Flower-like Fe₂O₃/reduced Graphene Oxide Composite for Electrochemical Energy Storage

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ABSTRACT

Fe₂O₃/reduced graphene oxide composite (FFGC) was fabricated by a [hydrothermal method](#) for the exploration of electrochemical energy storage, where the Fe₂O₃ nanoparticles (NPs) loaded onto the surface of reduced graphene oxide (rGO) sheet uniformly. Interestingly, the TEM image showed that visible micro-cracks were appeared on the surface of flower-like Fe₂O₃ NP, which did not interfere with its stably crystalline structure. Herein, FFGC was investigated as anode material for lithium-ion battery (LIB) as well as electrode material for supercapacitor (SC). For instance, the specific discharge capacity was of 1366 mAh g⁻¹ at 0.1 A g⁻¹ in LIB case, while the [specific capacitance](#) of 318.9 F g⁻¹ at 0.1 A g⁻¹ in SC experiment. On the other hand, FFGC exhibited the excellently steady performance in either LIB or SC experiment. Those results suggest the roseate future of FFGC in the application of energy issues.

Keywords: Flower-like Fe₂O₃, reduced graphene oxide, lithium-ion battery, supercapacitor.

1. Introduction

Since the middle of 20th century, the human life has been remarkably enriched by the immense industrial progress, which also is perplexed by such progress because of the concomitant energy crisis and environment deterioration. Hence, environment friendly and sustainable energy storage device with high performance becomes the new favorite, such as Li-ion battery (LIB) and supercapacitor (SC) [1-2]. For the former, small and light LIB possessed the high specific capacity and good cycle performance, which made it very suitable for electronic equipment and transportation. For the latter, due to its rapid charge/discharge rate, high power density, and excellent cycling stability [3], it may be preferable to LIB in some applications. Importantly, the selection of electrode material plays a key role on the capability of either LIB or SC device. Due to now, [graphite is the most widely used material in both devices, but it is also suffered by the low theoretical specific capacity](#) [4-7]. Recently, the chemist and the material scientist pay a lot of attention to explore the suitable substitute, such as [transition metal oxide \(\$M_xO_y\$ \), carbon nanotube, graphdiyne, graphene, \$MoS_2\$, and so on](#) [8-13].

For instance, economic and non-toxic hematite (Fe_2O_3) is a potential candidate with high theoretical specific capacity [14-17]. However, the application of pure Fe_2O_3 nanoparticles (NPs) was hindered by the insulating nature as well as the extreme volume expansion during the charge-discharge process [11, 18, 19], which was advanced by the hybridization with the conductive carbon material, especially famous graphene [12, 22]. In such composite, graphene effectively enhanced the transmission

of ions and electrons, whilst the existence of Fe_2O_3 NPs prevented the aggregation of graphene layers to increase the whole capacity [11, 21]. Significantly, in some cases reported [11, 23-26], the electrochemical performance of cracked Fe_2O_3 NPs was relatively better than that of common bulk material. In addition, the existence of micro-crack in the Fe_2O_3 NPs on Fe_2O_3 /graphene composite may form a multi-channel structure to facilitate transport of ions and electrons [25], which will greatly improve the electrochemical property. Commonly, because of the stable crystalline structure of Fe_2O_3 NPs, the typical micro-crack or defect was hardly generated, except for the special cruel experimental conditions [27-29].

In this paper, we reported the fabrication of flower-like Fe_2O_3 /reduced graphene oxide composite (FFGC) via a [hydrothermal method](#) for the exploration of electrochemical energy storage. The crystalline flower-like Fe_2O_3 NPs decorated with micro-cracks were incorporated with reduced graphene oxide (rGO) sheet homogenously. Briefly, the positively charged $\text{Fe}(\text{OH})_3$ colloid NPs were combined with the negative charged graphene oxide (GO) by the electrostatic attraction in solution. During the subsequent hydrothermal treatment process, Fe_2O_3 NPs with micro-cracks were formed and attached onto the surface of rGO. Herein, the electrochemical property of FFGC was studied in detail. For instance, as electrode material for LIB and SC, the specific discharge capacity was of 1366 mAh g^{-1} at 0.1 A g^{-1} in LIB case, while the specific capacity of 318.9 F g^{-1} at 0.1 A g^{-1} in SC experiment. This representation is excellent in the iron oxide/rGO series. On the other hand, sample FFGC also showed the outstandingly steady behavior even in 100 cycles for

LIB and 2000 cycles for SC. Those results suggest its potential application in energy storage device.

2. Experimental Section

2.1. Chemical reagents

Graphite flake (particle size = 150 μm) was purchased from Sigma-Aldrich. Concentrated sulphuric acid (H_2SO_4 , 98%), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2 , 30%), concentrated hydrochloric acid (HCl), ethanol and ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were obtained from Tianjin Chemical (Tianjin, China). All of the chemical reagents were analytical grade and used directly without any further purification. Deionized water was used throughout the whole experiment.

2.2. Preparation of GO, $\text{Fe}(\text{OH})_3$ colloid solution and FFGC

GO was synthesized by the modified Hummers' method reported previously [30, 31]. Positively charged $\text{Fe}(\text{OH})_3$ colloid solution was prepared by the modified hydrolysis of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ [20, 32].

The preparation of target product was designed by a simple colloidal electrostatic assembly route. In detail, 250 mg GO was dispersed into 500 mL deionized water by ultrasonication in 2 h to obtain the GO suspension. In the following, after 50 mL of $\text{Fe}(\text{OH})_3$ colloid solution was dropwisely added into the GO suspension, it was stirred in 2 h. The flocculent $\text{Fe}(\text{OH})_3/\text{GO}$ composite was centrifuged and subsequently washed by the deionized water for three times. Such precursor was treated in a hydrothermal process at 180 $^\circ\text{C}$ in 24 h. The raw product was collected and dried at 50

°C in 12 h to obtain one black powder composite that was named as FFGC. For the control experiments, the model rGO and Fe₂O₃ were synthesized under the same experimental condition.

2.3. Materials Characterization

Zeta potential of graphene and Fe(OH)₃ colloid NPs were recorded on a Zetasizer 3000 (Malvern Instrument), where the samples were diluted to 0.05 mg mL⁻¹. The microstructure of FFGC was obtained by transmission electron microscope (TEM) on JEOL, JEM-2010F (200 kV). Thermogravimetric analysis (TGA) of FFGC was carried out by a TA Instrument TGA-2050 from 25 to 800 °C at a heating rate of 10 °C min⁻¹ under air. The phase structure of sample was characterized by powder X-ray diffraction (PXRD) analysis on an X' Pert Pro system with Cu K α radiation in the 2 θ range of 0-80°. Fourier transform infrared (FT-IR) measurements were tested on Bruker IFS 66 v⁻¹ s infrared spectrometer using KBr as thinner. The X-ray photoelectron spectrum (XPS) was taken on a PHI-5702 multi-functional X-ray photoelectron spectrometer using pass energy of 29.35 eV and a Mg K α X-ray source. All Raman spectra were collected on a Renishaw RM-1000 Raman spectroscopy at 514 nm Ar-ion laser excitation. The Brunauer-Emmett-Teller (BET) Specific Surface Area (SSA) of FFGC was performed by nitrogen adsorption/desorption on Micromeritics ASAP 2420 at 77 K.

2.4. Electrochemical Measurement

The LIB study of the sample was evaluated by the coin cell. At first, a mixing slurry (80 wt% active materials, 10 wt% conductive carbon black (Super P) and 10 wt%

polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP)) was uniformly coated on the copper foil to obtain the work electrode. The amount of the active materials for the electrochemical test was 1.64 mg. Lithium tablet was used as the counter electrode and reference electrode, while the electrolyte was LiPF_6 in mixing solvent (ethylene carbonate : dimethyl carbonate = 1 : 1 in m/m). The coin cell was built up in the glove box under argon atmosphere. The galvanostatic charge-discharge (GCD) was conducted with a LAND battery system in the range from 0.01 to 3 V (vs Li/Li^+). Cyclic voltammogram (CV) was performed with a CHI 660E electrochemical workstation over potential range from 0.01 to 3 V (vs Li/Li^+) with voltage scan rate of 0.1 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) was recorded by CHI 660E electrochemical workstation in the frequency range from 100 k Hz to 0.01 Hz at open circuit potential.

The SC property was studied in a 6 M KOH electrolyte by the CV, GCD and EIS analysis. The active material FFGC, 12% Polytetrafluoroethylene (PTFE), and Super P were mixed (m : m : m = 80 : 10 : 10), and then coated on the nickel foam to form the work electrode. The amount of the active materials for the electrochemical test was 2.34 mg. EIS measurements were carried out in a three-electrode glass cell, where a saturate calomel electrode (SCE) and a Pt electrode were used as the reference and counter electrode, respectively. GCD and CV studies were carried out in a custom-built button type SC. GCD tests were conducted at the current densities of 0.1, 0.3, 0.5, and 1.0 A g^{-1} . The average specific capacity was calculated from the discharge slope by the following equation:

$$C = I\Delta t/(\Delta V \times m)$$

Where C is specific capacity, I is the current loading (A), Δt is the discharge time (s), ΔV is the potential change during discharge process, and m is the mass of active material in a single electrode (g).

3. Results and discussions

Insert Scheme 1

Commonly, GO prepared by the modified Hummers' method exhibits a negative charged surface [20]. In this paper, the zeta potential of GO as-prepared was measured at -45.43 mV, distinctly suggesting the negatively charged surface. Meanwhile, the prepared $\text{Fe}(\text{OH})_3$ colloidal NPs showed the zeta potential of +21.20 mV, which demonstrated its positively charged surface. As shown in Scheme 1, after $\text{Fe}(\text{OH})_3$ colloidal solution was added into the GO suspension, $\text{Fe}(\text{OH})_3$ colloidal NPs was easily absorbed onto GO sheets because of the strong electrostatic interaction. In addition, the combination was further reinforced by the other noncovalent interactions (van der Waals interaction and hydrogen bonding) as well as the chemisorptions between the $\text{Fe}(\text{OH})_3$ colloid NPs and the oxygenate groups on the GO sheet surface. Since that, brown flocculent precipitate $\text{Fe}(\text{OH})_3/\text{GO}$ has appeared in the bottom of the beaker. Subsequently, during the hydrothermal process, GO was reduced to rGO and $\text{Fe}(\text{OH})_3$ was decomposed to Fe_2O_3 spontaneously. Meanwhile, the adjacent tiny Fe_2O_3 NPs aggregated together and formed the flower-like Fe_2O_3 with micro-cracks loaded onto rGO sheet [34, 35]. This unique phenomenon is probably resulted from the aggregation of tiny Fe_2O_3 NPs during the dehydration process in the relatively

high temperature [29, 36, 37]. In addition, the deformation of micro-crack was also assisted by the physical squeezing of rGO sheets during the hydrothermal treatment. Finally, one black powder composite was obtained and named as FFGC.

Insert Fig. 1

Herein, the microstructure of sample FFGC was identified by TEM and HRTEM experiments. As shown in Fig. 1(a) and Fig. S1, it is clearly that the flower-like Fe_2O_3 NPs were loaded uniformly onto the rGO surface, the average size is about 50 nm. Importantly, no single Fe_2O_3 particle or rGO sheet was observed in this work, indicating the excellent combination between the two components. Furthermore, the morphology of Fe_2O_3 NPs is flower-like in the prepared composite, where the visible micro-cracks are randomly on its surface (Fig. 1(b) and (c)). As shown in Fig. 1(d), either distinctly resolved lattice from the HRTEM image (around 0.270 nm corresponding to the (104) plane of Fe_2O_3) or beautiful diffraction spots from the selected-area electron diffraction (SAED) pattern (JCPDS NO. 00-033-0664) [17], suggesting its refined crystal structure. Interestingly, micro-cracks did not interfere with the stably crystalline structure of Fe_2O_3 NPs. Moreover, the existence of these micro-cracks might efficiently increase the effective contact area between the active material and the electrolyte to improve the utilization of the active material.

Insert Fig. 2

The firm combination of Fe_2O_3 NPs and rGO sheet was further proved by the PXRD, FT-IR, Raman, and XPS analysis. As shown in Fig. 2(a), in comparison with model Fe_2O_3 , the positions and relative intensities of the diffraction peaks of sample

FFGC was consistent with hematite (JCPDS NO.00-033-0664, 24.1° (012), 33.1° (104), 35.6° (110), 40.8° (113), 49.5° (024), 54.1° (116), 57.6° (018), 62.5° (214) and 64.0° (300)) [4, 34]. The peak at $2\theta = 25.7^\circ$ (002, rGO) may ascribed to the reduction of GO to rGO [17]. Meanwhile, the disappearance of the single broad peak at $2\theta = 9.7^\circ$ (001) suggested that GO was completely converted to rGO in the hydrothermal process. In the FT-TR experiments, comparing to model GO and rGO (Fig. 2(b)), the characteristic peaks of carboxyl and epoxide were absent in sample FFGC, indicating the complete reduction of GO to rGO [40]. Moreover, the peaks at 1560 and 1200 cm^{-1} were corresponded to the C=C stretching vibration and C-O in-plane vibration of rGO, whilst the peaks at 532, 459, and 396 cm^{-1} were confirmed the presence of Fe_2O_3 in FFGC [40]. Similarly, as shown in Fig. 2(c), the G band at 1600 cm^{-1} was ascribed to the in-plane vibration of sp^2 -hybridized carbon atom and the D band at 1355 cm^{-1} represented the lattice defect of carbon atom in the Raman spectrum of sample FFGC according to those of references GO and rGO [17, 35, 43, 44]. The intensity ratio of D band to G band (I_D/I_G) is a valuable parameter to discuss graphene defects. As shown in Fig. 2c, the intensity ratio of D over G band in sample FFGC is 1.10 : 1, which is higher than that for rGO (1.05 : 1) and GO (1.01 : 1), which is consistent with the literature [20, 45]. On the other hand, the increased D band intensity of the FFGC clearly indicates the apparent structure interaction between Fe_2O_3 NPs and rGO sheets.

As well-known, the XPS experiment would show the detailed elemental composition in material science. Herein, as shown in Fig. 2(d), the C 1s, O 1s and Fe

2p peaks were obviously present in the XPS spectrum of FFGC. In comparison with that in GO sheet, both the weakened O 1s peak and the raised C 1s peak indicate the perfect reduction of GO. In addition, the shoulder peak at around 710 eV provided the evidence of Fe₂O₃, where the two peaks at 711.1 and 724.7 eV were corresponding to the Fe 2p_{3/2} and Fe 2p_{1/2} (Fig. 2(e)), respectively [46]. Moreover, the energy difference between Fe 2p_{3/2} and Fe 2p_{1/2} is of 13.6 eV, which is the typical Fe³⁺ state. Except those, weak Fe³⁺ satellite peak is also observable in the spectrum at 718.5 eV, almost in the middle of the Fe 2p_{3/2} and Fe 2p_{1/2} peaks. At last, the C 1s spectra of GO and FFGC (Fig. 2(f)) were analyzed by a multi-peak fitting mode. Briefly, there are four peaks at 284.8 eV (C-C), 286.3 eV (C-O), 288.1 eV (C=O) and 289.1 eV (O-C=O). On the other hand, in comparison with GO, sample FFGC showed the oxygen-related peaks weakened as well as the raised C-C peak, which was further proved the perfect conversion of GO.

In the TGA experiment under air atmosphere (Fig. S2(a)), there are two obviously weight loss. The light weight loss below 200 °C was attributed to evaporation of absorbed water. Another main weight loss about 35.9% was in the range of 350-500 °C, which was originated from the removal of rGO sheet [38]. Hence, the Fe₂O₃ content in FFGC is about 59.3 %, and the weight ratio of Fe₂O₃ to rGO is about 1.65 : 1. Herein, N₂ adsorption-desorption isotherm is used to measure the specific surface area (SSA) of FFGC. As shown in Fig. S2(b), that of FFGC is about 202.9 m² g⁻¹ and the total pore volume is 0.20 cm³ g⁻¹ in the scale from 1.7 to 300 nm. Additionally, there is a notable type IV hysteresis loop in the high relative pressures region,

suggesting the typically mesoporous structure.

Insert Fig. 3

As we know, the LIB performance commonly was tested in a coin cell. In this work, before the LIB experiment, the coin cell was built up in the glove box under argon atmosphere for the following CV, GCD and EIS measurements. In the coin cell, a mixing slurry (80 *wt%* active materials, 10 *wt%* conductive carbon black (Super P) and 10 *wt%* polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP)) was uniformly coated on the copper foil to form the work electrode. Lithium tablet was used as the counter electrode and reference electrode, while the electrolyte was LiPF₆ in mixing solvent (ethylene carbonate : dimethyl carbonate = 1 : 1 in m/m). As shown in Fig. 3(a), there are three platforms (~1.6 V, ~1.1 V and ~0.8 V) in the first discharge (lithium insertion) process corresponding to four stages (reactions (1)-(4)) as below, respectively [12, 39, 47-49]:

In the second discharge curve, only one platform at ~ 0.9 V was clearly observed, which indicated the irreversible anionic close-packing transform hexagonal to cubic [10, 41]. The charge (lithium extraction) curves showed a sloping platform at ~ 1.6 V, reflecting the oxidation of Fe shown in reaction (5) [12, 49]:

In this coin cell, the FFGC work electrode delivered a first discharge capacity of 1366 mAh g⁻¹ as well as a first charge capacity of 873 mAh g⁻¹, displaying the columbic efficiency of 63.9 % (Fig. 3(b)). The as-prepared FFGC actually shows lower electrochemical output than the high performance of reported Fe₂O₃/rGO composite [11], which is might be induced by the different experimental conditions and synthetic routes adopted. The excess capacity was attributed to the reaction between oxygen-containing function groups on rGO with lithium ions and the formation of SEI layer in the low-potential region [48, 50, 51]. The discharge capacities in the 2nd, 3rd, 4th and 5th cycles were 913, 898, 876, and 843 mAh g⁻¹, respectively. Even in 100 charge/discharge cycle, the reversible capacity was still keeping at 646 mAh g⁻¹. During the cyclic testing, the average columbic efficiency was 98% (Fig. 3(b)), showing a good capacity retention. In comparison with the control experiment, sample FFGC was obviously superior to separate component on cycling performance.

In the following CV experiments, sample FFGC and reference Fe₂O₃ were tested over potential range from 0.01 to 3 V (vs Li⁺/Li) at voltage scan rate of 0.1 mV s⁻¹ (Fig. 3(c) and S3(b)). Significantly, the peaks were favorably consistent with the charge/discharge platforms, representing the same processes (as reaction (1)-(5)), where shifted peaks and some absent peaks also proved the irreversible phase transformation [39, 47, 51].

Besides, the rate performance of FFGC was tested at different current rates for 10 cycles in the same cell (Fig. 3(d)). As shown in Fig. S3(e), a specific capacitance of the composite was about 630 mAh g⁻¹ at 0.2 A g⁻¹, while it lowered to 280 mAh g⁻¹ at

1 A g⁻¹. After the current back to 0.1 A g⁻¹, a reversible capacity recovered to 785 mAh g⁻¹ in this composite sample.

In this work, the EIS test was conducted in the frequency range of 0.01-100 kHz to profile the Nyquist spectrum (Fig. S3(c) and S3(d)). For instance, the first semicircle was corresponding to the resistance of Li⁺ migration on the SEI and the second one was the representation of the charge transfer resistance. The straight line part was resulted from the Warburg resistance, reflecting the Li⁺ diffusion in the inner of electrode materials [12, 52]. Obviously, sample FFGC showed the intermediate SEI resistance and interfacial charge-transfer resistance, because of the cooperation of Fe₂O₃ and rGO (Fig. S3(c)). As shown in Fig. S3(d), the Nyquist plot of FFGC after cycling showed smaller SEI and charge-transfer resistance than those of raw material before cycling. This result indicated that the transfer mode of ion and electron produced in the cycling process might make the Li⁺ insertion/extraction process easier. In addition, the space of rGO layer was probably expanded by the volume expansion of Fe₂O₃ NPs during the first discharge process to facilitate the Li⁺ transport [12].

Insert Fig. 4

Furthermore, the SC performance of FFGC was also investigated in a 6 M KOH electrolyte by the CV, GCD, and EIS analyses. Fig. 4(a) showed the CV curves of the FFGC at different scan rates (10, 20, 30, 50, 80, 100 mV s⁻¹) in the range of 0-0.6 V. The ideal rectangular shape was showed in lower scan rate, indicating its nature of double layer capacity. When the scan rate increased, the curves were deviated to quasi-rectangular, which was ascribed to the kinetics factor of the electron

transportation [53]. As shown in GCD curves (Fig. 4(b)), when the current intensity was gradually raised (0.1, 0.3, 0.5, 1, and 2 A g⁻¹) in the range of 0-1.2 V, the specific capacity of FFGC was decreased, from 318.9 to 128 F g⁻¹ shown in Fig. S4.

In addition, the composite cycling stability is measured by the conducting continuous charge-discharge cycle experiment at 0.3 A g⁻¹. In case FFGC (Fig. 4(c)), the change of specific capacity was relatively small, and the specific capacity still remained 81.9% (231.8 F g⁻¹) even after 2000 cycles. Herein, it is clear that cycling stability of FFGC is favorable, which can be a good candidate for SC application. On the other hand, the Nuquist plots of rGO, Fe₂O₃, and FFGC were figured by the EIS measurements in the range of 1-1000 KHz (Fig. 4(d)). Visibly, the profile of FFGC could be considered as a combination of Fe₂O₃ and rGO. In detail, the semicircle part in the high frequency region is similar to that of Fe₂O₃, corresponding to the charge-transfer resistance. Compared with Fe₂O₃, such decreased charge-transfer resistance of FFGC might be attributed to the presence of rGO and micro-cracks, which provided some new convenient channels for ion and charge transport as well as the increased interface between electrode and electrolyte. The straight line part in the low frequency region is very close to that of rGO, ascribed to the Warburg impedance. It also indicated that the diffusive resistance of FFGC was effectively reduced because of the rGO network.

4. Conclusions

In summary, FFGC was obtained by a hydrothermal method for the exploration of electrochemical energy storage, where the Fe₂O₃ NPs loaded onto the surface of rGO

sheet uniformly. The crystalline Fe_2O_3 NPs with amount of micro-cracks were formed onto rGO sheet via a facile normal treatment process without any other cruel technique or additive by using the $\text{Fe}(\text{OH})_3$ colloid as precursor. According to the results of LIB and SC experiments, FFGC shows its favorable capability, suggesting the roseate future in the application of energy issues.

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Figure captions:

Scheme 1. Construction process of FFGC.

Fig. 1 (a), (b) and (c) TEM images of FFGC, (d) HRTEM image of FFGC, the inset shows the SAED pattern of FFGC.

Fig. 2 (a) PXRD patterns of GO, rGO, Fe₂O₃ and FFGC, (b) FT-IR spectra of GO, rGO, Fe₂O₃ and FFGC, (c) Raman spectra of GO, rGO and FFGC, (d) XPS spectra of FFGC and GO, (e) the high spectrum of Fe from XPS spectrum of FFGC, (f) the high spectra of C 1s from XPS spectra of FFGC and GO.

Fig. 3 (a) The charge-discharge curves of the FFGC for LIBs at a current density of 0.1 A g⁻¹, (b) Cyclic performance of the FFGC for LIBs at a current density of 0.1 A g⁻¹, (c) The cyclic voltammogram (CV) curves of FFGC for LIBs at a scan rate of 0.1 mV s⁻¹, (d) the charge-discharge performances of the FFGC for LIBs at different current densities.

Fig. 4 (a) The cyclic voltammogram (CV) curves of FFGC for SC under the different scan rates of 10, 20, 30, 50, 80 and 100 mV s⁻¹, (b) GCD curves of FFGC for supercapacitors at different current densities, (c) comparison of the cycling performances of FFGC, Fe₂O₃ and rGO for supercapacitors at 0.3 A g⁻¹, (d) EIS of rGO, Fe₂O₃ and FFGC for supercapacitors, the inset shows the equivalent Randles circuit.

Scheme 1

Fig. 1.

Fig.2.

Fig.3.

Fig. 4.