analyses (TGA) were performed by Thermal Gravimetric Analyzer (Perkin Elmer, Pyris 1) under air from 30 to 700 ℃ at a rate of 10 ℃ min^{-1}. A Horiba spectrometer was carried out to record the Raman spectra with He-Ne laser excitation at 514 nm. The Brunauere EmmetteTeller (BET) measurements were used to measure the nitrogen (N_2) adsorption-desorption. The X-ray photoelectron spectroscopy (XPS) analysis was characterized by a Kratos-Axis spectrometer with monochromatic Al K_α (1486.71 eV) radiation (15 kV and 10 mA).

Electrochemical Measurements

The electrochemical measurements were performed on an electrochemical workstation (CHI 760e, Shanghai ChenHua Instruments Inc.) with a three-electrode configuration using 3 M KOH, Ag/AgCl and Pt foil as aqueous solution, reference and counter electrodes, respectively.

Galvanostatic charge/discharge (GCD) and cyclic voltammetry (CV) were performed from 0 to 0.64 V at various current density between 1 and 20 A g^{-1} and scanning rate between 2 and 100 mVs^{-1} at room temperature, respectively. The electrochemical impedance spectroscopy (EIS) measurements were carried out by applying an alternate current (AC) voltage with 5 mV amplitude.

As for the working electrodes, the as-prepared samples, acetylene black and polyvinylidene fluoride (PVDF) were sufficiently mixed at a weight ratio of 80 : 10 : 10 in N-methyl-2-pyrrolidone (NMP) followed by being uniformly pasted onto the Ni foams (1×2.5 cm^2). After drying at 60 ^{o}C for 24 h, the final mass loading of the active material on each Ni form was about 2 mg.

The ASC devices were assembled in CR2016-type coin cells, using cellulose paper as the separator, 3 M KOH solution as the electrolyte, MoO_2@C/CNT composite as the positive electrode and active carbon (AC) as the negative electrode respectively.

All the electrochemical measurements were carried out at room temperature and all the specific capacitances C (F g^{-1}) in this work were calculated according to the equation: $C = I\,\Delta t/m\,\Delta V$, where m (g) is the total mass of the active material in the electrode, ΔV (V) is the voltage window I (A) is discharge current, and Δt (s) is discharge time. The mass of the electrode material in ASC device was balanced according to the equation: $m_-/m_+ = (C_+\times\Delta V_+)/(C_-\times\Delta V_-),$ where ΔV is the potential range, C is specific capacitance of positive or negative electrode and m is mass of active material. The theoretical specific capacitance of ASC device is calculated by: $1/C_T = 1/C_p + 1/C_{n,}$ where C_T is the theoretical specific capacitance of the device, C_p and C_n are the capacitances of the positive and negative electrodes, respectively. The power density and energy density of the MoO_2@C/CNT//AC

ASC device are calculated according to $P = E/\Delta t$ and $E = CV^2/2$, where Δt is discharge time and V is the applied potential window.

Supporting Figures

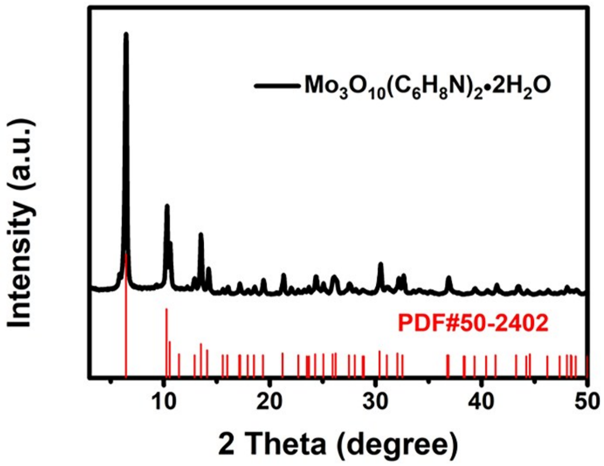

Fig. S1 XRD patterns of Mo-O-C precursor.

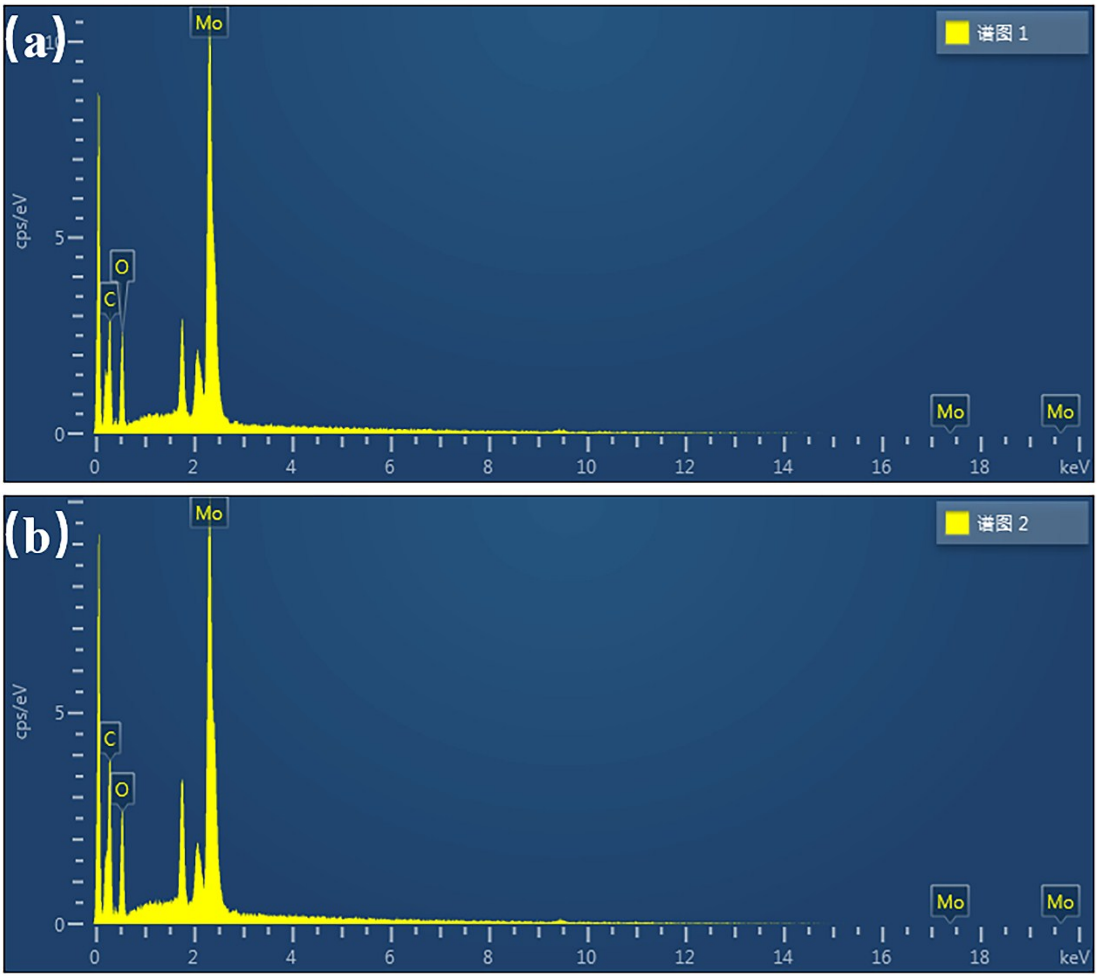

Fig. S2 EDX of MoO_2@C and MoO_2@C/CNT composites

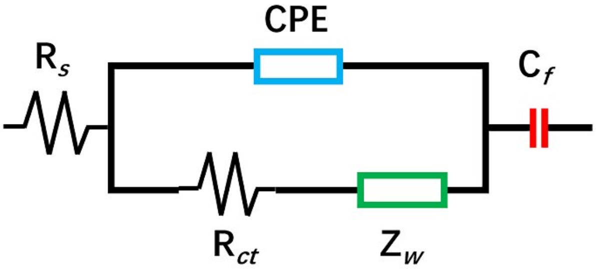

Fig. S3 Image of equivalent circuit.

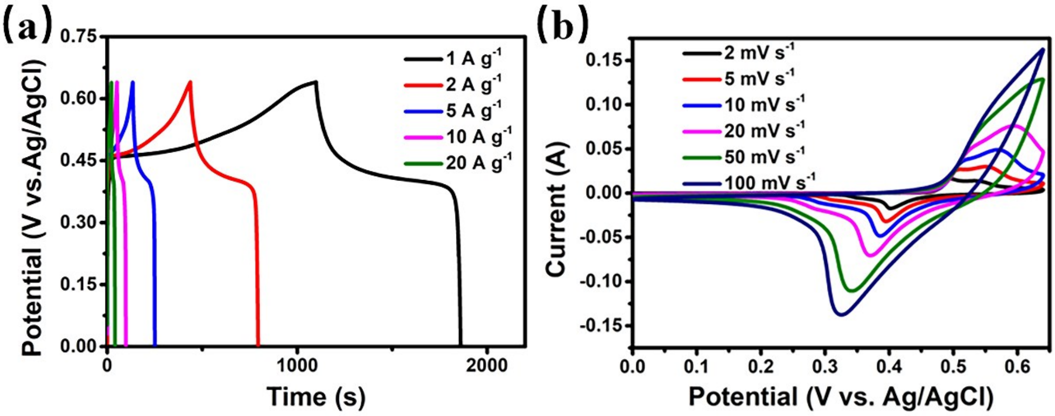

Fig. S4 Typical (d) GCD and (e) CV curves of MoO_2@C-0.1.

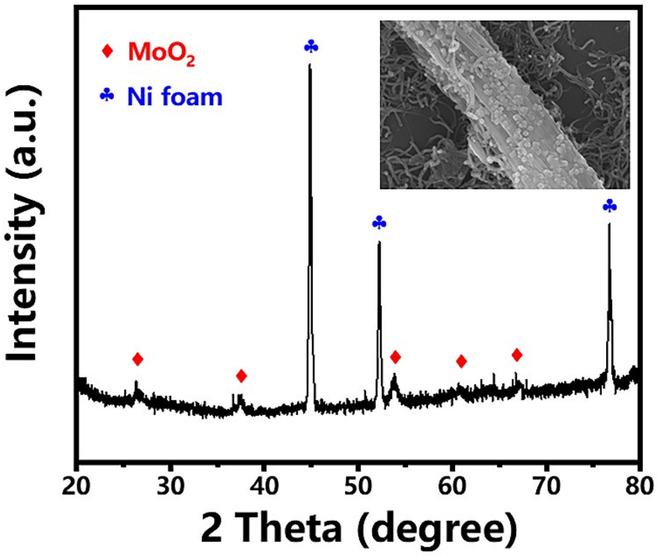

Fig. S5 Ex-situ XRD pattern and SEM image of the MoO_2@C/CNT after cycling.

Table. S1 Comparison of electrochemical performance based on Mo material in previously reported works.

Electrode materials	Electrolyte	Specific capacitance	Rate capability	Reference
MoO_2@C/CNT	3M KOH	1667.2 F g^{-1} (1 A g^{-1})	92.8% after 3000 cycles (5 A g^{-1})	This work
RGO@ MoO_2/C	3M KOH	1224.5 F g^{-1} (1 A g^{-1})	92% after 3000 cycles (5 A g^{-1})	[40]
MoO_2/Graphene	1M Na_2SO_4	290.9 F g^{-1} (0.1 A g^{-1})	92.5% after 1000 cycles (0.3 A g^{-1})	[42]
MoO_2 nanoparticles	1M H_2SO_4	620 F g^{-1} (1 A g^{-1})	90% after 1000 cycles (1 A g^{-1})	[44]
One-dimensional MoO_2 nanorods	1M H_2SO_4	140 F g^{-1} (1 mA cm^{-1})	86% after 50 cycles (1 mA cm^{-1})	[45]