Supporting information

Three-Dimensional Carbon Nanotube/Ethylvinylacetate/Polyaniline as High Performance Electrode for Supercapacitor

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

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Experimental methods

Preparation of CNT/EVA composites with 3D co-continuous phase structure

EVA containing 32% vinyl acetate (melt flow rate: 3.2 g $10min^{-1}$ at 230 °C and 2.160 kg) was supplied by Sinopec Group, Maoming petroleum Chemical Industry Limited Company, China. CNT NC7000 was obtained from Nanocyl S.A. CNT filled EVA composites membranes were prepared in the following procedure:

All the materials were adequately dried in a vacuum oven at appropriate temperatures. In order to improve the dispersion and the dosage of CNT in EVA, solution mixing process was used to prepare CNT/EVA composites. X mass of EVA, y mass of CNTs were dissolved in toluene, and they were mixed in a beaker. The resultant mixture was thoroughly homogenized using ultrasound and finally casted into thin sheets using cellulose hydrogel as substrates.

Preparation of CNT/EVA/PANI electrode

Firstly, 40wt% CNT/EVA composite was dipped into the ethyl alcohol solution containing aniline hydrochloride and then took out to volatilize ethyl alcohol completely. Therefore the aniline hydrochloride can stay inside CNT/EVA composite

to act as working electrode. Then, the continuous PANI network around CNT (denoted as PANI/CNT/EVA) was obtained via CV techniques in a conventional three-electrode cell using an electrochemical workstation (CHI 760E). The electrolyte consists of 0.3 M sodium sulfate. The reaction was under 0~1V with 50 mV s^{-1} for 50 cycles at room temperature.

Characteriazation

For mechanical testing, all specimens were conditioned at 25 °C and 50 % relative humidity for 5 days. Tensile properties were characterized using a Hounsfield THE 10K-S testing machine according to ASTM D 638. Five samples were tested from each compound and the average results were recorded. The resistivity of EVA/CNT thin sheets and conductive paper is measured by a standard four-probe method using a physical property measurement system (ST2253). The morphologies, chemical composition of the products were characterized by field emission scanning electron microscope (FE-SEM, Hitachi-S4800), TEM (TEM, JEM2010-HR, 200 KV), atomic force microscope (AFM, SPM-9500J3), XPS (XPS, ESCALab250, Thermo VG), X-ray diffraction (XRD, Empyrean) , Fourier transform infrared spectroscopy (FTIR, Nicolet6700) and Barrett-Emmett-Teller (BET, ASAP2020), respectively. The electrochemical properties of the products were investigated with cyclic voltammetry (CV), charge-discharge measurements and electrochemical impedance spectroscopy in a conventional three-electrode cell employing a CHI 760E electrochemical workstation (Chenhua, Shanghai). The electrochemical studies of the individual electrode were performed in a three-electrode cell, with a Pt counter electrode and the Hg/Hg_2Cl_2 reference electrode (SCE). All the electrochemical measurements for electrodes were performed in a 1 M H_2SO_4 solution at room temperature.

Data analysis:

The power density and energy density were calculated by using the following equations:

$$P = V^2 / [4RS] \qquad (1)$$

$$E = 0.5CV^2/S \quad (2)$$

where V is the applied voltage, R is the internal resistance calculated by equation (3), S is the total area of active electrode materials, and C is the measured total areal capacitance of electrode calculated by equation (4) :

$$R = \Delta V_{iR} / 2I \quad (3)$$

$$C = I\Delta t / [SV] \quad (4)$$

where I is the applied current, ΔV_{iR} is the voltage drop between the first two points from its top cut-off of discharge curve, Δt is the discharge time after the initial iR drop. The electrical resistivity is 18.5 Ω*cm for EVA/10%CNT, 0.56 Ω*cm for EVA/20%CNT, 0.10 Ω*cm for EVA/30%CNT, 0.051 Ω*cm for EVA/40%CNT. The electric conductivity is calculated by equation (5):

$$\sigma = 1/\rho \quad (5)$$

Figures:

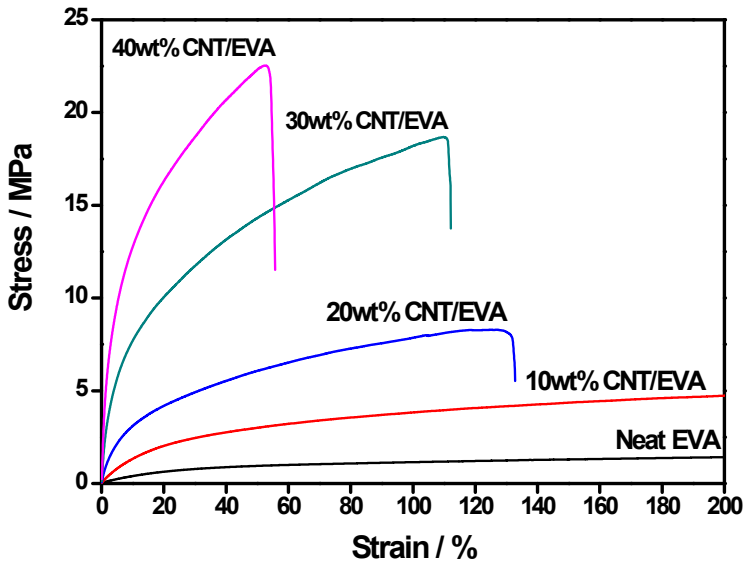

Figure S1. The stress-strain curves of CNT/EVA.

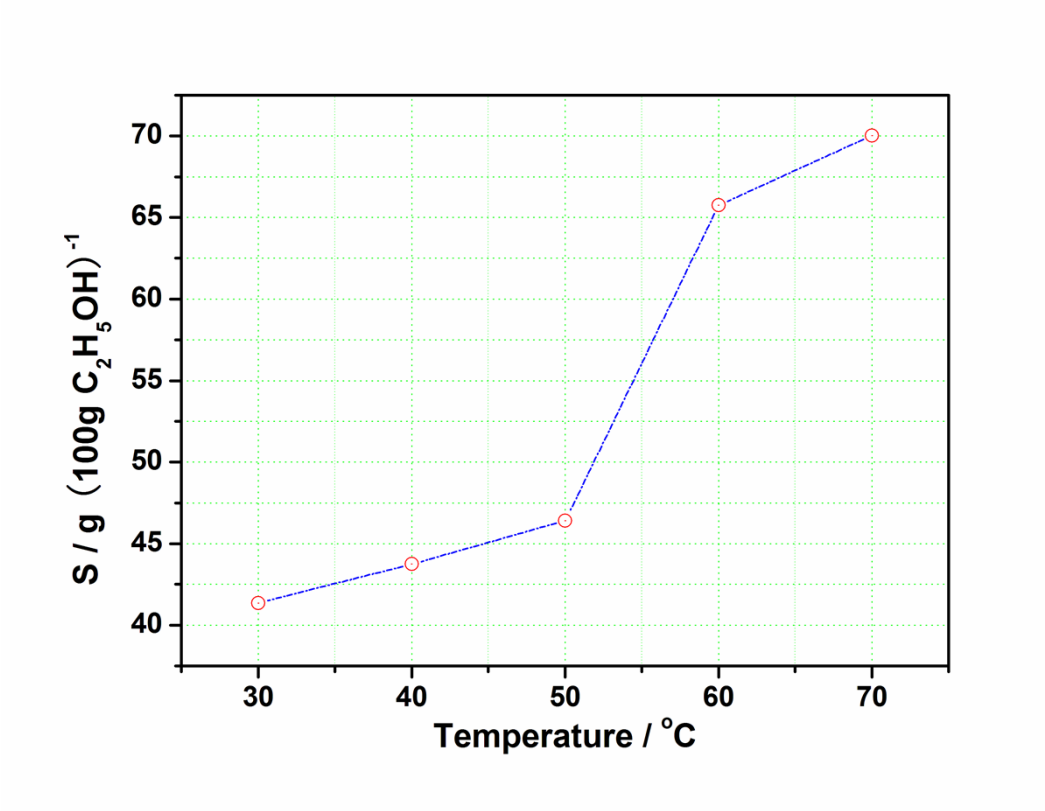

Figure S2. The solubility temperature curve of the aniline hydrochloride is easily dissolved in ethyl alcohol.

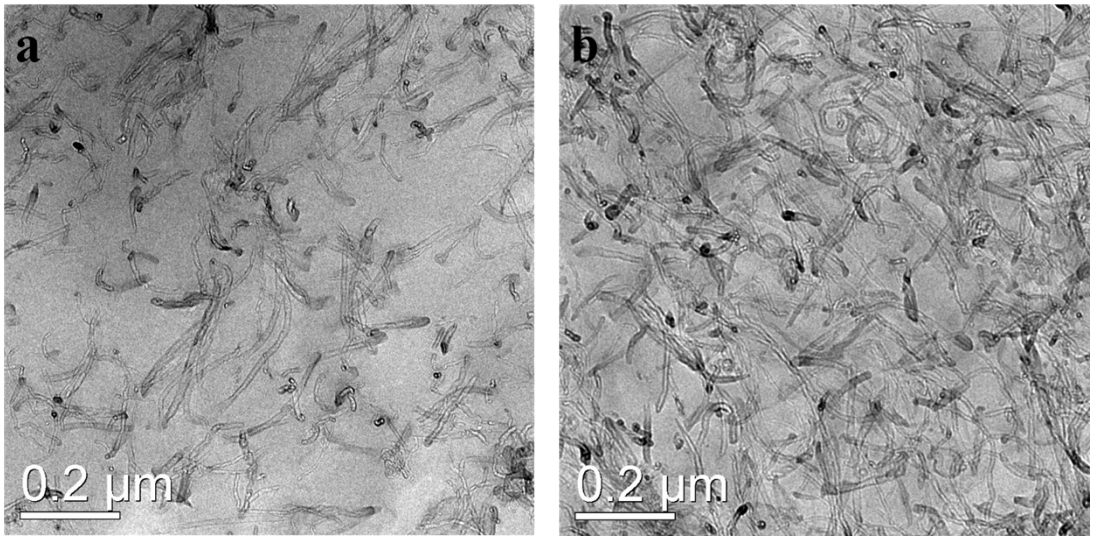

Figure S3. TEM image of (a) 40wt% CNT/EVA and (b) PANI/CNT/EVA.

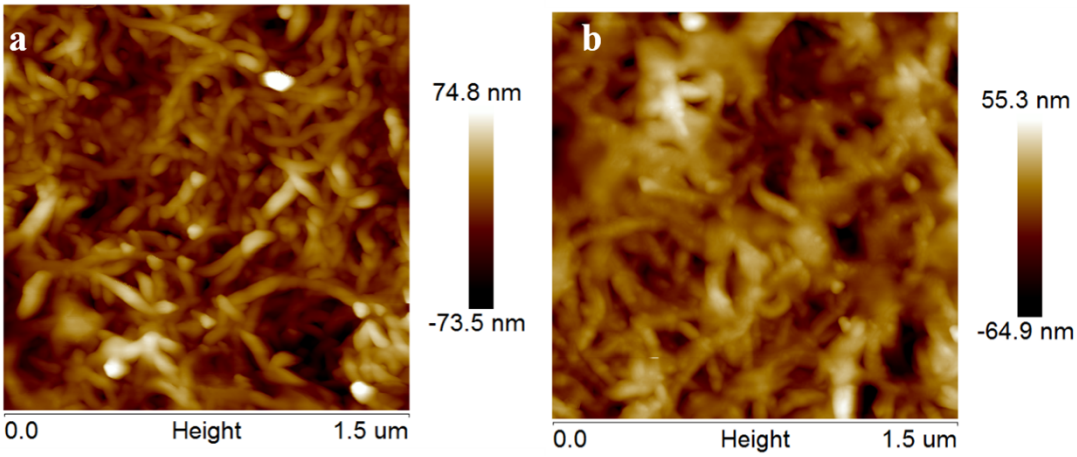

Figure S4. AFM height image (a) 40wt% CNT/EVA and (b) PANI/CNT/EVA.

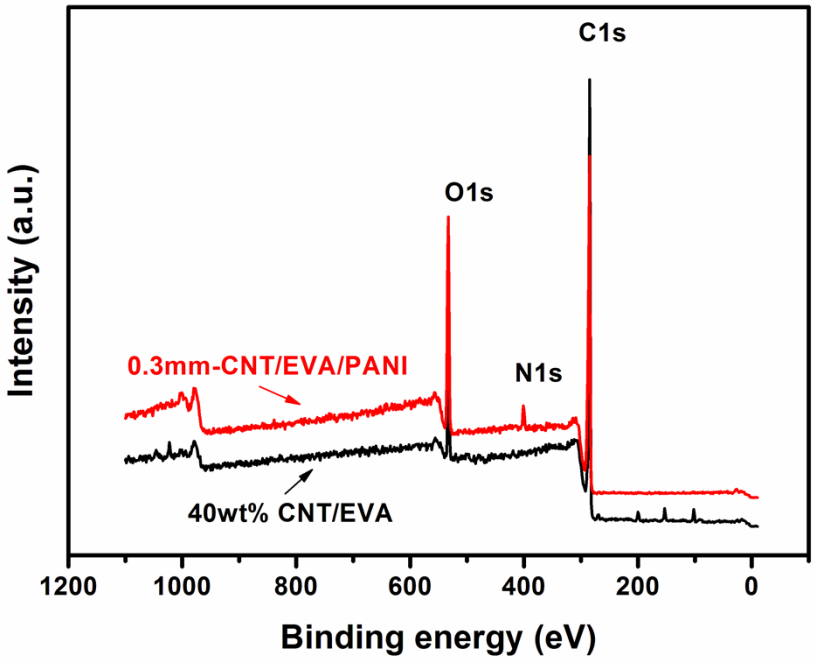

Figure S5. XPS spectra of 40wt% CNT/EVA and 0.3mm-CNT/EVA/PANI.

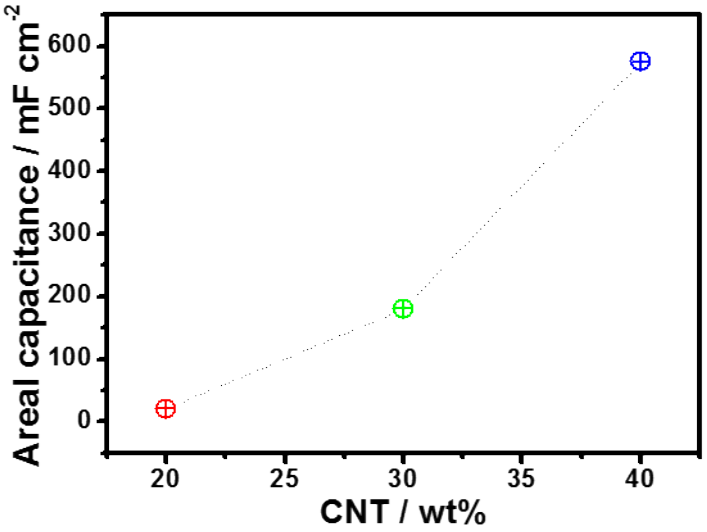

Figure S6. The calculated areal capacitances of PANI/CNT/EVA at the scan rate of 5 mV s^{-1}. PANI/CNT/EVA were fabricated from different content of CNT/EVA absorbed aniline hydrochloride at 70 °C. The detailed parameter of cyclic voltammetry method is: scan rates (50 mV s^{-1}), potential range (0 – 1 V), 50 cycles and electrolyte solution (0.3 M H_2SO_4).

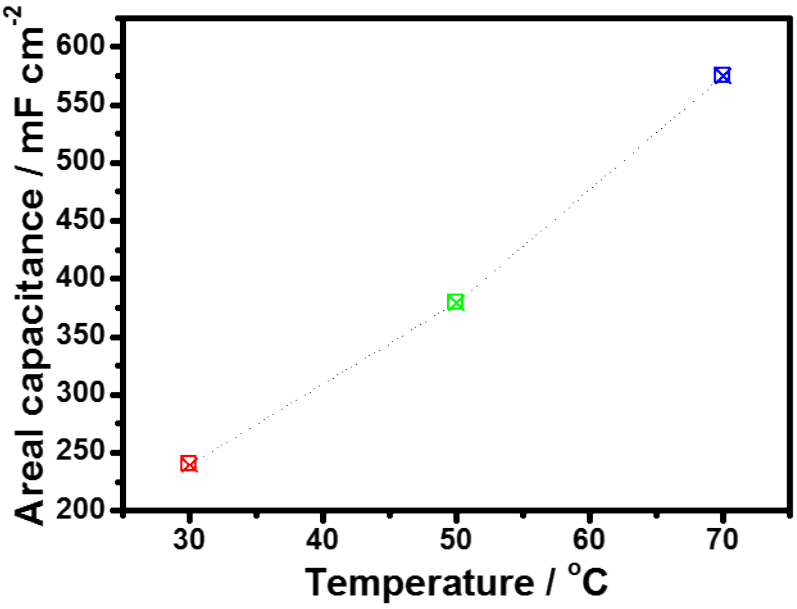

Figure S7. The calculated areal capacitances of PANI/CNT/EVA at the scan rate of 5 mV s^{-1}. PANI/CNT/EVA were fabricated from 40wt% CNT/EVA absorbed aniline hydrochloride at differet temperature. The detailed parameter of cyclic voltammetry method is: scan rates (50 mV s^{-1}), potential range (0 – 1 V), 50 cycles and electrolyte solution (0.3 M H_2SO_4).

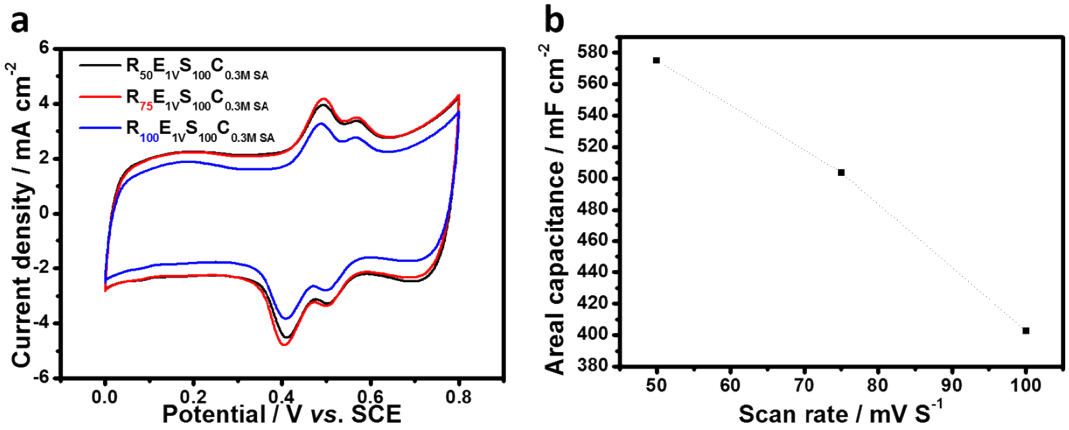

Figure S8. (a) CV curves and (b) the calculated areal capacitances of PANI/CNT/EVA at the scan rate of 5 mV s^{-1}. $R_xE_{1V}S_{100}C_{0.3M\ SA}$ is the detailed parameter of cyclic voltammetry method to fabricate PANI/CNT/EVA from 40wt%CNT/EVA absorbed aniline hydrochloride at 70 °C. R: the scan rates (mV s^{-1}); E_{1v}: potential range (0 – 1 V); S_{100}: 50 cycles; $C_{0.3M\ SA}$: electrolyte solution (0.3 M H_2SO_4).

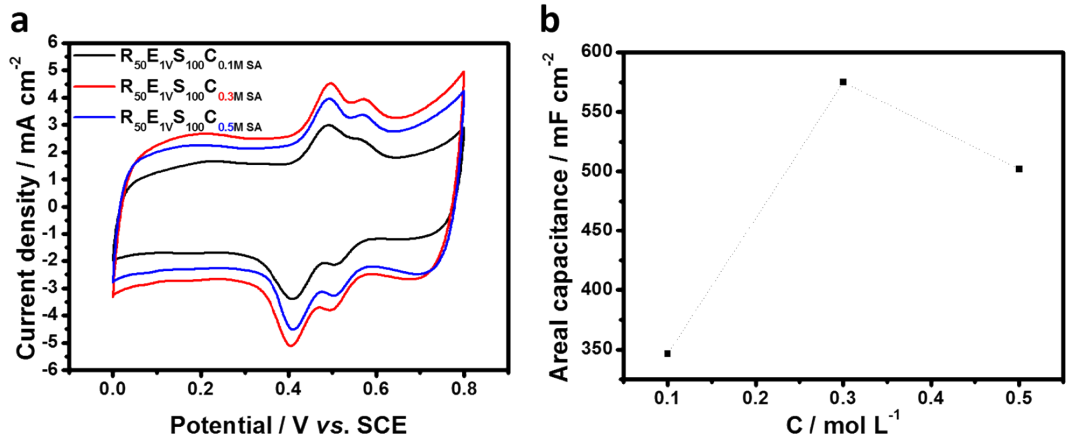

Figure S9. (a) CV curves and (b) the calculated areal capacitances of PANI/CNT/EVA at the scan rate of 5 mV s^{-1}. $R_{50}E_{1V}S_{100}C_{x\ M\ SA}$ is the detailed parameter of cyclic voltammetry method to fabricate PANI/CNT/EVA from 40wt%CNT/EVA absorbed aniline hydrochloride at 70 °C. R_{50}: the scan rates (50 mV s^{-1}); E_{1v}: potential range (0 – 1 V); S_{100}: 50 cycles; $C_{x\ M\ SA}$: electrolyte solution (x M H_2SO_4).

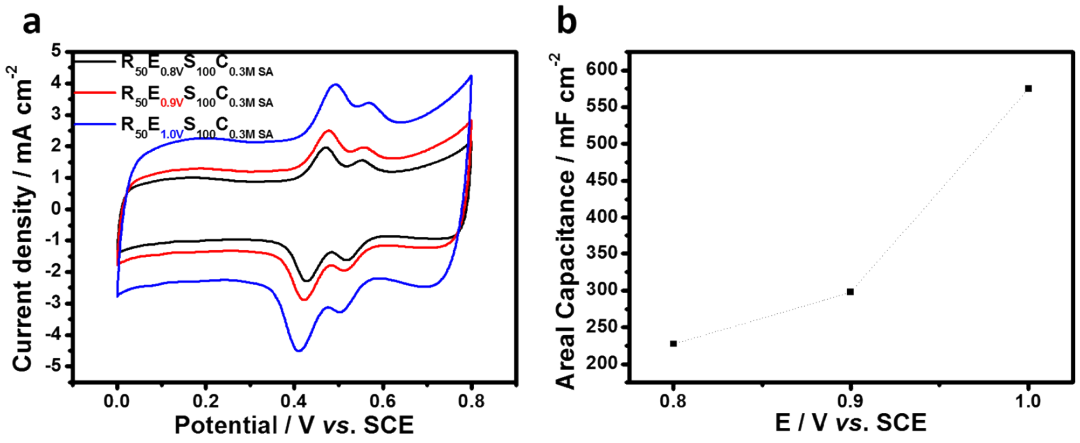

Figure S10. (a) CV curves and (b) the calculated areal capacitances of PANI/CNT/EVA at the scan rate of 5 mV s^{-1}. $R_{50}E_{xV}S_{100}C_{0.3M\ SA}$ is the detailed parameter of cyclic voltammetry method to fabricate PANI/CNT/EVA from 40wt%CNT/EVA absorbed aniline hydrochloride at 70 °C. R_{50}: the scan rates (50 mV s^{-1}); $E_{x\ V}$: potential range (0 – x V); S_{100}: 50 cycles; $C_{0.3M\ SA}$: electrolyte solution (0.3 M H_2SO_4).