Electronic Supplementary Information

Low-cost and high energy density asymmetric supercapacitors based on polyaniline nanotubes and MoO_3 nanobelts

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Experimental details

Materials: Aniline monomer (AN, Shanghai Chemical Works, China) was distilled under reduced pressure. D-tartaric acid (D-TA, Shanghai Chemical Works, China), ammonium persulfate (APS, Tianjin Damao Chemical Co., China) and sodium molybdate ($Na_2MoO_4·2H_2O$, Tianjing Chemical Co., China), solutions were prepared using deionized water. All other chemical reagents were in analytical grade.

Synthesis of PANI nanotubes: The PANI nanotubes were fabricated similar to our previous reported literature.[S1] In a typical process, aniline monomer (2 mmol) and D-tartaric acid (1 mmol) were dissolved in 10 mL of deionized water with magnetic stirring for 20 min at room temperature. After that, the resulting solution was cooled to 0-5 ^{o}C in an ice bath and an aqueous solution of ammonium persulfate (2 mmol in 5 mL of deionized water) cooled in advance was added drop-by-drop into the above solution. The reaction was carried out with magnetic stirring below 5 ^{o}C for 10 h. The resulting precipitate was washed several times with deionized water and ethanol, respectively. Finally, the product was dried at 60 ^{o}C for 12 h to obtain a dark green powder.

Synthesis of MoO_3 nanobelts: In a typical process, 4.84 g $Na_2MoO_4·2H_2O$ was dissolved in 10 ml deionized water. Then 16 ml 4 M $HClO_4$ was added dropwise to the molybdate solution under constant stirring. Finally, this solution was transferred into a 100 ml Teflon-lined stainless steel autoclave and heated at 140 ^oC for 24 h. After cooled to room temperature naturally, the resulting precipitates of MoO_3 were collected by filtration, washed with distilled water and absolute ethanol for several times to remove the residue of reactants, and then dried in vacuum at 60 ^oC for 12 h.

Materials Characterization

The morphologies of the as-prepared products were examined with field emission scanning electron microscopy (FE-SEM, JSM-6701F Japan) at an accelerating voltage of 5.0 kV. The structure of the PANI samples was characterized by a transmission electron microscopy (TEM, JEM-2010 Japan). X-ray diffraction (XRD) of samples was performed on a diffractometer (D/Max-2400, Rigaku) advance instrument using Cu Kα radiation (k =1.5418 Å) at 40 kV, 100 mA. The 2θ range used in the measurements was from 5 to 80°.

Three-electrode fabrication

For conventional three-electrode system, the glassy carbon electrode with a diameter of 5 mm was used as the working electrode. The working electrodes were fabricated similar to the literature.[S2] Typically, 4 mg of electrode material was ultrasonically dispersed in 0.4 mL of 0.25 wt% Nafion (DuPont, USA). The above suspension of 8 μL using a pipet gun was dropped onto the glassy carbon electrode and dried at room temperature. The three-electrode system was test in 1 M H_2SO_4 aqueous solutions, platinum electrode serves as the counter electrode, and standard calomel electrode (SCE) as the reference electrode, respectively.

Two-electrode cell fabrication

The capacitive performance of asymmetric supercapacitors was investigated using a two-electrode testing cell. The working electrode was prepared by mixing the electroactive material with polyvinylidene fluoride (PVDF) and commercial carbon black (8:1:1) in N-methyl-2-pyrrolidone (NMP) until homogeneous slurry. The slurry was coated on carbon plate (99.99%, 3 mm) with a working area of 1.0 cm^2 and the electrodes were dried at 120 ^oC for 12 h. To construct an ASC, the loading mass ratio of active materials (PANI//MoO_3) was estimated to be 0.89 from the specific capacitance calculated from their galvanostatic charge/discharge curves. The PANI positive electrode and MoO_3 negative electrode were pressed together and separated by a thin polypropylene film. The electrochemical measurements of the ASCs were carried out in a two electrode cell at room temperature in1 M H_2SO_4 electrolyte.

Electrochemical measurements

The electrochemical properties of the samples were investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge measurements in three-electrode cell and two-electrode configuration using a CHI 660D electrochemical workstation. The cycle-life stability was performed using computer controlled cycling equipment (LAND CT2001A, Wuhan China). Electrochemical impedance spectroscopy (EIS) measurements were performed with the Autolab PGSTAT 128N equipped (Eco-chemie, Netherland) with FRA module, the frequency ranging from 10 mHz to 100 kHz and an impedance amplitude of ±5 mV at open circuit potential.

The gravimetric capacitance from galvanostatic charge/discharge was calculated by using the formula of $C_s=4I\Delta t/(m\Delta V)$ for the two-electrode cells, while, $C_s^*=I\Delta t/(m\Delta V)$ for the three-electrode system, where I is the constant current (A) and m is the mass (g) of electrode material (For the two-electrode cells, m is the total mass of positive and negative electrodes), Δt the discharge time and ΔV the voltage change during the discharge process.

The specific energy density (E, Wh kg^{-1}) and power density (P, W kg^{-1}) for a supercapacitor cell can be calculated using the following equations: $E=1/2CV^2$ and $P=E/t$, where C is the specific capacitance of supercapacitor cell, V is voltage change during the discharge process after IR drop in V-t curve, and t is the discharge time.

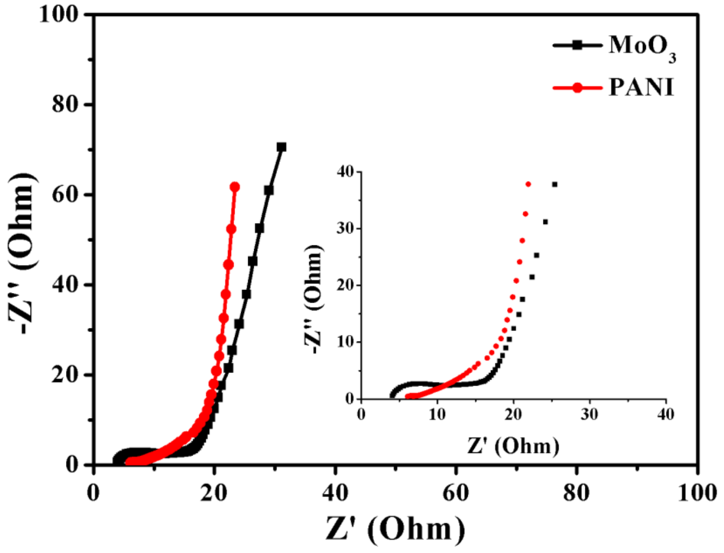

Figure S1. Nyquist plots of PANI and MoO_3 electrodes for three-electrode system and its expanded high frequency region (inset).

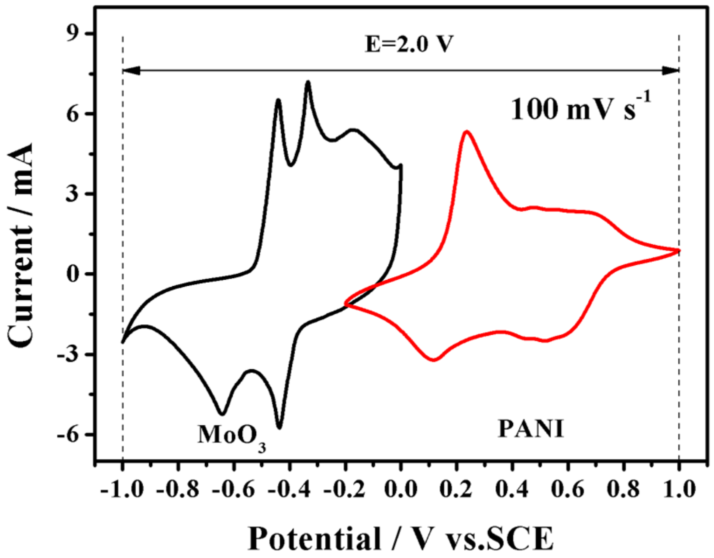

Figure S2. Comparative CV curves of PANI and MoO_3 electrodes performed in three electrode cell in 1 M H_2SO_4 electrolyte at a scan rate of 100 mV s^{-1}

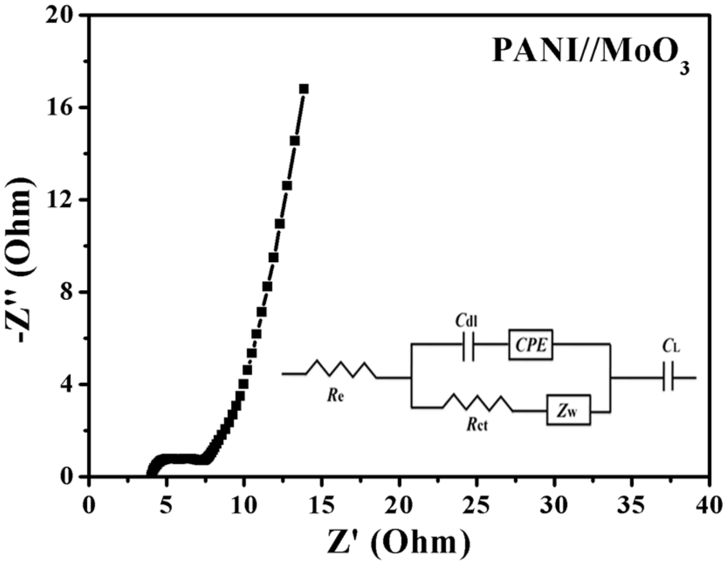

Figure S3. Nyquist plots of PANI//MoO_3 asymmetric supercapacitors for two-electrode system (the inset of modeled equivalent circuit of electrochemical impedance spectroscopy).

Table S1. Performances comparison of ASCs with positive and negative electrodes

ASCs structure	Electrolyte	Operation voltage (V)	Energy density (Wh kg^{-1})	Power density (W kg^{-1})	Ref.
$GrMnO_2//GrMoO_3$	Na_2SO_4	2.0	42.6	276	[S3]
$CNT/MnO_2//CNT/In_2O_3$	Na_2SO_4	2.0	25.5	50.3K	[S4]
RGO-RuO_2//RGO-PANI	KOH	1.4	26.3	150	[S5]
MnOOH@RGO//AC	KOH	1.6	41.1	400	[S6]
$Ni(OH)_2$/UGF//a-MEGO	KOH	1.8	13.4	85K	[S7]
CoO@PPy//AC	NaOH	1.8	43.5	87.5	[S8]
$Ni(OH)_2$/graphene// porous graphene	KOH	1.6	77.8	174.7	[S9]
$Ni(OH)_2$/graphene// RuO_2/graphene	KOH	1.5	48.0	230	[S10]
MnO_2//CNT	Na_2SO_4	2.0	47.4	200	[S11]
MnO_2//FeOOH	Li_2SO_4	1.85	24.0	450	[S12]
$NiCo_2O_4@MnO_2$	NaOH	1.5	35.0	163	[S13]
PbO_2//AC	H_2SO_4	1.8	31.6	201	[S14]
Ni-Zn-Co oxide/hydroxide// Porous carbon	Na_2SO_4	1.5	41.6	100	[S15]
PANI//MoO_3	H_2SO_4	2.0	71.9	254	Present

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