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Supporting information

1,3,6,8-pyrenetetrasulfonic acid anchored doping to prepare solution-processable polyaniline for electrochromic supercapacitors

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1. Experimental Section

1.1 Materials

All chemicals for synthesizing 1,3,6,8-pyrenetetrasulfonic acid (1,3,6,8-Psas) doped PANI/WO_3-FTO composite electrode were purchased from Aladdin and used without further purification. Ammonium paratungstate ($(NH_4)_{10}H_2(W_2O_7)_6$) was purchased from Aladdin to prepare WO_3 nanoarrays through a one-step hydrothermal method. Aniline (ANI), 1,3,6,8-Psas($C_{16}H_6Na_4O_{12}S_4$), Ammonium persulfate (APS), Sulfuric acid(H_2SO_4), Hydrogen Peroxide(H_2O_2), concentrated hydrochloric acid (HCl), ethanol (C_2H_6O), m-cresol (C_7H_8O) were used as received. fluoride-doped tin oxide (FTO) (thickness of 1.6 mm and square resistance of 14 Ω^{-1}) was purchased from Wuhan Geao education Instrument Co., Ltd.

1.2 Fabrication of WO_3 Nanoarray.

1g of $(NH_4)_{10}H_2(W_2O_7)_6$ was dissolved in 95mL deionized water, and 3mL of concentrated hydrochloric acid (HCl) was added one drop at a time. The solution changed from the original transparent state to a light-yellow precipitate. Then add 2mL of hydrogen peroxide (H_2O_2) and continue to stir to form a uniform and stable transparent solution. The conductive glass FTO formed an Angle with the polytetrafluoroethylene lining of the hydrothermal reactor and the conductive surface faced down. Slowly added the solution with good reaction to 70~80% of its total volume, and reacted for 1~4 hours at 150~160℃. After the reaction, cooled to room temperature, took out the FTO, washed with deionized water and ethanol (C_2H_6O), and then dried naturally.

1.3 Fabrication of PANI-WO_3/FTO film electrode.

A mount of 1 mL of ANI and 2.5 g of APS were added to 90 and 100 mL of 1 M HCl, respectively, both of which were carried out in an ice bath. Then, APS solution was added dropwise to ANI−acid mixed solution with constant stirring at 0-5 ℃ for 8 h. After purification with water and methanol, the collected PANI powder was put into a 0.1 M ammonia solution with continuous stirring for 24 h at room temperature. Afterward, the PANI-suspended solution was filtered and washed using deionized

water and methanol several times, followed by vacuum drying at 60 ℃ for 24 h. Then the PANI was added into m-cresol with constant stirring for 24 h, thus forming a black-green colored solution. Finally, spray the PANI spray solution on the WO_3/FTO substrate to form a film, and dry it in a vacuum oven at 100°C for 24 h. The prepared thin film electrode is designated as PANI-0.

1.4 Characterization.

The morphology of PANI-WO_3/FTO and 1,3,6,8-Psas doped PANI-WO_3/FTO film was investigated by using a field emission scanning electron microscope (SEM, FEI 3D, 20093075). The molecular structures of PANI-WO_3/FTO and 1,3,6,8-Psas doped PANI-WO_3/FTO film were investigated by a Fourier transform infrared spectrometer (FTIR, Nicolet 5700, A0071477) with a scan range from 500 to 4000 cm^{-1}. The phases of PANI-WO_3/FTO and 1,3,6,8-Psas doped PANI-WO_3/FTO film were characterized via X-ray diffraction (XRD) using a Bruker D8-Discover X-ray diffractometer with Cu Kα radiation in the range 2θ = 10−80°.

Cyclic voltammogram (CV) curves, galvanostatic charge−discharge (GCD) curves, and electrochemical impedance spectroscopy (EIS) were conducted on a CHI660E electrochemical workstation (Shanghai CH Instruments Co., China). EIS was performed in the frequency range of 10^5−1 Hz with the amplitude of 5 mV.

1.5 Electrochemical Test.

The electrochemical performance of film electrodes was investigated by using a three-electrode system in 1 M H_2SO_4, in which PANI-WO_3/FTO film or 1,3,6,8-Psas doped PANI-WO_3/FTO film, Ag/AgCl electrode, and 1cm×1cm Pt plate were used as working electrode, reference electrode, and counter electrode, respectively.

The specific capacitance (Cs) of film electrodes was calculated according to the following formula:

$$C_s = It/m\Delta V \quad (1)$$

where I is constant discharge current (A); t stands for discharge time (s); and ΔV and m present potential window (V) and area of integrated film electrode (cm^2).

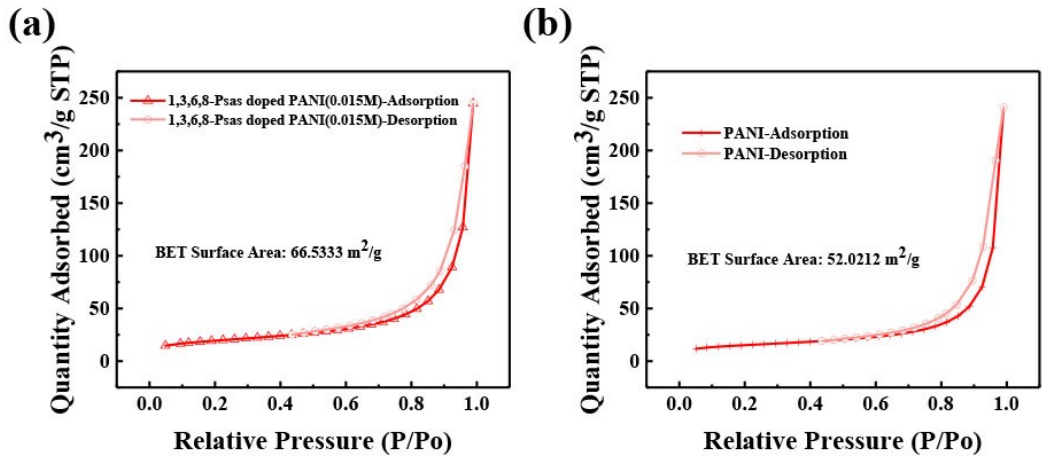

Fig. S1 BET images of (a) Pre/PANI-0.015; (b) PANI-0.