Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2017

# Supporting Information For

## **Elastic Soft Hydrogel Supercapacitor**

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#### **Experimental Section**

#### Synthesis of PVA/PPy hydrogel electrode

All the chemicals were of analytical grade and were used without further purification. During polymer synthesis, 0.4 g of ammonium persulfate (98%, Sigma Aldrich) was dissolved in 10 mL deionized (DI) water, and labelled as solution A. 4 g of PVA with 50 mL of deionized water was put in microwave reactor (800W) for 2 min to obtain a fully dissolved solution. Then, in an ice-water bath, 0.5 ml pyrrole (The mass ratio between PVA and pyrrole was 8:1) was added to the above PVA solution for about 30 min under vigorous agitation at 0-4°C to get the solution B. Subsequently, the A and B solutions were mixed under ice-water bath. After 1h, the mixture was subjected to three cycles of freeze-thawing, in which the mixture was frozen for 12h, and then thawed for 12h at room temperature as one cycle. To remove inorganic impurities and oligoaniline, the polyaniline hydrogel was purified by immersing into a large amount of deionized water for 3 days, and the deionized water was changed every 12 h. Then the swollen hydrogel was immersed in 1M H<sub>2</sub>SO<sub>4</sub> solution for 24 h and placed at room tempreture for 24 h. Finally, the PVA/PPy conductive polymer with high mechanical strength was obtained. As a reference, the pure PPy nanoparticles was also prepared by the same procedure without adding PVA and the pure PVA hydrogel was also

#### Preparation of CNTs films electrode

CNTs films electrodes were obtained by vacuum filtration.(The CNTss were purchased by Time/nano) First, 1g Triton X-100 and 60 mg CNTs were dispersed in 100 mL of deionized water under magnetically ultrasonic for 1 h in air. Then, the as-obtained solution was filtered on the PTFE membrane filter and the film was then dried and can be easily peeled off from the filtration paper.

#### Fabrication of deformable soft supercapacitor(DSS)

The DSS was assembled by using PVA/PPy conductive hydrogel as the negative electrode and CNTs film as the positive electrode and PVA/H<sub>2</sub>SO<sub>4</sub> gel as a quasi-solid electrolyte and separator. PVA/H<sub>2</sub>SO<sub>4</sub> gel was prepared as follows: in a typical process, 4g PVA was dissolved in 40mL deionized water with stirring at 85°C for 1h. Then, 1mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> (20 mL) were slowly dropped into the above solution at 85°C under stirring until the solution became clear.

At the bottom of the PVA/PPy conductive hydrogel, it was coated by PVA/H<sub>2</sub>SO<sub>4</sub> gel electrolyte and we repeated three or four times to ensure the uniform daub. Subsequently,

thanks to the viscosity of the gel electrolyte, the CNTs film electrode glued at the bottom of hydrogel, and then they were assembled together. The device was kept at freezer for 4 h to obtain the DSS.

#### Characterization

The obtained product was characterized by scanning electron microscopy (SEM,

Hitachi-4800), and energy dispersive spectroscopy (EDS), attached with SEM, respectively. The crystalline structures of the as-obtained products were characterized using X-ray diffractometer (XRD, Rigaku Dmax-2600/pc, Cu K $\alpha$  radiation,  $\lambda$ = 0.1542 nm, 40 KV, 150 mA). The structure properties of the as-synthesized samples were investigated by Raman spectroscopy (HR800) and a Thermo Scientific Nicolet iz10 FT-IR spectrophotometer using KBr pressed disks. Thermogravimetric analysis (TGA) was performed on a SDT Q600. The measured temperature of samples were ranging from 25°C to 800°C with a heating rate of 10°C min<sup>-1</sup> under the N<sub>2</sub> atmosphere. The water content in the hydrogel is about 38.32% which can be obtained from the thermogravimetric analysis (TGA) curves (Figure S6). The specific surface area of the as-prepared material was estimated using the Brunauer-Emmett-Teller (BET) equation based on the nitrogen adsorption isotherm obtained with a Belsorp-max. Field emission transmission electron microscopy (FETEM) was carried out by using the JEM-2100.

Electrochemical characteristics of the as-obtained products were studied on an CHI660 electrochemical work station (Chenhua, Shanghai) using cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) in a three-electrodes system in the 1 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> electrolyte, in which a Pt foil and a

saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. The electronic conductivity of PVA/PPy hydrogel at room temperature was tested using a standard four-point-probe method. The electronic conductivity was measured to be  $1.6 \times 10^{-2}$  S·cm<sup>-1</sup> at room temperature.

The compression test was performed on the universal testing machine (Instron 3344). In the compression tests, the hydrogel sample were shaped into cylindrical samples ( $\Phi$  40 mm × 40 mm) and placed on the lower plate and compressed by the upper plate. The strain rate during compression tests was set at 0.5 mm/min. The DSS sample was shaped into a cuboid (the length = 2 cm, the width = 0.5 cm and the height = 0.5 cm). The other parameters are constant.

#### Calculation Methods

The electrochemical performances of PVA/PPy composite and CNTs film were detected by cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) in a three-electrode system in the 1 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> electrolyte, in which a Pt foil and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively.

The capacitance ( $C_s$ , F g<sup>-1</sup>) of the pseudocapacitive electrode can be calculated in accordance with the following equation: <sup>[1, 2]</sup>

$$Cs = \frac{\int IdV}{vmV} \qquad S(1)$$

I is the response current density (A cm<sup>-2</sup>), V is the potential or cell voltage (V), v is the scan rate (mV s<sup>-1</sup>) and m is the mass of the active material (g cm<sup>-2</sup>). The PVA/PPy composite mass loading is about  $\approx$  10 mg. The average mass of PPy nanopaticles is about  $\approx$  5 mg. The average mass of CNTs film is about  $\approx$  35 mg.

It is necessary to maintain charge balance between positive and negative electrodes in a DSS device. That is

$$q^+ = q^- \qquad S(2)$$

Where  $q^+$  and  $q_-$  are electrical charges stored in the positive and negative electrodes, respectively. The optimal mass ratio between electrochemically active species in the positive and negative electrodes should satisfy the following equation:

$$R = \frac{m_{+}}{m_{-}} = \frac{C_{-}\Delta V_{-}}{C_{+}\Delta V_{+}}$$
(7) S(3)

Where  $m^+$  and  $m^-$  are the masses, C (F g<sup>-1</sup>) is the specific capacitance of electrode and  $\Delta V$  is the voltage change (V). The optimal mass ratio between PVA/PPy composite and CNTs film was calculated to be 1:3.4, on the basis of the Eqn. S(2) and (3) in supporting information.

In the case of the DSS device, its energy density (E, Wh kg<sup>-1</sup>) and power density (P, W kg<sup>-1</sup>) were calculated by generally adopted equations:

$$P=E/t \qquad S(4)$$
$$E=C\Delta V^2/2 \qquad S(5)$$

In the above equations, C is the specific capacitance of the asymmetric supercapacitors calculated according to the CV curves based on the total weight of the electroactive materials in two electrodes,  $\Delta V$  is the voltage scan range and t is the discharge time.

In order to get the bulk ionic conductivity of the PVA/PPy hydrogel, we have performed

the EIS measurements based on the hydrogel with a CHI electrochemical workstation (660C). The EIS data were obtained in the frequency range between 0.1 Hz and 1MHz with a perturbation of 5 mV.

Data processing:

The bulk ionic conductivity of the PVA/PPy are examined from the EIS by Equation

$$\sigma = L / (\mathbf{R} \times \mathbf{S}) \quad \mathbf{S}(6)$$

L, S and R are the thickness, area and bulk resistance, respectively, of the PVA/PPy sample. R is the bulk resistance obtained from EIS, which is the |Z| at the frequency where the phase angle approaches zero in Bode plots or the high-frequency intercept on the real impedance axis in the Nyquist plot.<sup>[3]</sup>



Figure S1 SEM images of the composite hydrogel. (a) Low-magnification SEM image. (b)

Enlarged SEM image. (c) High magnification SEM image.



Figure S2 EDS image of the composite hydrogel.



Figure S3 The XRD pattern of pure PPy nanopaticles and the composite hydrogel.



Figure S4 FTIR spectra of the composite hydrogel.



Figure S5 Typical nitrogen adsorption-desorption isotherm of (a) the pure PVA and (b) the

composite hydrogel.



Figure S6 Electrochemical characterizations of pure PPy nanoparticles in three electrodes system. (a) The charge/discharge curves at current densities ranged from 1.5 to 6 A g<sup>-1</sup>. (b)

The CV curves at scan rates between 5 and 200 mV s<sup>-1</sup>. (c) The specific capacitance as a function of the scan rates of pure PPy nanoparticles. (d) The charge/discharge curves of pure PPy nanoparticles before and after 8000th cycles. (e) Cycling performance at current density of 3 A g<sup>-1</sup>. (f) EIS spectras of pure PPy nanoparticles before and after 8000th cycles.



Figure S7 Comparative CV curves of pure PPy nanopaticles and Ni foam performed in a three-electrode cell at scan rate of 200 mV s<sup>-1</sup>.



Figure S8 Electrochemical characterizations of PVA/PPy composite in three electrodes system. (a) The charge/discharge curves at current densities ranged from 1.5 to 6 A g<sup>-1</sup>. (b) The CV curves at scan rates between 5 and 200 mV s<sup>-1</sup>. (c) The specific capacitance as a function of the scan rates of PVA/PPy composite. (d) The charge/discharge curves of PVA/PPy composite before and after 8000th cycles. (e) Cycling performance at current density of 3 A g<sup>-1</sup>. (f) EIS spectras of PVA/PPy composite before and after 8000th cycles and the inset is the local amplification figure of high frequency.



Figure S9 (a-b) The SEM images of PVA/PPy composite before and after 8000th cycles.



Figure S10 (a) Comparative GCD curves of pure PPy nanopaticles and PVA/PPy composite at current densities of 1.5A g<sup>-1</sup>. (b) Comparative CV curves of pure PPy nanopaticles and

PVA/PPy composite at scan rates of 200 mV s<sup>-1</sup>. (c) The Nyquist plots of pure PPy

nanopaticles and PVA/PPy composite measured in the same range from 100 kHz to 0.01 Hz.

(d) Cycling performances of pure PPy nanopaticles and PVA/PPy composite at current

density of 3 A g<sup>-1</sup>.



Figure S11 Electrochemical characterizations of CNTs film in three-electrode system. (a) The charge/discharge curves at current densities ranged from 1.5 to 6 A g<sup>-1</sup>. (b) The CV curves at scan rates between 5 and 200 mV s<sup>-1</sup>. (c) The CV curves at different bending states of the CNTs film. (d) The specific capacitance as a function of the scan rates of CNTs film. (e) The cycling performance at current density of 3 A g<sup>-1</sup> and the inset is the charge/discharge curves of CNTs film before and after 8000th cycles. (f) EIS spectras of CNTs film before and after 8000th cycles.



Figure S12 Schematic diagram of ion and charge transfer in the  $(PVA/PPy)_{(-)}//CNTs_{(+)}$  DSS device.



Figure S13 The specific capacitance of (PVA/PPy)(-)//CNTs(+) DSS device.



Figure S14 Fatigue resistance of hydrogel at 50% strain for 15 cycles.



Figure S15 The photograph of the flexible device.



Figure S16 The capacitance retention ratio of the fabricated  $(PVA/PPy)_{(-)}//CNTs_{(+)}$  DSS device.

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