

Supporting information

Raising the performance of 4 V supercapacitor based on EMIBF₄-single walled carbon nanotubes nanofluid electrolyte

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S1. Fabrication of supercapacitor cell and the test of capacitance

Electrode materials used in the present work were 80 wt% double walled carbon nanotubes (DWCNTs) and 20 wt% multiwalled carbon nanotubes (MWCNTs). Transmission electron microscope (TEM) images of DWCNTs were shown in the Fig.S1. They are mostly double walled carbon nanotubes with outer diameter of 2-3.5 nm. MWCNTs used here had a diameter of about 10 nm and length of at least 100 μm (Fig.S2). The effect of long MWCNTs was to link DWCNTs to fabricate a buckypaper with high strength and excellent electrical conductivity.

In detail, 80 wt% DWCNTs and 20 wt% MWCNTs in N-methyl pyrrolidone (NMP) solution were filtrated to form buckypaper with thickness of 300 μm. The buckypaper was cut into round sheet about 13 mm and was de-oxygen and de-water in nitrogen atmosphere at 120 °C for 24 hours and then put in a glove box with oxygen content of 0.7 mL/m³ and water content of 0.12 mL/m³. Each electrode's mass was about 12 mg.

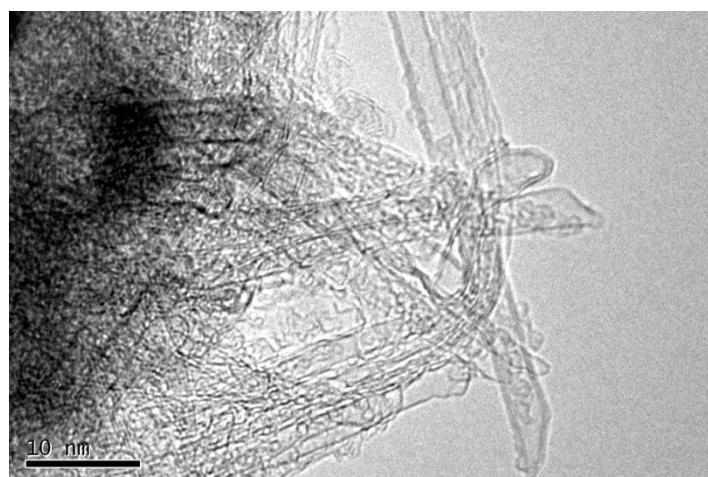


Figure.S1 TEM images of DWCNTs

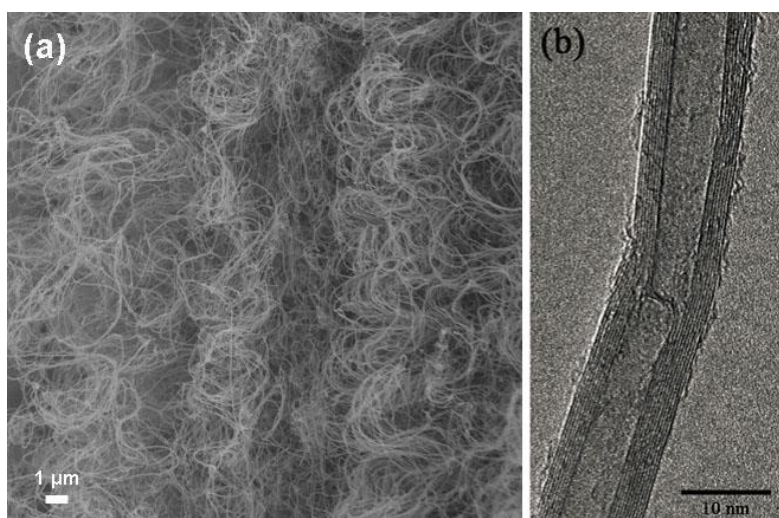


Fig.S2 SEM images of MWCNTs (a) and TEM images of MWCNTs (b)

Then the electrolyte was dipped onto the 13 mm buckypaper. The separator used was celgard membrane with thickness of 100 μm. These were sealed in a stainless steel cell as a supercapacitor.

The cell configuration was shown in the Fig.S3.

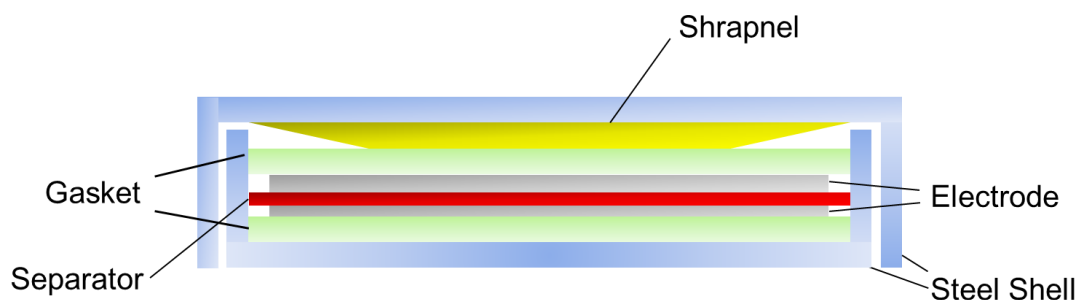


Figure.S3 Cell configuration of coin-like supercapacitor

The electrochemical performance such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of CNT-based supercapacitor was characterized by using a Solartron 1470E electrochemical station equipped with a 1455AFRA module. The CV curve and specific capacitance was tested under different scan rate of 0-200 mV/s from 0 to 4 V. Then the cycling ability was tested under the scan rate of 200 mV/s and in the range of 0-4 V for 4000 cycles.

S2. TEM image of SWCNTs used and SWCNTs coated with ILs

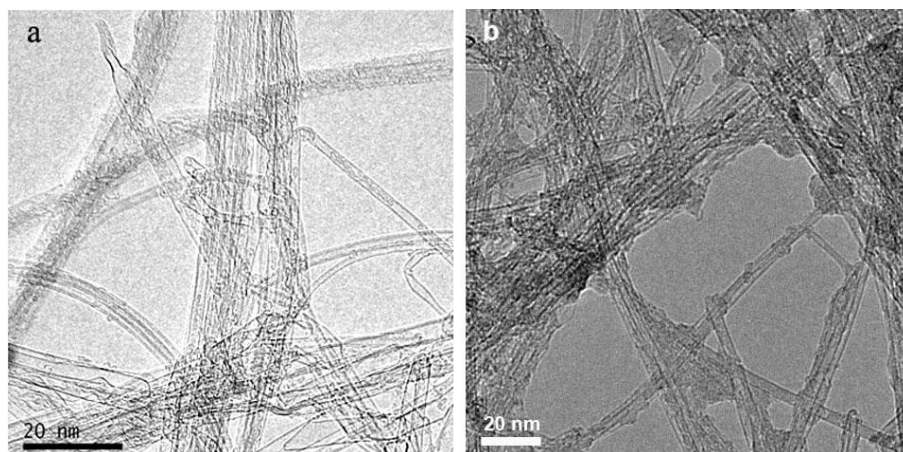


Figure.S4 TEM image of pristine SWCNTs (left) and ILs-coated SWCNTs (right), TEM instrument was JEOL 2010, 200kV.

Pristine SWCNTs had a diameter of 1-2 nm but they most existed as bundle with diameter of 5-25nm (Fig.S4, left). As they dispersed in ILs of EMIBF₄, most of them were mono dispersed (Fig.S4, right), due to the strong interaction of ILs with SWCNTs to de-bundle SWCNTs.

Each tube was coated with ILs, which made SWCNTs stably suspended in the bulk phase of ILs to form a nanofluid.

S3. Factors influencing the ionic conductivity

Actually, according to the conductivity equation:

$$\Lambda_m = \alpha(u_+ + u_-)F \quad \text{S-(1)}$$

Where Λ_m is the molar conductivity, α is the degree of ionization which means the density of the mobile ions, u_+ is the mobility of the cation, u_- is the mobility of the anion and F is the faraday constant.

This equation indicated that ionic conductivity depends on both the mobility and the ionic density. Brownian motion influenced the mobility of ions, whereas the presence of ion pairs or not contributed to the ionic density.

Considering the ion pairs after adding CNTs was unable to characterize by mass spectrum, we used another ionic liquids *N*-butyl-*N*-methyl pyrrolidiniumbis-(trifluoromethylsulfonyl) amide (EMINTF₂) mixed with the same mass of EMIBF₄ for the test. Actually, mixture of different ionic liquids which had the same cations, was effective to change the chemical balance S-(2) and S-(3) as below, resulting in breaking the ion pairs and increasing the ionic density of IL (Fig. S5).



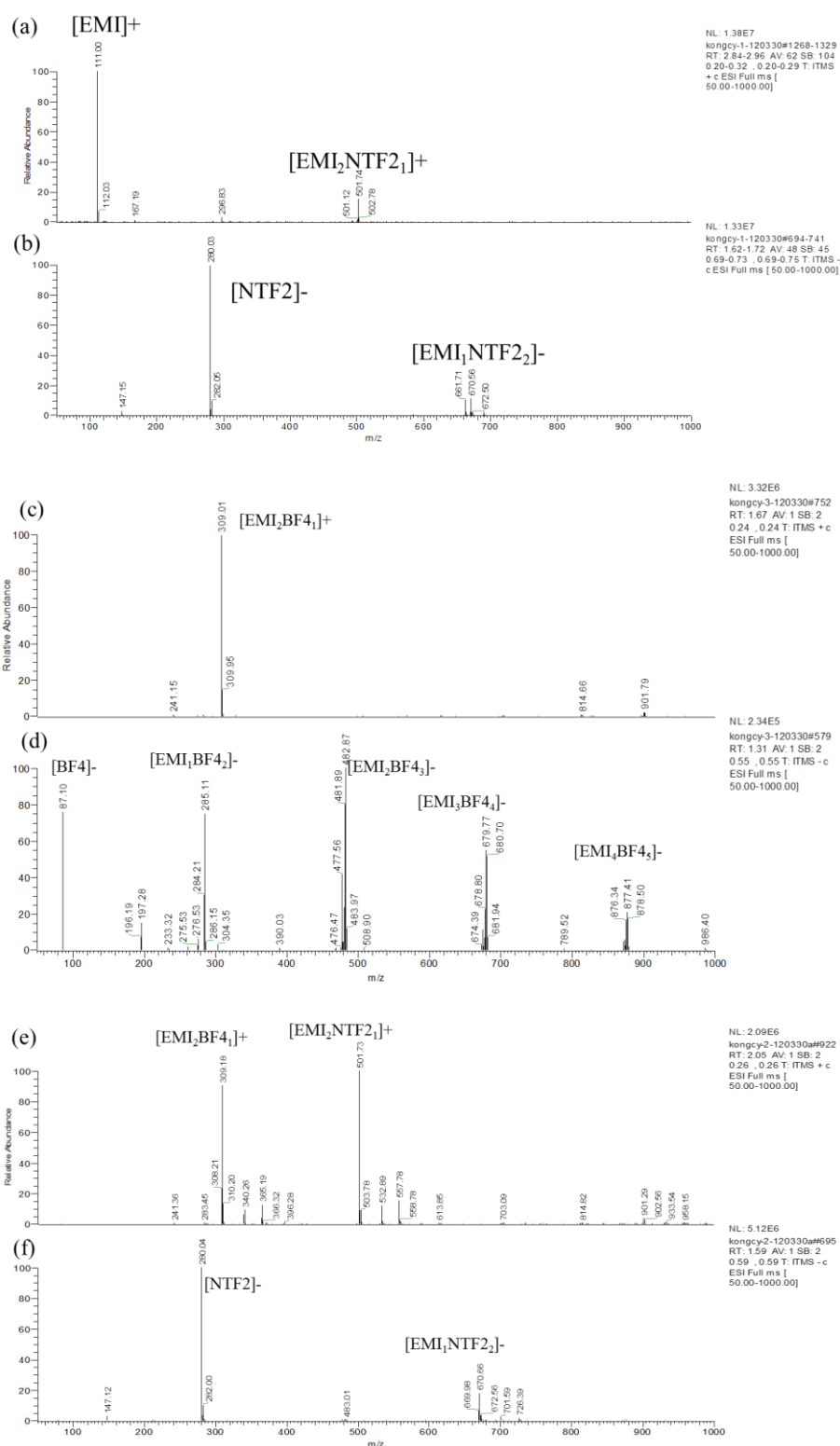


Figure.S5 Mass Spectrum of ILs: (a) the cation of pure EMINTF₂; (b) the anion of pure EMINTF₂; (c) the cation of pure EMIBF₄; (d) the anion of pure EMIBF₄; (e) the cation of the mixture containing 50 wt% EMINTF₂ and 50 wt% EMIBF₄; (f) the anion of the mixture containing 50 wt% EMINTF₂ and 50 wt% EMIBF₄. Lots of the ion pairs existed in the pure IL, but after mixing, the

ion pairs decreased and the single anions and cations increased accordingly. It proved that mixing the ILs could increase the ionic density.

If the increase of the ionic density contributed to the ionic conductivity significantly, the ionic conductivity of the mixture of ILs should be higher than both pure EMIBF₄ and EMINTF₂. However, the value was sustainably lower than that of pure EMIBF₄, regardless of the mass fraction of EMIBF₄ (Fig.S6). Thus, we concluded that the Brownian motion, not the increasing ionic density will be the dominant factor for increasing the ionic conductivity.

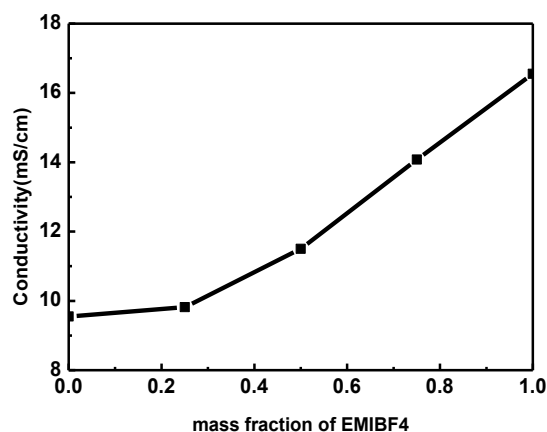


Fig.S6 Ionic conductivity of mixture of EMIBF₄ and EMINTF₂

S4. CV curve of electrode in different electrolyte in different scan rates.

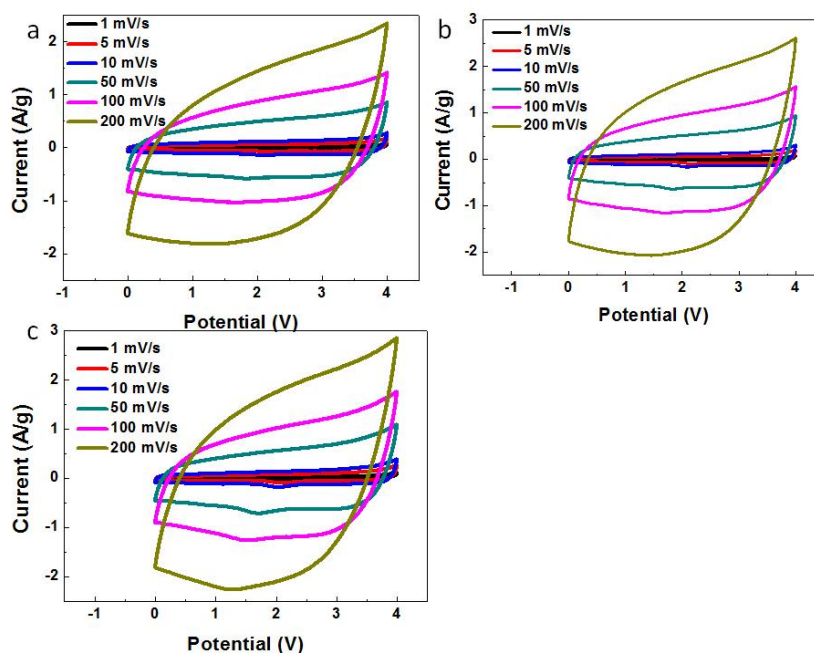


Figure.S7 CV curves of electrode in electrolyte Pure ILs (a); nanofluid electrolyte of EMIBF₄

containing 0.1 wt% SWCNTs (b) and nanofluid electrolyte of EMIBF₄ containing 0.5 wt% SWCNTs (c)

S5. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is a kind of common electrochemical analytical method, which the small amplitude sine wave potential or current acts as a disturbing signal to observe the response of the system at the steady state.

EIS needs us to set up a physical model firstly, and then calculate the parameters in the model through the imitation of the experimental results. According to the physical meaning of the parameters, we can understand the interior mechanism in the SCs. The Randles equivalent circuit is the most widely used model in the electrochemical field, which was also applied in our work.

In order to understand the interior mechanism, we put all the details in the following figure (Fig.S8 (a)). On the base of the relation of all the parameters, the Randles equivalent circuit is designed (Fig.S8 (b)). So the total impedance Z can be deduced to be the following equation:

$$Z = R_{\Omega} + \frac{1}{\frac{1}{Z_F} + j\omega C_d} = R_{\Omega} + \frac{Z_F}{1 + j\omega C_d Z_F} \quad \text{S-(4)}$$

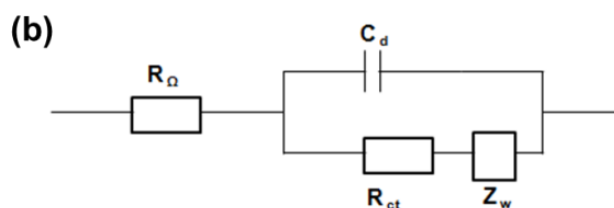
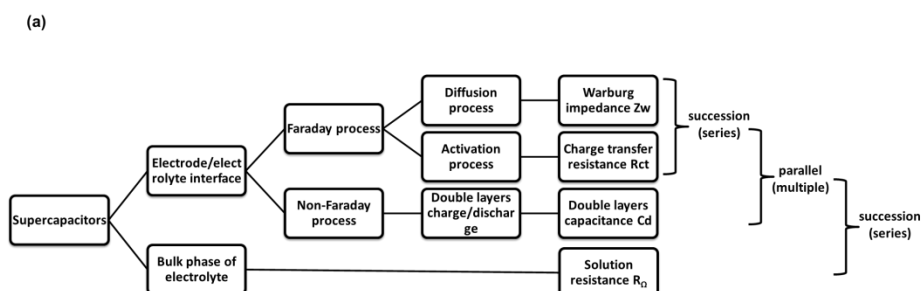


Figure.S8 (a) The interior mechanism of SCs and the physical meaning of the parameters. (b) The Randles equivalent circuit.

S6. Galvanostatic charge/discharge curves

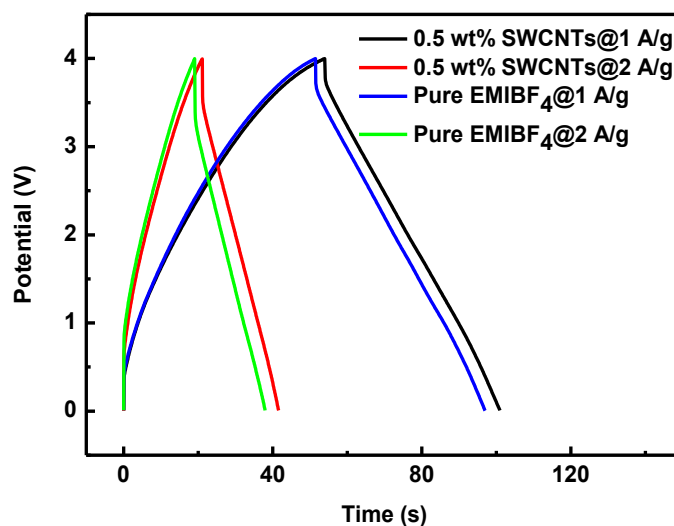


Figure.S9 Galvanostatic charge/discharge curves of using pure ILs or nanofluids electrolyte under different current densities.

According to

$$E = \int_0^t I_g U(t) dt \quad \text{S-(5)}$$

Where E is the energy density, I_g is the constant current, and U(t) is the voltage function vs. the time. The larger of the enclosed area, the higher of the energy density, in agreement with the CV curves. Moreover, IR drop became much smaller as adding 0.5 wt% SWCNTs. It further confirmed our conclusion.

S7. CV curve for long time cycle test.

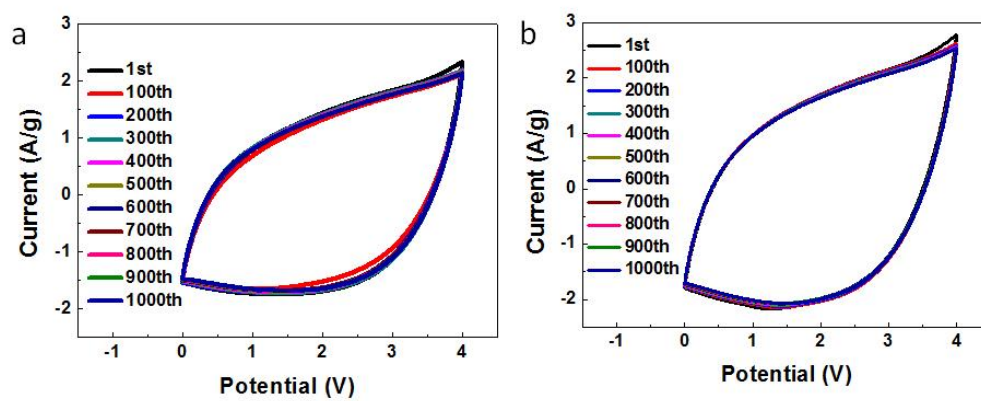


Figure.S10 CV curves of electrode in pure ILs electrolyte of EMIBF₄ at 200 mV/s and 4 V (a)

and in nanofluid electrolyte containing 0.5 wt% SWCNTs in EMIBF₄ at 200 mV/s and 4 V(b)