

Supporting Information for

Facile synthesize three dimensional flower-like MoO₂-Graphene nanostructure with enhanced electrochemical performance

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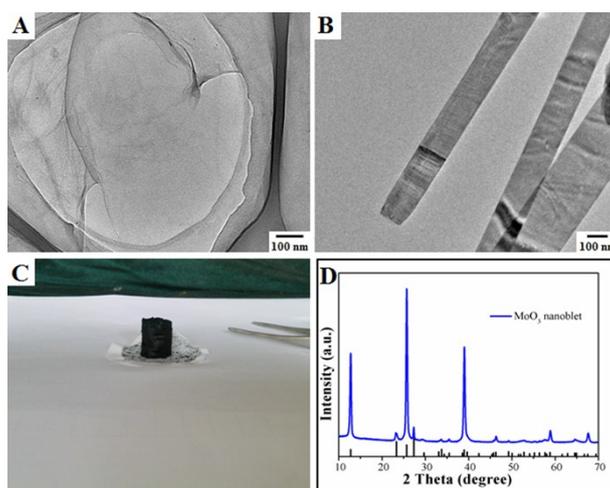


Figure S1 (A) TEM image of the as-prepared graphene oxide nanosheets (B) TEM image of the as-obtained MoO₃ nanobelts (C) photograph of the synthesized MoO₂-G samples (D) the XRD pattern of the MoO₃ nanobelts.

Experimental section

All the reagents are of analytical purity grade and received from commercial sources. In a typical preparation process, the as-synthesized MoO₃ nanobelts [1] (445 mg) and graphene oxide (67.7 mg) [2,3] were added into 54 ml deionized water under stirring for 30 min to form homogeneous solution. Then the obtained mixture was transferred into the stainless steel autoclaves with a Teflon liner of 100 ml in capacity, which was heated in an oven at 180 °C for 6 h. After the autoclave was air-cooled to room temperature, the products of MoO₂-GO were obtained by washed with distilled water and absolute ethanol for several times, followed by drying under vacuum at 60 °C for an overnight. As a comparison, the pure commercial MoO₂ particles were used for the electrochemical test.

SEM images were taken using a field-emission scanning electron microscope (JSM-6701F, JEOL) operated at an accelerating voltage of 5 kV. The X-ray diffraction spectra (XRD) measurements were performed on a Rigaku RINT-2000 instrument using Cu K radiation (40 kv). The XRD patterns were recorded from 10 ° to 80 ° with a scanning rate of 0.067 °/s. The oxidation states of the product were investigated through an ESCALAB 250Xi X-ray photoelectron

spectrometer (XPS) with non-monochromatized Mg K α X-ray as excitation source. TEM images were carried out by using an FEI Tecnai TF20 microscope operated at 200 kV.

2.3 Electrochemical measurements

The electrochemical properties were tested on a CHI660 (Chenhua, Shanghai, China) with three electrode system. All of the measurements were carried out in 1 M Na₂SO₄ aqueous electrolyte solution at room temperature. The working electrode was fabricated by mixing the electroactive material (8.5 mg), carbon black (1 mg) and poly(tetrafluoroethylene) (0.5 mg) at a weight ratio of 85:10:5 to form a homogeneous slurry. The resulting slurry was coated onto the nickel foam current collector using a blade. The mass of active materials on all electrodes is 8.5 mg. Then, the electrode was dried at 100 °C for 12 h. A saturated calomel electrode (SCE) and platinum sheet were used as the reference and counter electrodes, respectively. Cyclic voltammetry (CV) curves were carried out in a potential range from -0.5 V to 0.5 V at different scan rates, varying from 4 to 20 mV s⁻¹. Galvanostatic charge-discharge (GCD) measurements were recorded at different current densities within the potential range from -0.5 V to 0.5 V. Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from 10 mHz to 10⁵ Hz.

2.4 Fabrication of symmetric supercapacitor (AS) devices

The symmetric supercapacitor (SC) devices were fabricated in a two-electrode configuration using as prepared products as both the positive electrode and negative electrode. As typically, the as-synthesized electroactive MoO₂-G (8.5 mg), carbon black (1 mg) and poly(vinylidene fluoride) (0.5 mg) were mixed in a mass ratio of 85:10:5 to obtain a slurry and then coated on the Ni foam. Then, the electrode was dried at 100 °C for 12 h. The assembled electrodes were placed in a test cell rig, and the 1 M KCl aqueous solution was served as the electrolyte.

Reference

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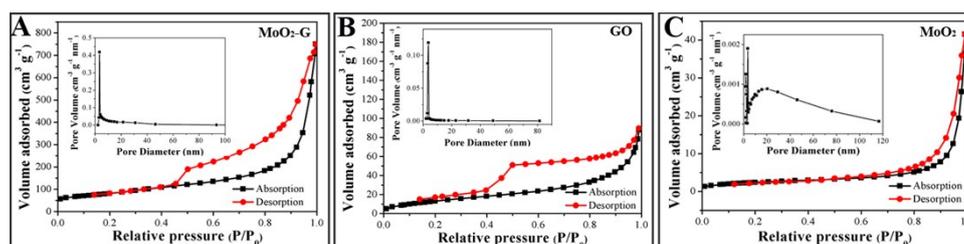


Fig. S2 (A) Nitrogen adsorption-desorption isotherm of the MoO₂-G (A), GO (B) and MoO₂ particles (C). Insets: the pore size distribution obtained from adsorption branches by the BJH method.

The Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption isotherm experiments have been performed to explore the surface area and nanochannels in the samples. Generally, the control of pore size distribution and the improvement of BET surface area are essential to improve the electrochemical activity. As shown in Fig. S2, all the adsorption-desorption isotherms could be identified as type IV.⁴⁻⁵ However, the surface areas vary a great deal with samples. More specifically, the as-prepared MoO₂-G possesses larger adsorption volume and a specific surface area (285.6 m²/g) than that of the graphene oxide (70 m²/g) and pure MoO₂ (8.8 m²/g). Furthermore, the main pore size distributions of the MoO₂-G and GO are generally in the range of 2-5 nm, suggesting the mesoporous structure in the samples. Be different to GO, the MoO₂-G shows the pore size distribution in the range of 5-40 nm, which may be ascribed to the 3D flower-like nanostructure. Furthermore, MoO₂-G has a larger pore volume (0.8 cm³ g⁻¹) than that of GO (0.08 cm³ g⁻¹) due to the well-developed flower-like structure, which benefits to the diffusion and transport of electrolyte ions during the rapid charge/discharge process. However, in the case of MoO₂ particles, no primary pore size distribution has been observed. These results suggest that the surface area was enhanced by rational fabrication of 3D flower-like MoO₂-G architecture.

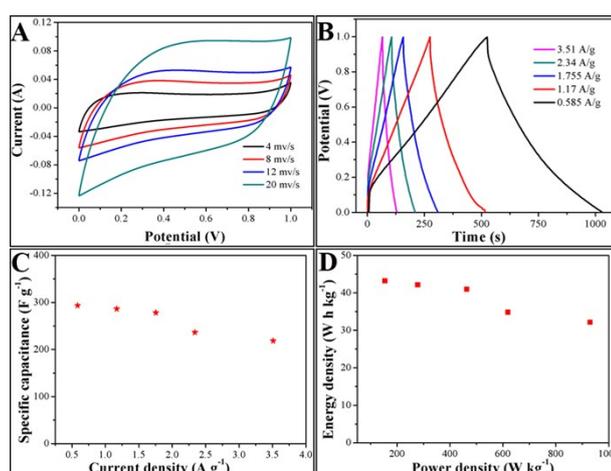


Fig. S3 CV curves (A) of the symmetric supercapacitor at different scan rates and Galvanostatic charge-discharge curves (B) of the symmetric supercapacitor at different scan rates (C) specific capacitance of the symmetric supercapacitor at different current densities (D) Ragone plot of the estimated energy density and power density at different current densities for the symmetric supercapacitor.

To evaluate the MoO₂-G electrode and highlight the ion exchange effect for practical applications, the symmetric supercapacitor device was assembled using the as-prepared sample as both the positive electrode and negative electrode with one piece of cellulose paper acting as the separator. As typically, the as-synthesized electroactive MoO₂-G (8.5 mg), carbon black (1 mg) and poly(vinylidene fluoride) (0.5 mg) were mixed in a mass ratio of 85:10:5 to obtain a slurry and then coated on the Ni foam. The assembled electrodes were placed in a test cell rig, and the 1 M KCl aqueous solution

was served as the electrolyte. As shown in Fig. S3A, the CV curves of the two-electrode device with the voltage window of 0-1 V present nearly rectangular shape without redox peaks, indicating an almost ideal capacitive behavior despite the absence of the polarization phenomenon.⁶ So the maximum voltage window can be chosen from 0 V to 1 V, implying the potential of the assembled system in practical application. As the scan rate increases from 4 to 20 mV/s, the specific capacitances (C_s) of the device are 242.6, 205.9, 185 and 176.5 $F g^{-1}$, respectively.

Fig. S3B presents the galvanostatic charge-discharge curves of the device at various current density values. All the curves are almost symmetric, indicating the electrochemical capacitive behavior with remarkable reversible redox reaction.^{7,8} More specifically, the device capacitances were measured to be 293.6, 286.4, 278.3, 236.55 and 218.5 $F g^{-1}$ at 0.585, 1.17, 1.755, 2.34 and 3.51 $A g^{-1}$, respectively. The Ragone plots of the MoO_2 -G electrode are shown in Fig. S3D. At a power density of 0.15 $kW kg^{-1}$, the supercapacitor delivers an energy density of 43.2 $W h kg^{-1}$. Even at a high power density of 0.9 $kW kg^{-1}$, the energy density of the device could reach 32.1 $W h kg^{-1}$.

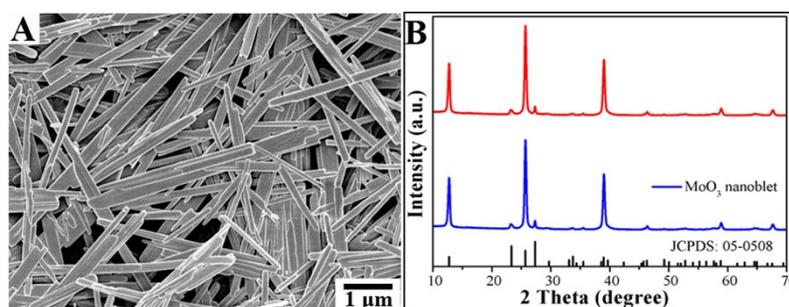


Fig. S4 (A) SEM image of MoO_3 nanobelts through hydrothermal reaction (B) XRD patterns of the MoO_3 nanobelts and MoO_3 nanobelts through hydrothermal reaction.

The control experiment which MoO_3 nanobelts are treated under the same hydrothermal conditions without adding GO has been conducted. It is clearly that the nanobelts morphology did not change as shown in the SEM image of the product (Fig. S4A). It is can be seen that the product keeps the nanobelts morphology with an average width of about 100 nm. Moreover, the XRD pattern (Fig. S4B) shows that no MoO_2 and only MoO_3 were obtained, which is completely consistent with the MoO_3 nanobelts (JCPDS: 05-0508).

Reference

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