# Journal of Materials Chemistry A

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# ARTICLE

Cite this: DOI: 10.1039/xoxxooooox

Identifying Pseudocapacitance of Fe<sub>2</sub>O<sub>3</sub> in Ionic Liquid and its Application in Asymmetric Supercapacitors

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Received ooth January 2012, Accepted ooth January 2012

DOI: 10.1039/x0xx00000x

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Pseudocapacitance is commonly associated with surface or near-surface reversible redox reactions, as observed with transition metal oxides in alkaline aqueous electrolytes. Here, we demonstrate that a pseudocapacitive behavior of Fe<sub>2</sub>O<sub>3</sub> can occur in 1-ethyl-3methylimidazolium tetrafluoroborate (EMIMBF<sub>4</sub>) ionic liquid (IL), and it is closely related to the chemical state variation between Fe<sup>3+</sup> and Fe<sup>2+</sup> on the surface of Fe<sub>2</sub>O<sub>3</sub> electrode during the charging/discharging process. By taking advantage of such pseudocapacitance, we prepare a promising electrode material, i.e., graphene nanosheets-supported  $Fe_2O_3$  nanoparticles (denoted as  $Fe_2O_3(\alpha GNS)$ , and then build high-performance asymmetric supercapacitors (ASs) using  $Fe_2O_3$  (CMR) as the battery-type electrode material, commercial activated carbon (AC)/or activated polyaniline-derived carbon nanorods (denoted as APDC) as the capacitortype electrode material, and EMIMBF<sub>4</sub> IL as the electrolyte. As-made ASs are able to work reversibly in a full operation voltage region of  $0 \sim 4$  V and exhibit very high energy density. Especially, the AS of Fe<sub>2</sub>O<sub>3</sub>@GNS//APDC gains an extremely high energy density of 177 Wh·kg<sup>-1</sup> and shows superior combination of high energy and power density (the energy density still remains 62.4 Wh·kg<sup>-1</sup> even at a high power density of 8 kW·kg<sup>-1</sup>).

# Introduction

Supercapacitors, also called as electrochemical capacitors, have attracted considerable attention in recent years because they are able to provide high power density, fast charge process, long cycle life and low maintenance cost.<sup>1,2</sup> Supercapacitors have been currently used in various energy storage systems; however, the major drawback of lower energy density compared to rechargeable batteries severely limits their extended applications.<sup>3-6</sup> By the formula of  $E=1/2 \ CV^{2}$ ,<sup>7</sup> the increase of the energy density (E) can be achieved by maximizing the specific capacitance (C) and the operation voltage (V). It is now widely recognized that asymmetric supercapacitors (ASs), combining a capacitor-type electrode and a battery-type Faradaic electrode, not only can increase the specific capacitance but also can enlarge the operation voltage, resulting in the greatly enhanced energy density.<sup>8-10</sup> Concerning the capacitortype electrode, various carbon materials are commonly used as electrochemical double layer capacitance (EDLC) materials to boost the power density due to their excellent chemical stability, high rate capacity and acceptable cost.<sup>11-13</sup> Concerning the battery-type electrode, different pseudocapacitive materials, in particular transition metal (Ru, Mn, Co, Ni, Fe, V, Sn, etc.) oxides are widely used to enlarge the operating voltage and enhance the energy storage capacity due to their desired redox potential and outstanding pseudocapacitive properties.<sup>2,9,10,14,15</sup> It is well known that pseudocapacitance is commonly associated with surface or nearsurface reversible redox reactions of pseudocapacitive materials in aqueous electrolytes.<sup>16,17</sup> However, in aqueous media the potential windows of ASs are limited in the range of 0~2.5 V due to the low

decomposition potential of water,18-20 resulting in the still unsatisfactory energy density (below 80 Wh kg<sup>-1</sup>).<sup>21,22</sup> Therefore, exploring suitable non-aqueous electrolytes, where two charge storage mechanisms (EDLC and pseudocapacitance) are able to act together, is one of the most important tasks in the field of ASs.

Ionic liquids (ILs), a class of room-temperature molten salts, are a kind of potential electrolytes for EDLC supercapacitors.<sup>23,24</sup> Recent studies have demonstrated that the operation voltage of carbon materials in ILs is able to reach 2.5~4 V, resulting in high energy density.<sup>25-28</sup> However, excepted for RuO<sub>2</sub>, MnO<sub>2</sub> and CuO.<sup>29-32</sup> the pseudocapacitive behavior of other transition metal oxides in ILs is rarely reported to date. Thereby, to bulid high-performance ASs with ILs, it is very necessary to exploit other alternative transition metal oxides, which have obvious pseudocapacitance in given ILs, and which are also inexpensive, natural abundance and environmental friendliness.

Iron is the second most abundant metal in the earth crust and iron oxides are low cost and environmentally benign nature. In this work, the pseudocapacitive behavior of Fe<sub>2</sub>O<sub>3</sub> in an IL electrolyte, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF<sub>4</sub>), is first identified. It is closely related to the chemical state variation between Fe<sup>3+</sup> and Fe<sup>2+</sup> on the surface of Fe<sub>2</sub>O<sub>3</sub> electrode during the charging/discharging process. Furthermore, in order to increase the specific capacitance of Fe<sub>2</sub>O<sub>3</sub> material in EMIMBF<sub>4</sub>, graphene nanosheets-supported Fe<sub>2</sub>O<sub>3</sub> nanoparticles (denoted as Fe<sub>2</sub>O<sub>3</sub>@GNS) are prepared through a simple hydrothermal synthesis. On this basic, advanced ASs are successfully fabricated by using as-prepared

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Fe<sub>2</sub>O<sub>3</sub>@GNS as the battery-type electrode material, commercial activated carbon (AC)/or we prepared activated polyaniline-derived carbon nanorods (denoted as APDC) as the capacitor-type electrode material, and EMIMBF<sub>4</sub> as the electrolyte. As-made ASs are able to work reversibly in a full operation voltage region of 0~4 V and thus exhibit extremely high energy density (118 Wh·kg-1 for the AC//Fe<sub>2</sub>O<sub>3</sub>@GNS AS and 177 Wh·kg<sup>-1</sup> for the APDC//Fe<sub>2</sub>O<sub>3</sub>@GNS AS).

#### Experimental

#### Materials and chemicals

High-purity graphite powder (99.9%, 325 mesh) was purchased from Qingdao Huatai Tech. Co., Ltd., China. EMIMBF<sub>4</sub> IL was obtained from the Center for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. All conventional chemicals were of analytical grade and were used without further purification. Ultrapure water was used in all experiments.

#### Synthesis of Fe<sub>2</sub>O<sub>3</sub>

In a typical synthesis,<sup>33</sup> 2 mmol of FeCl<sub>3</sub> was dissolved in 20 ml of ultrapure water. After magnetic stirring for 30 min, the solution was transferred to a Teflon-lined stainless autoclave. The autoclave was sealed and heated at 140 °C for 12 h and then cooled to room temperature naturally. The obtained Fe<sub>2</sub>O<sub>3</sub> particles were filtered, washed with ethanol and water, and then dried at 60 °C in vacuum.

#### Synthesis of Fe<sub>2</sub>O<sub>3</sub>@GNS

Graphene oxide (GO) nanosheets were synthesized from natural graphite flake by a modified Hummers method, as described elsewhere.<sup>34</sup> GNSs were obtained by reducing GO nanosheets in 0.5 mol L<sup>-1</sup> NaOH solution at 80 °C for 1 h.<sup>35</sup> For the preparation of Fe<sub>2</sub>O<sub>3</sub>@GNS, 40 mL of GNS aqueous suspension (1 mg mL<sup>-1</sup>) was prepared with aid of sonication, and then slowly added into 10 mL of FeCl<sub>3</sub> solution (0.1 mol  $L^{-1}$ ). The mixture was heated to 85 °C and kept at this temperature for 5 h. The obtained Fe<sub>2</sub>O<sub>3</sub>@GNS product was filtered, washed with water, and then dried at 60 °C in air.

#### Synthesis of APDC

Polyaniline (PANi) nanorods were synthesized by oxidative polymerization of aniline with ammonium per-sulfate in an aqueous solution containing citric acid.<sup>36</sup> As-prepared PANi nanorods were pyrolyzed at 800 °C for 1 h under argon atmosphere to obtain PANiderived carbon (PDC). Subsequently, KOH activation was carried out as follows. Typically, 0.4 g of PDC was impregnated with 3.2 g of KOH in aqueous phase with the aid of sonication. After the removal of water, the dried PDC/KOH mixture was heated at 800 °C for 1 h under argon atmosphere. After being cooled down to room temperature, the product was washed with dilute HCl solution and ultrapure water until the pH value of the washing water reached 7, and then dried at 60 °C in air.

#### Structural characterization

Field emission scanning electron microscopy (FESEM; JSM 6701F), transmission electron microscopy (TEM; JEOL 2100 FEG), powder X-ray diffraction (XRD; Rigaku D/Max-2400, Cu-Ka radiation) and Raman spectroscopy (JY-HR800, the excitation wavelength of 532 nm) were employed to investigate the structure of as-prepared electrode materials. The nitrogen adsorption-desorption

isotherm measurements were performed on a Micromeritics ASAP 2020 volumetric adsorption analyzer at 77 K. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area. The pore-size distribution was determined by a nonlocal density functional method using the nitrogen adsorption data, and assuming a slit pore model. The changes of surface chemical compositions of Fe<sub>2</sub>O<sub>3</sub> electrode after charging and discharging were examined by X-ray photoelectron spectroscopy (XPS; Perkin-Elmer PHI-5702) with 1486.6 eV radiation as the excitation source.

#### Electrode preparation and electrochemical measurements

The working electrodes were prepared as follows: 80 wt % of sample was mixed with 7.5 wt % of acetylene black and 7.5 wt % of conducting graphite in an agate mortar until a homogeneous black powder was obtained. To this mixture, 5 wt % of poly(tetrafluoroethylene) was added with a few drops of ethanol. After briefly allowing the solvent to evaporate, the resulting paste was pressed at 10 MPa to the nickel gauze with a nickel wire for an electric connection. The assembled electrodes were dried for 12 h at 60 °C in air.

Electrochemical measurements of each electrode material were firstly performed using an electrochemical working station (CHI660D, Shanghai, China) in a three-electrode system in EMIMBF<sub>4</sub> IL electrolyte at room temperature. A platinum gauze electrode and a saturated calomel electrode (SCE) served as the counter electrode and the reference electrode, respectively. In threeelectrode system, each electrode contains about 5 mg of electroactive material and has a geometric surface area of about 1 cm<sup>2</sup>. The average specific capacitance value (C) was calculated from the galvanostatic discharge curves, using the following equation:

 $C = I/[(dE/dt) \times m] \approx I/[(\Delta E/\Delta t) \times m] (F \cdot g^{-1})$ (1)Where I is constant discharge current,  $\Delta t$  is the time period for a full discharge, *m* indicates the mass of the corresponding active electrode material, and  $\Delta E$  represents the voltage change after a full discharge.

A two-electrode cell configuration was used to measure the performances of as-made ASs in EMIMBF<sub>4</sub> electrolyte. The loading mass ratio between positive and negative materials was optimized according the reported methods and our earlier work.<sup>8,9,52</sup> Here the mass loading of positive material (commercial AC or as-prepared APDC) and negative material (Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>2</sub>O<sub>3</sub>@GNS) was 3 mg and 2 mg, respectively. For building a cell, in a glove box filled with argon, two electrodes separated by a porous nonwoven cloth separator were pressed together and assembled into a coin cell (2032 style). After injecting EMIMBF<sub>4</sub> electrolyte, the cell was covered by pressure. The energy density (E) of ASs can be achieved by the specific capacitance (C) and the cell voltage (V) according to the following equation: (g<sup>-1</sup>)

$$E=0.5 \ CV^2$$
 (Wh·k

The power density (P) of ASs can be achieved by the E and the discharging time (t) according to the following equation:  $P = E/t (W \cdot kg^{-1})$ (3)

# **Results and discussion**

As shown in Figure 1a, as-synthesized Fe<sub>2</sub>O<sub>3</sub> presents homogeneous and cubic particles. In the X-ray diffraction (XRD) pattern shown in Figure 1b, all diffraction peaks are in good agreement with the bulk  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystal phase (PDF#33-0664) and no additional peaks of other phase have been detected, indicating high purity and good crystallinity of Fe<sub>2</sub>O<sub>3</sub> product. Transmission electron microscopy (TEM) image and the corresponding selective area electron diffraction (SAED) pattern further verify the cubic α-

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Fe<sub>2</sub>O<sub>3</sub> crystal structure (see Figure S1 in Supporting Information). The existence of these diffraction rings indicates the polycrystalline nature of the single cubic particle, and the measured *d*-spacing from SAED pattern could be assigned to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, which is consistent with the result of XRD. To study the pseudocapacitive behavior of Fe<sub>2</sub>O<sub>3</sub> in an IL electrolyte, EMIMBF<sub>4</sub> was chosen because it has high conductivity and low melting point,<sup>37,38</sup> and it is the most common IL in reported nanocarbon-based symmetric supercapacitors.<sup>39-41</sup> Figure 1c shows the cyclic voltammetry (CV) curve of as-prepared α-Fe<sub>2</sub>O<sub>3</sub> particles measured in EMIMBF<sub>4</sub> electrolyte at a scan rate of 5 mV·s<sup>-1</sup>. There are distinct redox peaks in the CV curve, indicating the high reactivity and obvious pseudocapacitive behavior of Fe<sub>2</sub>O<sub>3</sub> particles in EMIMBF<sub>4</sub> electrolyte. In addition, as shown in Figure 1d, the electrochemical impedance spectroscopy (EIS) plot of asprepared Fe<sub>2</sub>O<sub>3</sub> in EMIMBF<sub>4</sub> is very similar to that of Fe<sub>2</sub>O<sub>3</sub> in aqueous electrolyte.<sup>42</sup> The distinct Warburg region (45° phase angle) in the low frequency range indicates the high ion diffusion resistance,43,44 and the obvious semicircle at high frequency range indicates the low electronic conductivity and intrinsically high charge-transfer resistance at the Fe2O3 electrode.45 The exactly fitting data of Nyquist plots of Fe<sub>2</sub>O<sub>3</sub> is shown in Table S1.



**Figure 1.** Structure characteristics of as-prepared Fe<sub>2</sub>O<sub>3</sub> and its electrochemical properties in EMIMBF<sub>4</sub> electrolyte under a threeelectrode system: (a) SEM image, (b) XRD pattern, (c) CV curve at a scan rate of 5 mV s<sup>-1</sup>, and (d) Nyquist plot. Inset shows the equivalent circuit and the data of high frequency range.

We believe that the pseudocapacitive behavior of  $Fe_2O_3$  particles in EMIMBF<sub>4</sub> should be closely related to a chemical state variation of  $Fe_2O_3$  in the process of charging and discharging. To verify the reaction mechanism, the  $Fe_2O_3$  electrode after discharging and charging in EMIMBF<sub>4</sub> at the scan rate of 5 mV·s<sup>-1</sup> was examined by X-ray photoelectron spectroscopy (XPS), and the corresponding  $Fe_{2p}$ and large-region (200~750 eV) XPS spectra are shown in Figure 2.

In Figure 2a, the Fe<sub>2p</sub> XPS spectrum of the charged electrode can be fitted into three peaks, the peak of Fe<sub>2p3/2</sub> at 711 eV, the peak of Fe<sub>2p1/2</sub> at 725 eV and the satellite peak of Fe<sub>2p3/2</sub>(Fe<sub>2p3/2,sat</sub>) at 718.6 eV, which are well consistence with the signals of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.<sup>46</sup> It indicates that the valence state of Fe element is +3 in the electrode after charging. In comparison, as shown in Figure 2b, the Fe<sub>2p</sub> XPS spectrum of the discharged electrode can be fitted into four different peaks, the peak of Fe<sub>2p3/2</sub>(Fe<sub>2p3/2,sat</sub>) at 718.6 eV, and the peak at around 716 eV. Compared with Figure 2a, the main differences are the remarkable intensity reduction of the peak of Fe<sub>2p3/2,sat</sub> and the appearance of the peak at 716 eV. It is reported that the peak at around 716 eV is normally assigned to the satellite structure of the Fe<sup>2+</sup> ions, analogous to the spectrum of FeO.<sup>47,48</sup> This result suggests that some trivalent Fe would change to bivalent Fe during the discharging process. In turn, during the charging process, the valence state of the reduced bivalent Fe can change to trivalent Fe in the electrode as shown in Figure 2a.



**Figure 2.** Well-fitted  $Fe_{2p}$  XPS spectra of the  $Fe_2O_3$  electrode after charging (a) and discharging (b) in EMIMBF<sub>4</sub> electrolyte at a scan rate of 5 mV·s<sup>-1</sup>, (c) large-region XPS spectra of the  $Fe_2O_3$  electrode after charging and discharging.

Moreover, as shown in Figure 2c, the  $N_{1s}$  signal that comes from [EMIM]<sup>+</sup> appears in the discharged curve and disappears in the charged curve. It indicates that [EMIM]<sup>+</sup> ions exist on the discharged electrode surface accompanied by the formation of Fe<sup>2+</sup> ions and then disappear on the charged electrode surface. Based on the above results, Figure 3 shows a schematic of the pseudocapacitive mechanism of Fe<sub>2</sub>O<sub>3</sub> in EMIMBF<sub>4</sub> electrolyte during charge/discharge and the corresponding reactions. The peaks of the CV curve presented in Figure 1c are caused by redox reactions of Fe<sub>2</sub>O<sub>3</sub> in EMIMBF<sub>4</sub> electrolyte.

The deoxidization peak is caused by the following reaction:

 $Fe^{III}_{2}O_{3}+x[EMIM]^{+}+xe \leftrightarrow Fe^{III}_{2}Fe^{III}_{2-x}O_{3}[EMIM]_{x}$ 

The oxidation peak is caused by the reversed reaction:  $Fe^{III}_{2}Fe^{II}_{2-x}O_{3}[EMIM]_{x} \leftrightarrow Fe^{III}_{2}O_{3}+x[EMIM]^{+}+xe^{-1}$ 

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Figure 3. A schematic showing the pseudocapacitive mechanism of  $Fe_2O_3$  occurring in EMIMBF<sub>4</sub> during the charging/discharging process.

The successful identification of the pseudocapacitance behavior of Fe<sub>2</sub>O<sub>3</sub> in EMIMBF<sub>4</sub> makes it be possible to devise advanced ASs using Fe<sub>2</sub>O<sub>3</sub> as the battery-type electrode material and EMIMBF<sub>4</sub> as the IL electrolyte. Then, in order to enhance the electrochemical performance of Fe<sub>2</sub>O<sub>3</sub> particles in EMIMBF<sub>4</sub> electrolyte, GNSs were used as templates to grow Fe<sub>2</sub>O<sub>3</sub> nanoparticles (see Figure S2 in Supporting Information). The adding of GNSs can enhance the electrical conductivity of as-prepared Fe<sub>2</sub>O<sub>3</sub>@GNS composite, but also confine the size of the Fe<sub>2</sub>O<sub>3</sub> nanoparticles. Figure 4a and 4b display the XRD patterns and Raman spectra of as-prepared Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>@GNS, which both prove the coexistence of graphene and Fe<sub>2</sub>O<sub>3</sub> phases in Fe<sub>2</sub>O<sub>3</sub>@GNS. Figure 4c and 4d are TEM images of Fe<sub>2</sub>O<sub>3</sub> nanoparticles grown on a GNS. As the images show,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles are uniformly distributed on this GNS, and their sizes are usually smaller than 5 nm. Additionally, as-prepared Fe<sub>2</sub>O<sub>3</sub>@GNS shows an obvious mesoporous structure (see Figure S3 in Supporting Information) with a high specific surface area of 290.2  $m^2 \cdot g^{-1}$  and an average pore size of 3.1 nm.

A comparison of the electrochemical properties between Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>@GNS in EMIMBF<sub>4</sub> electrolyte under a three-electrode system was carried out, and Figure 4e-4h and Figure S4 show the corresponding results. As the CV curves show (Figure 4e), Fe<sub>2</sub>O<sub>3</sub>@GNS also has a pseudocapacitive behaviour, and its CV area is much larger than that of Fe<sub>2</sub>O<sub>3</sub>, meaning that Fe<sub>2</sub>O<sub>3</sub>@GNS possesses a higher specific capacitance. Figure 4f displays the galvanostatic charge/discharge (GCD) curves of as-prepared Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>@GNS in EMIMBF<sub>4</sub> electrolyte at a current density of 1 A g<sup>-1</sup>. Nearly symmetric potential-time curves imply the high charge/discharge columbic efficiency and low polarization of Fe<sub>2</sub>O<sub>3</sub>. Such triangular curves with a slight curvature are similar to that of MnO<sub>2</sub> in IL electrolyte,<sup>31</sup> indicating good electrochemical reversibility. As shown in Figure 4g, the specific capacitance values of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>@GNS are 53.5 and 143  $F \cdot g^{-1}$  at 0.2  $A \cdot g^{-1}$ . With increasing the current density, Fe<sub>2</sub>O<sub>3</sub>@GNS still shows much higher capacitances than Fe<sub>2</sub>O<sub>3</sub>. Moreover, as the Nyquist plots show in Figure 4h and the exactly fitting data of Nyquist plots show in Table S1, compared with the Fe<sub>2</sub>O<sub>3</sub> electrode, the Fe<sub>2</sub>O<sub>3</sub>@GNS electrode features a higher phase angle (exceeding 45°) in the low frequency range, indicating the faster ion transfer behaviour; the Fe<sub>2</sub>O<sub>3</sub>@GNS electrode has a smaller semicircle in the high frequency range, indicating the obviously decreased charge transfer resistance; the  $Fe_2O_3$  (a) GNS electrode shows a smaller real axis intercept (inset of Figure 4h), indicating a much smaller bulk resistance. We believe that the remarkably improved electrochemical properties of the Fe<sub>2</sub>O<sub>3</sub>@GNS electrode mainly derive from its unique structure: the quantum-size Fe<sub>2</sub>O<sub>3</sub> particles increase the electrochemical utilization

of the active material, the electro-conductive GNSs accelerate the electron transfer inside the electrode material, and the high surface area of  $Fe_2O_3$ @GNS facilitates the rapid transport of the ions of the electrolyte.



**Figure 4.** Structure characteristics of as-prepared  $Fe_2O_3@GNS$ : (a) XRD patterns of  $Fe_2O_3$  and  $Fe_2O_3@GNS$ , (b) Raman spectra of  $Fe_2O_3$ , GNSs and  $Fe_2O_3@GNS$ , and (c and d) TEM images of  $Fe_2O_3@GNS$  with low and high magnifications. Inset of (d) shows the HRTEM image of an individual  $Fe_2O_3$  nanoparticle. A comparison of electrochemical properties between  $Fe_2O_3$  and  $Fe_2O_3@GNS$  in EMIMBF<sub>4</sub> electrolyte under a three-electrode system: (e) CV curves at a scan rate of 5 mV s<sup>-1</sup>, (f) GCD curves at a current density of 1 A g<sup>-1</sup>, (g) the specific capacitance as a function of discharge current density, and (h) Nyquist plots. The insets show the equivalent circuit and the data of high frequency range.

AC materials, with high BET surface area and well-controlled pore structure, enable the formation of effective EDLC to facilitate the fast transport of electrolyte ions, and thus can fulfill the demand of high power delivery performance from ASs.<sup>2,8,9</sup> In this study, two kinds of ACs including commercial AC and we prepared APDC were chosen to combine with as-made Fe<sub>2</sub>O<sub>3</sub>@GNS respectively, to build ASs. As shown in Figure S5, as-prepared nanorods-like APDC exhibits a type-IV isotherm for mesoporous characteristic and its specific surface area is about 3350 m<sup>2</sup>·g<sup>-1</sup>. In comparison, commercial AC shows a type-I isotherm for microporous characteristic and its specific surface area is about 2200 m<sup>2</sup>·g<sup>-1</sup>. Figure S6 displays the electrochemical characteristics of two ACs in EMIMBF<sub>4</sub> electrolyte under the three-electrode system. They both have nearly rectangular shaped CV curves, relatively linear-andsymmetrical GCD curves and low impedance. The specific Journal Name

capacitances for commercial AC and APDC are about 150 and 230  $F \cdot g^{-1}$  at the current density of 0.5 A  $\cdot g^{-1}$ . Even at a relatively high current density of 5 A  $\cdot g^{-1}$ , APDC still retains a high capacitance of 165  $F \cdot g^{-1}$ . These results indicate that the two ACs, especially APDC, can deliver high specific capacitance and good rate ability, making them suitable to pair with as-prepared  $Fe_2O_3@GNS$  to build advanced ASs.



**Figure 5.** Electrochemical characteristics of as-made ASs: (a) Schematic of the assembled structure. (b) CV curves at a scan rate of 20 mV·s<sup>-1</sup>, (c) GCD curves at a current density of  $1 \text{ A} \cdot \text{g}^{-1}$ , (d) the specific capacitance as a function of discharge current density, (e) Nyquist plots (inset showing the data of high frequency range), and (f) capacitance retention and Coulombic efficiency of Fe<sub>2</sub>O<sub>3</sub>@GNS//APDC at a current density of  $1 \text{ A} \cdot \text{g}^{-1}$ .

In order to actually utilize the pseudocapacitive behaviour of  $Fe_2O_3$  in EMIMBF<sub>4</sub> IL electrolyte, three ASs including  $Fe_2O_3//AC_2$ Fe<sub>2</sub>O<sub>3</sub>@GNS//AC and Fe<sub>2</sub>O<sub>3</sub>@GNS//APDC were respectively built. Figure 5a shows the schematic of the assembled structure for the ASs. The operated voltage of the Ass is optimized by compared the electrochemical performance of Fe2O3@GNS//AC AS at different range within the limiting operating voltage of [EMIM]BF<sub>4</sub> ionic liquid electrolyte  $(0{\sim}4 \text{ V})$ .<sup>28</sup> From Figure S7 we can find at the same scan rate the electrochemical performance of Fe2O3@GNS//AC is best within the operated voltage ranging from 0 to 4 V. The optimized operated voltage is ragging from 0 to 4 V. Figure 5b shows the CV curves of as-made ASs measured at a scan rate of 20 mV s<sup>-1</sup>. In the full operated voltage ranging from 0 to 4 V, all CV curves exhibit a relatively quasi-rectangular shape and possess obvious redox peaks. Among them, Fe<sub>2</sub>O<sub>3</sub>@/GNS//APDC shows the largest CV area, indicating that it possesses the highest specific capacitance. Figure 5c shows GCD curves of the ASs at the current density of 1 A·g<sup>-1</sup>. For Fe<sub>2</sub>O<sub>3</sub>@GNS//AC and Fe<sub>2</sub>O<sub>3</sub>@GNS//APDC, a good liner relation of the charging/discharging potentials with time is observed, indicating a rapid current-potential response and small equivalent series resistance.<sup>8,49,50</sup> Also, their curves display quasitriangular shape, demonstrating the good electrochemical reversibility and Columbic efficiency. The specific capacitance is calculated from the discharge curves with values of 44.2, 57.1 and 79.6  $F \cdot g^{-1}$  at the current density of 0.1  $A \cdot g^{-1}$  for  $Fe_2O_3//AC$ , Fe<sub>2</sub>O<sub>3</sub>@GNS//AC and Fe<sub>2</sub>O<sub>3</sub>@GNS//APDC, respectively. As showed in Figure 5d, at a relatively high current density of 3 A  $g^{-1}$ the specific capacitance still remains at 17.0, 28.7 and 41.0  $F \cdot g^{-1}$ , respectively. EIS spectra (Figure 5e) further show that as-fabricated

Fe<sub>2</sub>O<sub>3</sub>@GNS//AC and Fe<sub>2</sub>O<sub>3</sub>@GNS//APDC have lower electronic and ionic resistances at high frequency range, and more vertical line characteristic of capacitive behaviour at low frequency range, indicating the fast charging/discharging behaviour. Furthermore, as shown in Figure 5f, for Fe<sub>2</sub>O<sub>3</sub>@GNS//AC, there is 81.5% capacitance retention after 2000 cycles in EMIMBF<sub>4</sub> electrolyte at 1 A·g<sup>-1</sup>, indicating its good electrochemical stability. In addition, it displays excellent Columbic efficiency during the whole cycling test.

Figure 6a shows Ragone plots of as-fabricated three ASs. As the plots show, Fe<sub>2</sub>O<sub>3</sub>@GNS//APDC has the highest energy and power density. It can gain a maximum energy density of 177 Wh kg<sup>-1</sup> at a low power density of 200 W kg<sup>-1</sup> and it remains 62.4 Wh kg<sup>-1</sup> at a high power density of 8 kW kg<sup>-1</sup>, indicating superior combination of high energy and power density. Furthermore, this maximum value of energy density is much higher than other reported different types of supercapacitors summarized in Figure 6b, including aqueous ASs  $Wh \cdot kg^{-1}$ ) such as AC//Co(OH)<sub>2</sub> (25.7 and porous graphene//Ni(OH)2@GNS (77.8 Wh·kg<sup>-1</sup>),<sup>8,51</sup> lithium-ion hybrid supercapacitors such as H<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>//mesoporous carbon (90 Wh·kg<sup>-1</sup>) and TiO2@GNS//AC (42 Wh kg<sup>-1</sup>),<sup>52,53</sup> supercapacitors using IL electrolytes such as GNS//GNS (85.6 Wh kg<sup>-1</sup>) and AC//MnO<sub>2</sub> (67.5 Wh·kg<sup>-1</sup>).<sup>29,31</sup>



Figure 6. (a) Ragone plots (energy density vs. power density) of asmade ASs. (b) A comparison among our ASs with other reported different types of supercapacitors. 1 Our work. Fe<sub>2</sub>O<sub>3</sub>@GNS//APDC in EMIMBF<sub>4</sub> electrolyte; 2. our work: Fe<sub>2</sub>O<sub>3</sub>@GNS//AC in EMIMBF<sub>4</sub> electrolyte; 3. GNS//GNS in EMIMBF<sub>4</sub> electrolyte; 4.  $AC//MnO_2$  in IL electrolyte; 5. H<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>//mesoporous carbon in Li<sup>+</sup>-containing organic electrolyte; 6. TiO<sub>2</sub>@GNS//AC in Li<sup>+</sup>-containing organic electrolyte; 7. porous graphene//Ni(OH)2@GNS in KOH aqueous electrolyte; 8. AC//Co(OH)<sub>2</sub> in KOH aqueous electrolyte.

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#### Conclusions

To summarize, we have indentified the pseudocapacitive behavior of Fe<sub>2</sub>O<sub>3</sub> in EMIMBF<sub>4</sub> IL, and proved that it is closely related to the chemical state variation between Fe<sup>3+</sup> and Fe<sup>2+</sup> on the surface of Fe<sub>2</sub>O<sub>3</sub> electrode during the charging/discharging process. Also, by taking advantage of GNSs, we have prepared a promising supercapacitor electrode material, i.e., graphene nanosheetssupported Fe<sub>2</sub>O<sub>3</sub> nanoparticles. Such mesoporous Fe<sub>2</sub>O<sub>3</sub>@GNS, with a high specific surface area and quantum-size  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, provides the right combination of an electrode active material in supercapacitors with enhanced specific capacitance and improved electron and ion transfer capability in EMIMBF<sub>4</sub> electrolyte. On this basic, we have successfully built two advanced ASs, i.e., Fe<sub>2</sub>O<sub>3</sub>@GNS//AC and Fe<sub>2</sub>O<sub>3</sub>@GNS//APDC, by taking advantage of pseudocapacitive behavior of Fe<sub>2</sub>O<sub>3</sub> and EDLC behavior of ACs. They are able to work reversibly in a full operation voltage region of 0~4 V and thus exhibit very high energy density. Especially, Fe<sub>2</sub>O<sub>3</sub>@GNS//APDC gains a maximum energy density of 177 Wh kg<sup>-1</sup> and shows superior combination of high energy and power density (the energy density still remains 62.4 Wh kg<sup>-1</sup> even at a high power density of 8 kW·kg<sup>-1</sup>). The results presented here may provide a new direction to explore the energy storage behavior and mechanism of more transition metal oxides in IL electrolytes, and give a new insight for designing and fabricating high-performance ASs.

# Acknowledgement

This work was supported by the Top Hundred Talents Program of Chinese Academy of Sciences and the National Nature Science Foundations of China (21203223 and 21303234).

# Notes and references

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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We indentify the pseudocapacitive behaviour of  $Fe_2O_3$  in ionic liquid electrolyte, and build high-performance asymmetric supercapacitors by utilizing such pseudocapacitance.

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