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Molecular chain bonding synthesis of nanoporous, flexible and conductive polymer composite with outstanding performance for supercapacitors

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Experimental data

Preparation of CNT/EVA: 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 (MWCNT, NC7000) was obtained from Nanocyl S.A., and its average diameter, average length, purity and specific surface area are 9.5nm, 1.5μm, 90% and 250-300 m^2 g^{-1}, respectively. 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 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 xylol, 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/c-EVA: The as prepared dense CNT/EVA was dipped into the ethyl acetate solution containing various content of dicumyl peroxide (DCP, cross-linking agent) and then took out to volatilize ethyl acetate completely, resulting various DCP uniformly dispersed in the EVA matrix. The as prepared samples were heated to 160 °C for an hour, and various dosage of EVA could be changed to c-EVA. In a word, CNT/EVA was changed to CNT/EVA/c-EVA. Finally, CNT/EVA/c-EVA was washed with xylol to remove the dissoluble EVA but remained CNT/c-EVA, thus CNT framework in porous c-EVA matrix was successfully constructed.

Fabrication of CNT-SSCs: CNT-SSCs were assembled by two uniform electrodes (work area: 2 cm ×0.5 cm) with H_2SO_4/PVA gel electrolyte as solid state electrolyte and a filter paper as separator sandwiched in between. H_2SO_4/PVA gel electrolyte was simply prepared as follows: 2 mL H_2SO_4 (98wt%), 20 mL distilled water and 2g PVA were mixed together and heated at 80 °C for 30 min under vigorous stirring. All the electrodes and separator were soaked with the H_2SO_4/PVA solution and make them solidified at room temperature for about 3h. Then they were assembled together and kept at 40 °C for another 3h to remove excess water in the electrolyte. The area and thickness of the fabricated SSCs are about 1cm2 and 0.06 cm, respectively.

Preparation of PANI/CNT/c-EVA: PANI was electrodeposited on the CNT/c-EVA through cyclic voltammetry technique in a conventional three-electrode cell with a Pt counter electrode and a saturated calomel reference electrode on an electrochemical workstation (CHI 760E). The reaction was performed in a mixed solution (volume ratio of water and ethanol 1: 1) of 0.1 M aniline and 1 M H_2SO_4. And the detailed parameter of cyclic voltammetry method is: potential range: 0 – 1 V, scan rate 50 mV s^{-1}, cycles: 5, 10, 30, 50 and 70.

Material Characterization and Electrochemical Measurement: 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. Six samples were tested from each compound and the average results were recorded. The bend of the CNT/c-EVA and CNT-SSCs was conducted on a programmable motorized precision translation stage (NL03STA-150). The resistivity of CNT/EVA and CNT/c-EVA thin sheets is measured by a standard four-probe method using a physical property measurement system (ST2253). The morphologies, chemical compositions and pore structure properties of the products were characterized by field emission scanning electron microscope (FE-SEM, Hitachi-S4800), Barrett-Emmett-Teller (BET, ASAP2020) and Mercury intrusion porosimetry (AutoPore IV 9500 V1.09), respectively. The electrochemical properties of the products were investigated with cyclic voltammetry (CV), charge-discharge measurements in a conventional three-electrode cell employing a CHI 760E electrochemical workstation (Chenhua, Shanghai). The electrochemical impedance spectroscopy

(EIS) analysis were conducted in Autolab PGSTAT302N electrochemical workstation. 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 CNT/c-EVA electrodes were performed in a 0.5 M Na_2SO_4 solution at room temperature. All the electrochemical measurements for PANI/CNT/c-EVA electrodes were performed in a 1 M H_2SO_4 solution at room temperature.

Data analysis

The electric conductivity is calculated by equation (1):

$$\sigma = \frac{1}{\rho} \quad (1)$$

where ρ is electrical resistivity.

The specific capacitance, areal capacitance and volumetric capacitance are calculated by using the following equations:

$$C_s = \frac{Q}{m * \Delta V} \quad (2)$$

$$C_a = \frac{Q}{S * \Delta V} \quad (3)$$

$$C_v = \frac{Q}{V * \Delta V} \quad (4)$$

where Q is the average electric quantity of the electrode in the CV measurement of charge and discharge, ΔV is operating voltage window for the electrode, m is the active material mass in the electrode, S is the tested total area of active electrode materials, and V is the tested volume of the electrode.

Figure

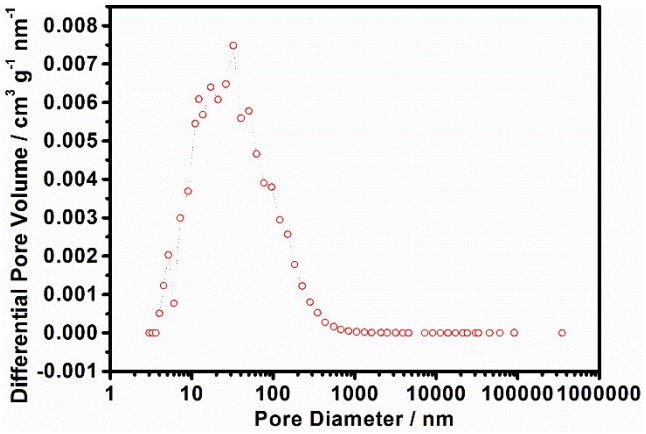

Fig. 1 Pore structure properties of 54.2wt% CNT/c-EVA tested by the mercury porosimeter.

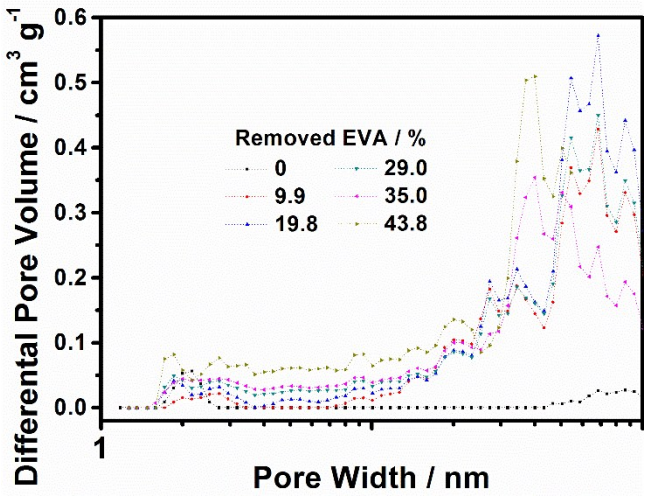

Fig. 2 DFT pore size distributions of CNT/c-EVA.

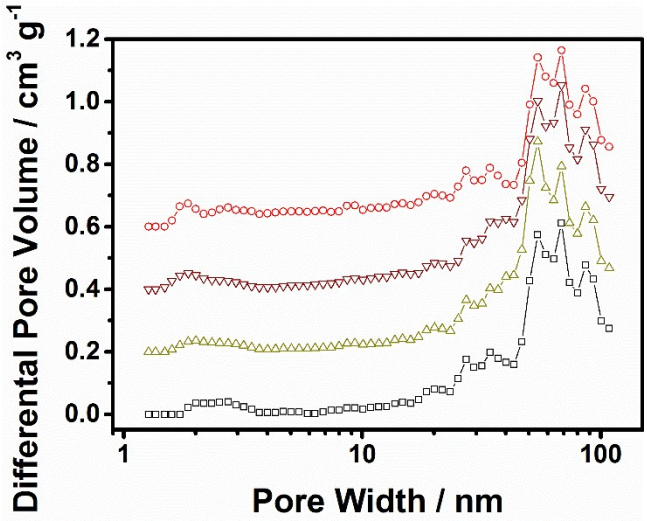

Fig. 3 The pore size distributions of CNT/c-EVA prepared from 10wt% (□), 20wt% (△), 30wt% (▽) and 40wt% (○) CNT/EVA under the same experimental conditions (0.001M DCP). The curves of the latter three are offset vertically by 0.20, 0.40, and 0.60 cm^3 g^{-1}, respectively.

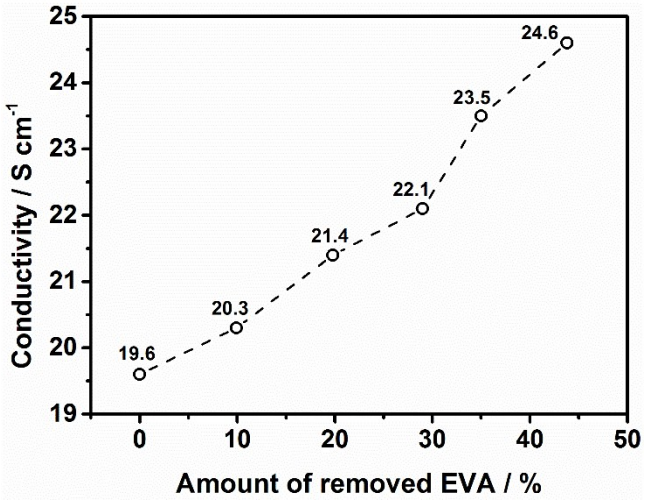

Fig. 4 The conductivity of CNT/c-EVA as a function of the amount of removed EVA.

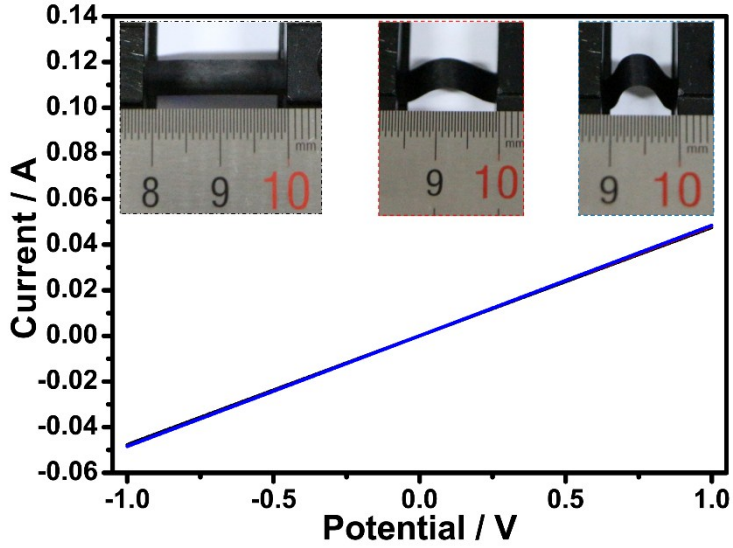

Fig. 5 Linear sweep voltammograms (LSV) curves collected for CNT/c-EVA under various bending angles

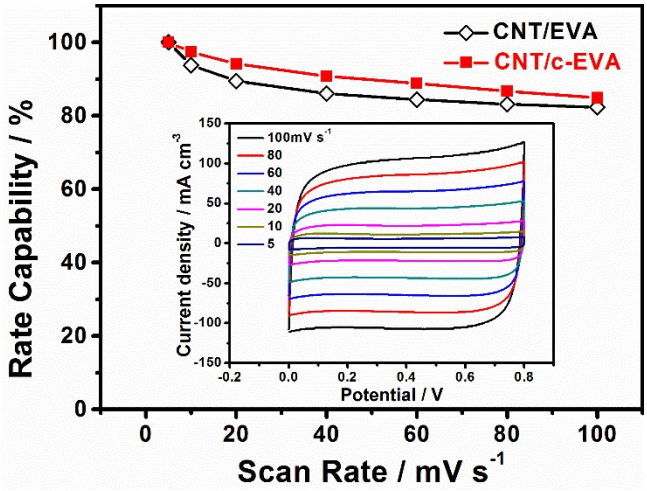

Fig. 6 Rate capability as a function of scan rate of CNT/EVA and CNT/c-EVA. Inset: CV curves of CNT/c-EVA collected at various scan rate from 5 to 100 mV s^{-1}.

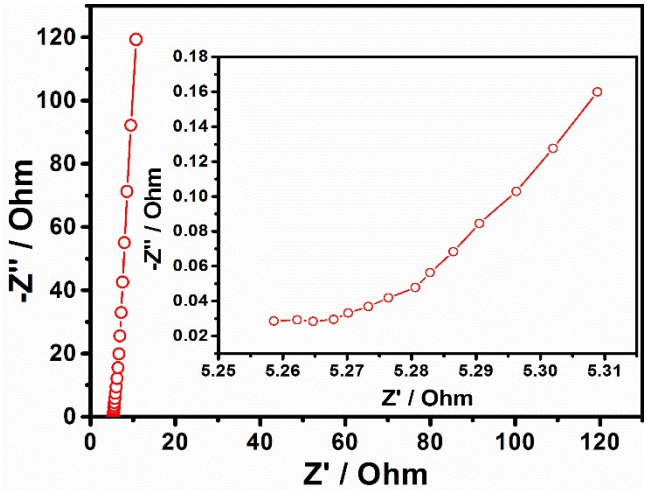

Fig. 7 Nyquist plots of CNT/c-EVA. The plots don't show semicircle regions, which could be attributed to the low faradaic resistances of CNT/c-EVA. The high-frequency meets with X-axis in a point, equivalent series resistance (Rs), which consists of the electrolyte solution resistance, the intrinsic resistance of active material and the contact resistance at the electrode–electrolyte interface. Thus, the Rs of CNT/c-EVA is around 5.25 Ω cm^{-2}. In the low-frequency part, nearly vertical line represents an idea capacitive behavior, which indicates good ion diffusion in the nanoporous structure.

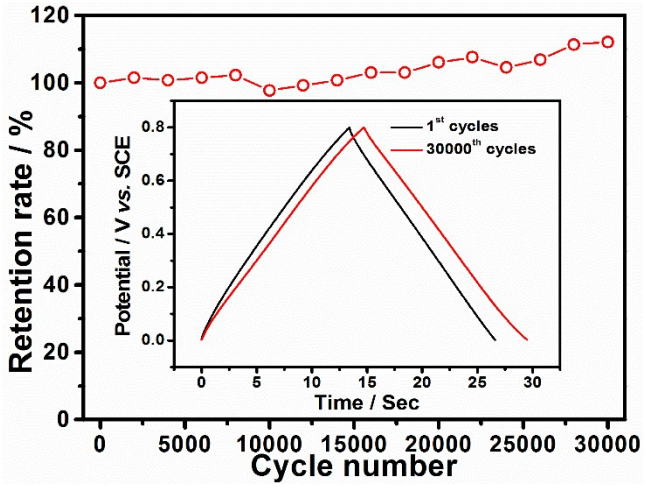

Fig. 8 Cycling performance of CNT/c-EVA during continuous galvanostatic charge-discharge process at current density of 1mA·cm^{-2}. Inset: galvanostatic charge-discharge curves of 1st and 30000th cycles.

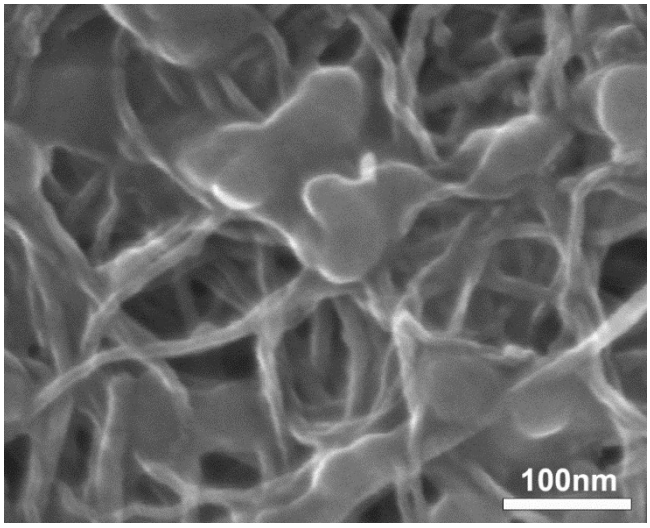

Fig. 9 The surface SEM images of PANI/CNT/c-EVA.

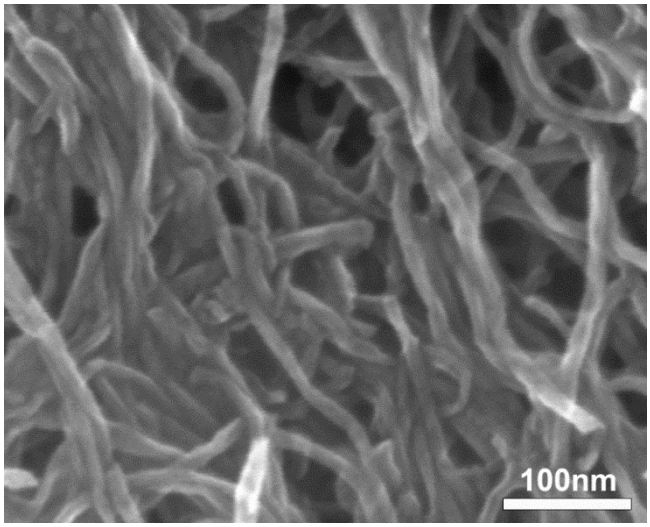

Fig. 10 The cross-sectional SEM images of PANI/CNT/c-EVA.

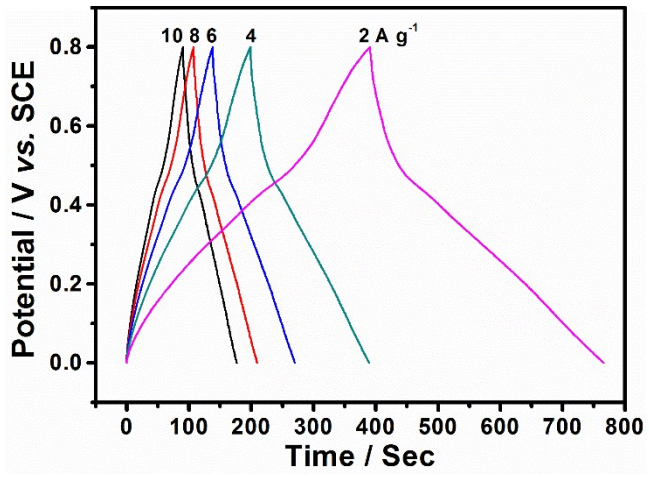

Fig. 11 Galvanostatic charge-discharge curves of PANI/CNT/c-EVA collected at the current density from 2 to 10 A g^{-1}.

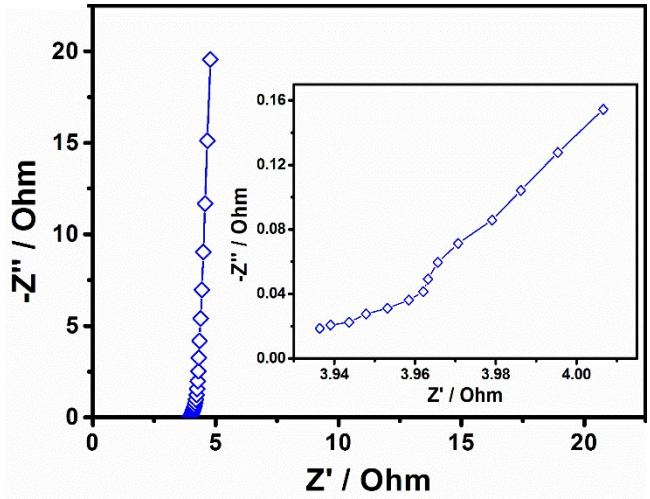

Fig. 12 Nyquist plots of PANI/CNT/c-EVA. The Rs of CNT/c-EVA is around 3.93 Ω cm^{-2}.

Table

Table 1 Pore parameters of CNT.

sample	BET surface area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)
CNT	223.56	0.840

Table 2 Pore parameters of CNT/EVA and CNT/c-EVA with various amount of removed EVA.

Removed EVA (%)	BET surface area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)
0	30.38	0.019
9.9	36.54	0.229
19.8	54.84	0.289
29.0	54.01	0.247
35.0	51.91	0.247
43.8	76.09	0.447

Table 3 Pore parameters of CNT/c-EVA prepared from CNT/EVA containing 10wt%, 20wt%, 30wt% and 40wt% CNT/EVA under the same experimental conditions (0.001M DCP).

sample	BET surface area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)
CNT/c-EVA prepared from 10wt% CNT/EVA	40.93	0.265
CNT/c-EVA prepared from 20wt% CNT/EVA	41.92	0.372
CNT/c-EVA prepared from 30wt% CNT/EVA	48.81	0.397
CNT/c-EVA prepared from 40wt% CNT/EVA	76.09	0.447

Table 4 Composition variation in preparation of CNT/c-EVA from 40wt% CNT/60wt% EVA.

C_{DCP} ($mol{\cdot}L^{-1}$)	Molecular chain bonding	$m_{EVA}/m_{EVA+c-EVA}$ (%)	$m_{c-EVA}/m_{EVA+c-EVA}$(%)	Removed EVA
0.001	40.0wt% CNT/26.3wt% EVA/33.7wt% c-EVA	43.8%	56.2%	54.2wt% CNT/c-EVA
0.01	40.0wt% CNT/21.0wt% EVA/39.0wt% c-EVA	35.0%	65.0%	50.6wt% CNT/c-EVA
0.1	40.0wt% CNT/17.4wt% EVA/42.6wt% c-EVA	29.0%	71.0%	48.4wt% CNT/c-EVA
0.5	40.0wt% CNT/11.9wt% EVA/48.1wt% c-EVA	19.8%	80.2%	45.4wt% CNT/c-EVA
1	40.0wt% CNT/5.9wt% EVA/54.1wt% c-EVA	9.9%	90.1%	42.5wt% CNT/c-EVA

Table 5 Mechanical index of CNT/EVA and CNT/c-EVA.

Removed EVA (%)	Elastic modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
0	372.9	22.3	55.3
9.9	576.8	11.5	4.7
19.8	530.0	17.0	8.9
29.0	452.8	22.4	24.2
35.0	362.8	23.6	35.6
43.8	350.2	18.3	31.5