Facilely synthesized Fe₂O₃–graphene nanocomposite as novel electrode materials for supercapacitors with high performance

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ABSTRACT

Fe₂O₃–graphene nanocomposite with high capacitive properties had been prepared friendly and facilely by hydrothermal method in one-step. The morphology and structure of the obtained material were examined by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) and transmission electron microscope (TEM) techniques. It was revealed by TEM images that Fe₂O₃ nanoparticles grow well on the surface of graphene and the formation of Fe₂O₃ nanoparticles hinders the aggregation of graphene (reduced graphene oxide, namely, RGO). Electrochemical properties of the synthesized materials were characterized by serials of electrochemical measurements in 1 M Na₂SO₄ electrolyte. Fe₂O₃–graphene nanocomposite electrode show higher specific capacitance than graphene, indicating an accelerative effect of Fe₂O₃ and graphene on improving the electrochemical performance of the electrode. The specific capacitance of Fe₂O₃–graphene nanocomposite is 226 F/g at a current density of 1 A/g. These attractive results indicate it is possible to seek and develop the promising, environmentally benign and commercial electrodes material based on Fe₂O₃ and graphene.

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1. Introduction

Since the continuous increase of the world's population, the shortage of energy has become one of the major issues in many countries worldwide, in recent years. Supercapacitors are typical energy storage devices which have attracted much attention because of its important features including high power density and long cycle life [1–3]. Compared with conventional capacitors, supercapacitors possess higher power capability and relatively larger energy density, which is a promising potential to meet the increasing power demands of energy storage systems [4]. The energy stored in supercapacitors mainly by means of either ion adsorption at the electrode/electrolyte interface (namely, electrical double layer capacitor EDLCs) or fast and reversible faradic reactions (namely, pseudocapacitors) [5]. In order to obtain supercapacitors with well electrochemical properties, variety of materials has been investigated as possible supercapacitor electrode.

Graphene, a two-dimensional carbon material with unique mechanic and electronic properties, offers promising prospects and draws extensive attentions since 2004. As a low dimensional material, graphene has a huge theoretical specific area of 2600 m²/g and presents an excellent electrical conductivity of 7200 S/m at room

temperature [6–11]. These encouraging characteristics make such new materials have a wide range of potential applications and attracted great interests in developing graphene composites with other materials [12,13]. Graphene based composites with metal oxides (RuO₂, MnO₂, ZnO, SnO₂, Co₃O₄) or conducting polymers (polyaniline, polypyrrole, and polythiophene) have also shown unique electronic and electrochemical properties [14–24]. Among these metal oxides used as supercapacitor, the research on Fe₂O₃ is relatively rare, however, Fe₂O₃ is abundant, low cost, and non-toxic and is therefore deserves being investigated as supercapacitors [25,26].

Recently, lots of work, which focused on ferric nanocomposite, have been reported [27–39]. Among them, ferric and graphene nanocomposite are newly reported. Ruoff's group has prepared graphene–Fe₂O₃ nanosheet materials as a high performance anode material in two steps [27]. Wang's group has prepared different morphology of Fe₂O₃ nanoparticles deposit on graphene with the additional of NH₄H₂PO₄ [28]. Yu's group has prepared the graphene@Fe₂O₃ core–shell nanostructures by three steps: pre-modification of MOs with amine groups, coating of a graphene oxide (GO) layer, and finally conversion of the GO shell to graphene [29]. Yan's group has prepared graphene–Fe₂O₃ nanocomposites through a solvothermal method using ethanol as solvent and ammonia to adjust the pH value and the formation of Fe₂O₃ [30]. Although graphene–Fe₂O₃ nanocomposites with different properties were prepared by the above groups, the preparation methods are time

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consuming or the materials are toxic, besides, these are all about graphene-Fe₂O₃ used for lithium ion batteries. Herein, we report a simple and green method to fabricate graphene-Fe₂O₃ nanocomposites and the electrochemical properties are discussed in detail.

2. Experimental

2.1. Preparation of graphite oxidate and Fe₂O₃-graphene nanocomposites

Graphene oxide (GO) was prepared from natural graphite powder through a modified Hummers' method [40]. Fe₂O₃-graphene nanocomposites was synthesized hydrothermally as followed, 0.5 g GO was dispersed in H₂O and stirred for 12 h to form a homogeneous aqueous dispersion. Then 0.08 g Fe(NO₃)₃ and certain amount of urea were added into the GO dispersion followed by stirring at room temperature overnight, the obtained mixture was transferred to a 100 mL Teflon-lined autoclave and maintained at 180 °C for 24 h. The products were washed with ethanol for several times. The synthesis of graphene was similar to that of Fe₂O₃-graphene except the addition of Fe(NO₃)₃.

2.2. Material characterizations

X-ray diffraction (XRD) patterns of all samples were carried out by a Rigaku powder diffractometer (D/MAX-RB) using Cu K α radiation ($\lambda = 0.15418$ nm) at a scanning rate of 4°/min in $2\theta = 10$ –70°. The structures of the electrode materials were characterized by transmission electron microscopy (TEM, JEOL 3010). Adsorption and desorption isotherms of nitrogen were measured with a NOVA 1200 gas sorption analyser at liquid nitrogen temperature (–196 °C). Before the measurements, the samples were degassed under vacuum condition at 180 °C for 8 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area using adsorption data acquired in a relative pressure (P/P_0) range of 0.5–0.25. The total pore volume was estimated from the amount adsorbed at a relative pressure of about 0.99. The pore size distribution curves were calculated from the analysis of the desorption branch of the isotherm based on the Barrett–Joyner–Halenda (BJH) algorithm. The micropore volume and micropore surface area were estimated by a t -plot method.

2.3. Electrochemical measurements

The electrochemical performances of the as-prepared material electrodes were measured using a cyclic voltammetry (CV) method, galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) on an electrochemical workstation (CHI 660D, Shanghai CH Instrument Company, China) with a typical three-compartment cell at ambient temperature. The as-synthesized electrode materials, a platinum wire electrode and a saturated calomel electrode (SCE) were used as working electrode, counter electrode and reference electrode, respectively. The working electrode was prepared by mixing sample (80 wt.%) as active material with poly(tetrafluoroethylene) (PTFE, 20 wt.%) in ethanol to produce a homogeneous paste. Then the resulting mixture was coated onto the Ni foam substrate. The foam was dried at 80 °C in air for 12 h to remove the solvent. The measurement was carried out in 1 M Na₂SO₄ aqueous electrolyte at room temperature. CV tests were conducted between –1.2 and –0.2 V (vs SCE) at scan rates of 5, 10, 20, 30, 40, 50 and 100 mV s^{–1}. Galvanostatic charge/discharge curves were measured in the potential range of –1 to 0 V at different current densities, and the EIS measurements were also carried out in the frequency range from 100 kHz to 0.1 Hz at open circuit potential with an ac perturbation of 5 mV.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-prepared GO, RGO, Fe₂O₃ and Fe₂O₃-RGO. Fig. 1c is the pattern of Fe₂O₃ nanoparticles, the characteristic peaks are consistent with that of Fe₂O₃ crystals (PDF 33-0664). From Fig. 1d, the broad peak in range of 20–30° is corresponded to the (002) diffraction of graphene. For sample Fe₂O₃-RGO, the characteristic peaks of Fe₂O₃ such as (012), (104), (110), (214), (300) can be seen, while the (002) plane peak of RGO becomes broad and its intensity becomes weak. The peak of GO is similar with the reported [41]. And the phenomenon is in agreement with the other studies, which reports that the diffraction peaks become weak or even disappear if the regular stacks of graphite oxide or graphene are destroyed (for example by exfoliation) [42]. It means that the regular layered structure of graphite oxide or graphene is collapsed. Besides, to confirm the reduction of GO, FTIR of GO and RGO are given in the Supplementary material (Fig. S1).

Fig. 1. XRD patterns of GO (a), RGO (b), Fe₂O₃ (c) and Fe₂O₃-RGO (d).

In order to confirm that the formation of Fe₂O₃ prevent the restacking of graphene nanosheets, nitrogen cryosorption were done to obtain the surface area and porous data of RGO and Fe₂O₃-RGO. The corresponding specific surface area of Fe₂O₃-RGO and RGO are about 357.6 and 40.95 m² g^{–1}, respectively (Fig. 2). The nitrogen adsorption/desorption isotherm of Fe₂O₃-RGO could be considered as a combination of type I and type IV according to the IUPAC classification [43], while RGO shows a typical II characteristics (Fig. 2a). For sample Fe₂O₃-RGO, an H₂-type hysteresis loop is observed in the region of relative pressure of 0.38–0.68 [44]. It is confirmed by the pore distribution shown in Fig. 2b, the pores of Fe₂O₃-RGO are mainly mesopores structure. Sample with high specific surface area and mesopores is favorable for improving both the main pseudocapacitance of metals and the electric double-layer (EDL) capacitance of graphene because of the easily accessible of the hydrated ions in the electrolyte to the exterior and interior pore surfaces [45,46].

The TEM images (Fig. 3) shows the transparent structure of GO and Fe₂O₃ anchored on graphene. It is apparent that the graphene nanosheets are decorated by Fe₂O₃ nanoparticles, and they are mainly 50–80 nm in size (Fig. 3b). However, there was a detectable agglomeration of Fe₂O₃ despite the presence of graphene nanosheets support. The co-formation of Fe₂O₃ on graphene in the presence of urea can be represented as follows:

The electrochemical behavior of the obtained Fe₂O₃-RGO and RGO nanocomposites are investigated using a three-electrode system in a 1 M Na₂SO₄ electrolyte between –1.2 and –0.2 V at different scan rates and the results are shown in Fig. 4A and B. For RGO electrode material, the cyclic voltammetric curves show relatively rectangular in shape for scan rates up to 50 mV/s, indicating an obvious supercapacitive behavior of the RGO electrode. As the scan rate increased (100 mV/s), the peak current increases and the shape of CV curve shows some distortions from an ideal capacitor, it maybe due to the bad rate capability of RGO electrodes. For sample Fe₂O₃-RGO, the CV curves are a bit different from the curves of RGO because the overall capacitance of Fe₂O₃-RGO derives from the combined contribution of the redox pseudocapacitance of Fe₂O₃ and the EDL capacitance of graphene in the composite, while

Fig. 2. N₂ adsorption–desorption isotherm (a) and pore size distribution (b) of RGO and Fe₂O₃-RGO samples at 77 K.

Fig. 3. TEM images of samples GO (A) and Fe₂O₃-RGO nanocomposite (B).

the capacitance of RGO is from EDL capacitance [47]. Furthermore, the CV curve of the Fe₂O₃-RGO electrode exhibits nearly a mirror-image current response on voltage reversal indicating an excellent capacitive property and good reversibility [48]. It is obvious that Fe₂O₃-RGO electrode shows higher integrated area than RGO electrode, indicating the synergistic effect of RGO and Fe₂O₃. The specific capacitances (C_s) were calculated from the CV curves according to the following equation:

$$C_s = \frac{\int IdV}{v m \Delta V}$$

where C_s is the specific capacitances (F/g), I is the response current A, ΔV is the potential window (V), v is the potential scan rate (mV/s), and m is the mass of the electroactive materials in the electrodes (g). The specific capacitance value calculated from the CV curve at 5 mV s⁻¹ is found to be 193.18 and 120 F/g for Fe₂O₃-RGO and RGO, respectively. Fig. 4C and D give the variation of specific capacitances with different current density for RGO and Fe₂O₃-RGO. The capacitance of sample Fe₂O₃-RGO is much higher than the reported a-Fe₂O₃/MWNT [49] and even graphene/Fe₃O₄ [50], this could be ascribed as follows: (i) the pseudocapacitance of Fe₂O₃ and the EDL capacitance of RGO; (ii) the residual C–O and C=O function groups from the partially reductive of GO; (iii) less aggregation of the graphene nanosheets due to the introducing of Fe₂O₃ particles.

The galvanostatic charge/discharge curves of Fe₂O₃-RGO and RGO in 1 M Na₂SO₄ at different current densities are shown in

Fig. 5A and B, respectively. The specific capacitances (C_s) of the electrodes can be calculated according to the following equation:

$$C_s = \frac{It}{(\Delta V)m}$$

where I (A) is the discharge current, m (g) is the mass of the active material in the film electrode, ΔV (V) is the potential window, t is the discharge time, and C_s (F g⁻¹) specific capacitance. It is apparent that the shapes of the discharge curves of the two samples are different mainly owing to the pseudocapacitance of Fe₂O₃, which is in agreement with the analysis of CV measurement. The discharge time of sample Fe₂O₃-RGO is longer than that of RGO at the same current density and mass of the active materials. Table 1 gives the specific capacitance values of the two samples at different current density. The discharge specific capacitance of the Fe₂O₃-RGO electrodes at the current density of 1 A/g is 226 F/g, which is higher than the newly reported [51]. The remarkably increased capacitance of Fe₂O₃-RGO may be caused by the combination of electric double-layer capacitance of RGO and faradic pseudocapacitance of Fe₂O₃. With the increase of the current density, the capacitance of Fe₂O₃-RGO electrode is decrease from 226 to 90.8 F/g. This trend of the capacitance indicates that the partial surface of the electrode is in accessible at the high current density.

EIS analysis is a tool to examine the fundamental behavior of the electrode materials for supercapacitors. For further understanding, the impedance of RGO and Fe₂O₃-RGO composites were measured in the frequency range of 100–0.1 kHz at open circuit

Fig. 4. CV curves of RGO (A) and Fe₂O₃-RGO (B) electrodes at different scan rate; Relationship between specific capacitance and the scan rate (RGO (C), Fe₂O₃-RGO (D)).

Fig. 5. Charge-discharge behavior of Fe₂O₃-RGO (A) and RGO (B) electrodes at different current density.

potential with an ac perturbation of 5 mV before charge process. Fig. 6 shows the Nyquist plots of the electrodes, it indicates that all spectra contain a semicircle in the high frequency region, a straight line inclined at a constant phase in the mid-frequency region, and an almost vertical capacitive line in the low frequency region. The semicircle at high frequency range is due to the charge transfer reaction at the interface of the electrolyte/oxide electrode; and it corresponds to the charge transfer resistance (R_{ct}) [52]. Warburg impedance is related to the diffusional impedance of the elec-

Table 1

Specific capacitance values of electrodes RGO and Fe₂O₃-RGO calculated from charge/discharge curves measured at different current densities.

Electrode	Current density				
	1 A/g	2 A/g	3 A/g	4 A/g	5 A/g
Fe ₂ O ₃ -RGO	226 F/g	177.6 F/g	132.6 F/g	104.8 F/g	90.8 F/g
RGO	116.2 F/g	106 F/g	69.6 F/g	57.6 F/g	52.4 F/g

Fig. 6. Nyquist plots of RGO and Fe_2O_3 -RGO nanocomposite electrodes with a frequent range of 0.1 Hz–100 kHz in 1 M Na_2SO_4 electrolyte.

trochemical systems [53–55], which is employed to fit the straight line at intermediate frequencies, followed by a near-vertical line at low frequency region, it is a typical capacitive behavior. It indicates that the capacitance of Fe_2O_3 -RGO electrode may be due to the faradic reaction, while the unstraight line of RGO may be because of the partial redox of GO. It is clearly shown that the R_{ct} of Fe_2O_3 -RGO is smaller than that of RGO, indicating that the electrochemical reaction on the electrode/electrolyte interface is more facile for Fe_2O_3 -RGO. This confirms that the formation of Fe_2O_3 nanoparticles indeed make the electronic resistance of the electrode decrease. Meanwhile, the value of the intercept at the real axis (R_Ω) in the high frequency range can be used to estimate the rate that the supercapacitor can be charged/discharged, and it is an important factor in determining the power density of a supercapacitor. R_Ω of Fe_2O_3 -RGO is lower than that of RGO electrode. These results infer that the formation of Fe_2O_3 nanoparticles on RGO can significantly improve the electrical performance due to the intrinsic resistance change of the active material and less aggregation of the graphene nanosheets.

4. Conclusions

Fe_2O_3 -RGO nanocomposites were synthesized successfully by a simple and green hydrothermal method using urea to adjust the pH value for the formation of Fe_2O_3 . The electrochemical properties were studied in detail. Compared with RGO, the capacity of Fe_2O_3 -RGO was enhanced greatly with the deposition of Fe_2O_3 . The existence of Fe_2O_3 nanoparticles make the charge-transfer resistance of Fe_2O_3 -RGO electrode decrease, which results in Fe_2O_3 -RGO nanocomposite electrode shows a specific capacitance of 226 F/g at a current density of 1 A/g. This material takes the advantage both of the electrical double layer capacitor from RGO, and pseudocapacitance of Fe_2O_3 nanoparticles. The Fe_2O_3 -RGO nanocomposites is a potential promising electrode material for energy storage/conversion device with excellent performance and deserves to be studied further.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jallcom.2012.11.071>.

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