Electrostatic Self-Assembly of Fe$_3$O$_4$ Nanoparticles on Graphene Oxides for High Capacity Lithium-Ion Battery Anodes

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Abstract: Magnetite, Fe$_3$O$_4$, is a promising anode material for lithium ion batteries due to its high theoretical capacity (924 mA h g$^{-1}$), high density, low cost and low toxicity. However, its application as high capacity anodes is still hampered by poor cycling performance. To stabilize the cycling performance of Fe$_3$O$_4$ nanoparticles, composites comprising Fe$_3$O$_4$ nanoparticles and graphene sheets (GS) were fabricated. The Fe$_3$O$_4$/GS composite disks of μm dimensions were prepared by electrostatic self-assembly between negatively charged graphene oxide (GO) sheets and positively charged Fe$_3$O$_4$-APTMS [Fe$_3$O$_4$ grafted with (3-aminopropyl)trimethoxysilane (APTMS)] in an acidic solution (pH = 2) followed by in situ chemical reduction. Thus prepared Fe$_3$O$_4$/GS composite showed an excellent rate capability as well as much enhanced cycling stability compared with Fe$_3$O$_4$ electrode. The superior electrochemical responses of Fe$_3$O$_4$/GS composite disks assure the advantages of: (1) electrostatic self-assembly between high storage-capacity materials with GO; and (2) incorporation of GS in the Fe$_3$O$_4$/GS composite for high capacity lithium-ion battery application.

Keywords: lithium-ion battery; anode; iron oxide; magnetite; graphene; self-assembly
1. Introduction

Lithium-ion batteries (LIBs) are being intensively pursued for the emerging large-scale applications in many electrified vehicles and energy storage system (ESS), etc. [1–3]. In commercial LIBs, graphitic carbon has long been used as the anode material since the first introduction of LIBs in 1991 due to its excellent cycling stability and relatively low cost. However, more advanced anode material that provides higher energy and power densities than graphitic carbon is required to meet the growing demands.

Nanostructures of iron oxides (α-Fe2O3 and Fe3O4) that store 6~8 Li ions per formula unit via electrochemical “conversion reaction” shown below have been extensively studied as potential high capacity anode materials [4–13]. They have low toxicity and high intrinsic density (5.17 g cm−3 for Fe3O4 vs. 2.16 g cm−3 for graphite), and are abundant. In spite of these highly appealing features, their use in LIB anodes is hampered by low electrical conductivity, and fast capacity fading due to severe aggregation of iron oxides particles and large volume changes inherent in the conversion reaction process [5,8,14]. Their hybridization with conductive matrices such as carbon is mostly adopted to resolve these problems. However, it is hard to get homogeneous dispersion of iron oxide nanostructures in carbon matrices. Rendering the high electrical conductivity of composites with post thermal-treatment of carbon precursors is also problematic issue due to the limited thermal stability of iron oxide nanostructures [5,9]. Among many carbon matrices, graphene is regarded as the most attractive ones because of its unique properties such as superior electrical conductivity, high thermal and chemical stability, high mechanical ductility and large surface area. Hence, graphene has been successfully used to support metal oxides including iron oxide nanostructures by employing chemical co-precipitation or solvothermal processes [7,8,15,16]:

\[
\begin{align*}
\text{Fe}_2\text{O}_3 + 6\text{Li}^+ + 6\text{e}^- &\leftrightarrow 2\text{Fe}^0 + 3\text{Li}_2\text{O} \\
\text{Fe}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- &\leftrightarrow 3\text{Fe}^0 + 4\text{Li}_2\text{O}
\end{align*}
\]

Herein, we report an instant electrostatic self-assembly to fabricate Fe3O4/graphene sheets (GS) composite. For this purpose, Fe3O4 nanoparticles grafted with (3-aminopropyl)trimethoxysilane (Fe3O4-APTMS) were added into a slightly acidic dispersion of graphene oxides (GO) followed by in situ chemical reduction of GO. This process yielded Fe3O4/GS disks of μm dimensions in which Fe3O4 nanoparticles are in intimate contacts with GS and are ideally dispersed between GS layers. As an anode material for LIB, the Fe3O4/GS composite disks with unique morphology exhibited a high reversible discharge capacity of 674 mA h g−1 at 100 mA g−1 with an excellent cycling stability up to 100 cycles. The Fe3O4/GS disks also showed high rate capability, i.e., ~300 mA h g−1 at the current as high as 2000 mA g−1.

2. Results and Discussion

Scheme 1 illustrates the electrostatic self-assembly process between Fe3O4-APTMS and GO to prepare Fe3O4/GS composite disks. In an acidic solution, the positively charged Fe3O4-APTMS is homogeneously bound on the surface of negatively charged GO sheets by instant electrostatic interactions. The Fe3O4/GO composite was subsequently reduced in situ with hydrazine to give Fe3O4/GS composite disks.
Scheme 1. Schematic diagram for the electrostatic self-assembly process.

Figure 1a compares the Fourier transform infrared spectroscopy (FTIR) spectra of Fe₃O₄ and Fe₃O₄-APTMS. In the spectrum of Fe₃O₄, a strong band at 500–700 cm⁻¹ due to the Fe–O stretching vibration and a broad band at 3400–3600 cm⁻¹ due to the stretching vibration of the surface –OH groups of Fe₃O₄ was observed [17,18]. The surface –OH groups attack the labile methoxy-groups in APTMS to form Fe–O–Si bonds at elevated temperature. Different from the spectrum of bare Fe₃O₄, that of Fe₃O₄-APTMS clearly showed the stretching vibration band of Si–O bonds in Fe–O–Si at 1050–1100 cm⁻¹ with the stretching vibration bands of C–H in alkyl chains at 2850 cm⁻¹, 2925 cm⁻¹ and 2956 cm⁻¹. The bands at 3423 cm⁻¹ and 1635 cm⁻¹ correspond to N–H stretching and bending vibrations in free amines, respectively, and the band at 1385 cm⁻¹ corresponds to C–N stretching vibration. The FTIR spectrum of Fe₃O₄-APTMS indicates that the surfaces of Fe₃O₄ nanoparticles were successfully grafted with APTMS. As shown in Figure 1b, the X-ray diffraction (XRD) patterns of Fe₃O₄ nanoparticles and Fe₃O₄/GS composite disks match well with that of magnetite (JCPDS No. 19-0629). With the Scherrer’s formula, \( D = \frac{0.89\lambda}{\beta \cos \theta} \), to the line width of (311) diffraction, the average particle size of Fe₃O₄ was estimated to be 10.1 nm. The magnetite structure was preserved in the Fe₃O₄/GS composite after in situ chemical reduction with hydrazine.

Figure 1. (a) Fourier transform infrared spectroscopy (FTIR) spectra: (i) Fe₃O₄ and (ii) Fe₃O₄-APTMS; (b) X-ray diffraction (XRD) patterns: (i) Fe₃O₄ and (ii) Fe₃O₄/GS [inset is the XRD patterns of graphene oxides (GO) and reduced GO (rGO)].
Figure 2 presents photographs of GO and Fe₃O₄-APTMS dispersions in acidic solution, and hydrazine-reduced Fe₃O₄/GS. GO and Fe₃O₄-APTMS formed homogeneous dispersions by sonication in acidic solution as shown in Figure 2a,b, respectively. Right after the two dispersions are mixed together, Fe₃O₄/GO aggregates were precipitated due to electrostatic assembly. After addition of hydrazine, the reduced Fe₃O₄/GS composite floated to the surface of clear solution (Figure 2c), indicating hydrophobic nature of composite surface and complete electrostatic assembly between Fe₃O₄-APTMS and GO sheets.

**Figure 2.** Photographs: (a) GO dispersion; (b) Fe₃O₄-APTMS dispersion; and (c) reduced Fe₃O₄/GS solution.

Figure 3 shows X-ray photoelectron spectroscopy (XPS) spectrum of Fe₃O₄/GS composite. Insets are the high-resolution spectra of the Si 2p (left) and C 1s (right) regions. A small Si 2p peak with binding energy of 102.0 eV was detected, providing additional evidence of successful grafting of APTMS on Fe₃O₄ [17]. The two Fe peaks with binding energies of 710.9 eV and 724.4 eV were attributed to Fe 2p₃/2 and Fe 2p₁/2, respectively, for trivalent Fe in the Fe₃O₄. The C 1s spectra showed an intense peak at 284.6 eV due to the C–C bonds in GS with substantially low peak intensities assignable to the C–O moieties in pristine GO, supporting high degree of GO reduction with hydrazine [19].

**Figure 3.** X-ray photoelectron spectroscopy (XPS) spectrum of Fe₃O₄/GS composite. Insets are the high-resolution spectra of Si 2p and C 1s regions.
The amount of Fe$_3$O$_4$ in the composite was estimated to be 54.5 wt% by thermogravimetric analysis (TGA) profile shown in Figure 4a, for which mass loss below 200 °C was assumed to be adsorbed water. The scanning electron microscopy (SEM) image of Fe$_3$O$_4$/GS composites in Figure 4b, showed disk-shaped aggregates of 1–3 μm in size with thicknesses of 0.5–1 μm. The size of composite disks is comparable to that of pristine flake graphite used to prepare GO. The structure of Fe$_3$O$_4$/GS composite was further investigated by transmission electron microscopy (TEM). As shown in Figure 4c, Fe$_3$O$_4$ nanoparticles with a size range of 10–20 nm are dispersed on GS and are in close contact with very thin layers of GS. The lattice d-spacings of 0.47 nm, 0.297 nm and 0.25 nm corresponding to (111), (220) and (311) planes of Fe$_3$O$_4$, respectively, were identified in the high resolution TEM image (Figure 4d).

**Figure 4.** (a) Thermogravimetric analysis (TGA) profile; (b) scanning electron microscopy (SEM) image; (c) and (d) transmission electron microscopy (TEM) images of Fe$_3$O$_4$/GS composite.

The electrochemical properties of Fe$_3$O$_4$/GS composite were tested in comparison to those of Fe$_3$O$_4$ nanoparticles by cyclic voltammetry (CV) and galvanostatic cycling tests. Figure 5a,b shows the CV curves for the initial five cycles. In the first cathodic scan of Fe$_3$O$_4$ electrode, a strong reduction peak was observed at 0.55 V due to the electrochemical reduction of Fe$^{3+}$ and Fe$^{2+}$ to Fe$^{0}$ [9,20,21]. In the subsequent cycles, the obvious peak at 0.55 V was shifted to 0.6–0.7 V due to the polarization. In the first anodic scan, two broad peaks were recorded at 1.72 V and 1.82 V assignable to the oxidation of Fe$^{0}$ to Fe$^{2+}$ and Fe$^{3+}$, respectively [8,14,21]. In the subsequent cycles, however, the peak at 1.82 V is hardly observed indicating the redox cycle between Fe$^{0}$ and Fe$^{2+}$ would be the major process. Overall, the integrated areas of both cathodic and anodic scans of Fe$_3$O$_4$ electrode were substantially decreased in five cycles, indicating electrochemical irreversibility. Figure 5b shows much stabilized CV responses for the Fe$_3$O$_4$/GS composite. The major cathodic and anodic peaks were recorded at 0.65 V and 1.67/1.81 V, respectively. The Fe$_3$O$_4$/GS showed much less polarization after the first scan than Fe$_3$O$_4$ alone and the CV curves of subsequent cycles almost overlapped indicating excellent...
electrochemical reversibility. In particular, in the Fe$_3$O$_4$/GS composite, two anodic peaks at 1.67 V and 1.81 V due to Fe$^0$ oxidation to Fe$^{2+}$ and Fe$^{3+}$, respectively, were repeatedly observed. The voltage difference between cathodic and anodic process was also decreased in comparison to that of Fe$_3$O$_4$ alone possibly due to the enhanced conductivity in Fe$_3$O$_4$/GS. Figure 5c,d presents the voltage-capacity profiles of Fe$_3$O$_4$ nanoparticles and Fe$_3$O$_4$/GS composite, respectively, for the initial five cycles at a current density of 100 mA g$^{-1}$. In the first discharge curves, both electrodes showed long voltage plateaus at around 0.8 V vs. Li$^+$/Li due to the reduction of Fe$^{3+}$ and Fe$^{2+}$ to Fe$^0$ followed by downward sloping voltage profiles due to the combined effects of the formation of solid electrolyte interphase (SEI) layers and possibly interfacial lithium storage [8,22]. In the first charge profiles, both electrodes showed sloping voltage plateaus in 1.25–2.0 V mainly due to the oxidation of Fe$^0$ to Fe$^{2+}$ and Fe$^{3+}$. After the first cycle, the charge and discharge capacities of Fe$_3$O$_4$ decreased rapidly with cycling while those of Fe$_3$O$_4$/GS were maintained at around 700 mA h g$^{-1}$.

**Figure 5.** Cyclic voltammetry (CV) curves of (a) Fe$_3$O$_4$ and (b) Fe$_3$O$_4$/GS; voltage profiles of (c) Fe$_3$O$_4$ and (d) Fe$_3$O$_4$/GS cycled at the current of 100 mA g$^{-1}$.

As shown in Figure 6, the Fe$_3$O$_4$ electrode exhibited very high discharge and charge capacities of 1478 mA h g$^{-1}$ and 949 mA h g$^{-1}$ in the first cycle, respectively, resulting in a coulombic efficiency (CE) of 64.2%. However, it lost most of its capacity after ten cycles and delivered less than 200 mA h g$^{-1}$ at the 50th cycle. On the other hand, Fe$_3$O$_4$/GS composite showed much enhanced cycling stability. The initial discharge and charge capacities of Fe$_3$O$_4$/GS were 1126 mA h g$^{-1}$ and 674 mA h g$^{-1}$, respectively, corresponding to the CE of 59.9%. In the following cycles, the reversible discharge capacity was more than 600 mA h g$^{-1}$ and the capacity retention at the 100th cycle was about 80%. The GS electrode delivered the reversible capacity on the order of 200 mA h g$^{-1}$. Of the capacity (674 mA h g$^{-1}$) of Fe$_3$O$_4$/GS, the contribution by the GS is estimated to be 91 mA h g$^{-1}$ (13.5%) considering that the weight fractions of Fe$_3$O$_4$ and GS equal to 55.5% and 45.5%, respectively.
Hence, Fe$_3$O$_4$ in the composite delivered about 583 mA h g$^{-1}$, which was slightly larger than the one calculated with its theoretical capacity (924 mA h g$^{-1} \times 55.5\% = 513$ mA h g$^{-1}$) possibly due to the interfacial lithium storage [8,22].

**Figure 6.** Cycling performances of GS, Fe$_3$O$_4$ and Fe$_3$O$_4$/GS at the current of 100 mA g$^{-1}$. Open and filled symbols denote discharge and charge capacities, respectively.

The Fe$_3$O$_4$/GS also exhibited excellent rate performances, as shown in Figure 7. On average, the capacity retentions at 500 mA g$^{-1}$, 1000 mA g$^{-1}$ and 2000 mA g$^{-1}$ were about 78%, 61% and 57% of the capacity at 100 mA g$^{-1}$. When the current was returned back to 100 mA g$^{-1}$ after 45 cycles, the initial capacity was completely recovered, indicating an excellent electrochemical reversibility of Fe$_3$O$_4$/GS. The enhanced electrochemical responses of Fe$_3$O$_4$/GS compared with unsupported Fe$_3$O$_4$ could be attributed to the combined effects: (1) the high dispersion of Fe$_3$O$_4$ nanoparticles on GS layers by employing the electrostatic self-assembly method, which suppresses the agglomeration of metal oxide particles and the consequential capacity fade upon cycling; (2) the flexible and electrically conductive nature of GS layers that accommodates mechanical stresses inherent in the conversion reaction of Fe$_3$O$_4$ and maintains electrically conductive-networks through the electrode; and (3) relatively high wettability of electrolytes in the layers between Fe$_3$O$_4$ nanoparticles and GS, which can result in enhanced rate capability.

**Figure 7.** Rate performances of Fe$_3$O$_4$/GS.
3. Experimental Section

3.1. Synthesis of Fe₃O₄ Nanoparticles and GO

Fe₃O₄ nanoparticles were synthesized by the hydrothermal liquid-interface reaction in the literatures [8,9]. In a 20 mL glass vial, Fe(NO₃)₃·9H₂O (0.40 g) was dissolved in ethylene glycol (EG, 5 mL). The vial was placed into a 30 mL Teflon autoclave that contained 28% ammonia solution (5.3 mL). The autoclave was sealed and placed in a furnace. The furnace was heated to 180 °C for 12 h. After cooling, the powder was washed with ethanol by centrifugation and filtration for several times. GO was synthesized by the modified Hummers method with commercial flake graphite (230 U Grade, Asbury Carbons, Asbury, NJ, USA) [23–25]. The GO was diluted to make a ~6% w/w in water and was subjected to sonication to get an aqueous dispersion of GO sheets.

3.2. Preparation of Fe₃O₄-APTMS and Fe₃O₄/GS Composite

Fe₃O₄ nanoparticles (0.1 g) were dispersed into dry toluene (10 mL) via sonication in an argon-filled flask. After 30 min, APTMS (0.1 mL) was poured into the solution and refluxed for 24 h under a N₂ atmosphere and washed with ethanol by centrifugation and filtration to obtain amine-functionalized Fe₃O₄ nanoparticles (Fe₃O₄-APTMS). Fe₃O₄-APTMS powder (0.1 g) was re-dispersed in ethanol (100 mL). The pH values of Fe₃O₄-APTMS dispersion in ethanol and GO dispersion in water were adjusted to be around 2 by adding appropriate amount of hydrochloric acid solution. An acidic condition was employed to make sure that the surface of APTMS-Fe₃O₄ is rendered with positive charge [26]. The Fe₃O₄/GS composite was fabricated via electrostatic self-assembly between positively charged Fe₃O₄-APTMS and negatively charged GO in acidic solution (pH = 2), followed by chemical reduction with hydrazine. Fe₃O₄-APTMS solution (0.50 mg mL⁻¹, 200 mL, pH = 2) was added into aqueous GO solution (0.18 mg mL⁻¹, 125 mL, pH = 2) under stirring. After stirring for 1 h, a small amount of hydrazine solution (35 wt% in water) was added into the obtained dark brownish solution under stirring. The self-assembled composites were further reduced overnight at room temperature. The supernatant was decanted and resulting black dispersion was washed with distilled water for several times and dried at 80 °C overnight to obtain the Fe₃O₄/GS powder. For comparison, GS (rGO) sample was prepared by hydrazine reduction of GO.

3.3. Materials Characterization

FTIR spectra were collected on a Nicolet 380 spectrometer using wafers formed by mixing the sample (2–3 wt%) with KBr powder and then pelleted. The powder XRD patterns of samples were recorded on an Ultima IV, Rigaku model D/MAX-50 kV system (Cu-Kα radiation, λ = 1.5418 Å). XPS was performed on a Thermo Electron Corporation spectrometer with an Al Kα (1486.6 eV) radiation. The carbon content in Fe₃O₄/GS was determined by the weight loss in a TGA run to 800 °C at a ramping rate of 10 °C min⁻¹ in an air flow. The morphology of Fe₃O₄/GS was investigated by using SEM (JEOL JSM-35CF operated at 10.0 kV, JEOL Ltd., Tokyo, Japan) and TEM (JEOL JEM-2010 operated at 200.0 kV, JEOL Ltd., Tokyo, Japan).
3.4. Electrochemical Measurements

Electrochemical tests were conducted using R-2032 coin cell with Li foil as the counter-electrode. The working electrodes (35–40 μm thick) were prepared by casting a paste consisting of 80 wt% active material [Fe₃O₄ nanoparticles, GS (rGO) or Fe₃O₄/GS composite], 10 wt% conductive additive (Super P-Li, TIMCAL Ltd., Bodio, Switzerland) and 10 wt% poly(vinylidene fluoride) (PVDF) binder onto a copper foil. The typical mass loading of the working electrode was 2.5–3.0 mg cm⁻². A polypropylene membrane (Celgard 2400) was used as the separator. 1.0 M LiPF₆ in an ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/DEC) mixture (3:4:3 v/v/v) provided by Panax Etech Ltd. (Busan, Korea) was used as the electrolyte. The cells were assembled in an argon-filled glove box. Cyclic voltammograms were recorded in the voltage range of 3.0–0.01 V vs. Li⁺/Li at 0.1 mV s⁻¹. The cells were galvanostatically cycled in the cut-off voltage range of 3.0–0.01 V vs. Li⁺/Li using a galvanostat/potentiostat system (WonATech, Seoul, Korea).

4. Conclusions

Fe₃O₄/GS composite disks, in which Fe₃O₄ nanoparticles were ideally dispersed in GS layers, were prepared by electrostatic self-assembly of positively charged Fe₃O₄-APTMS nanoparticles on negatively charged GO sheets in acidic aqueous solution followed by in situ chemical reduction. Thus prepared Fe₃O₄/GS composite showed an excellent rate capability as well as much enhanced cycling stability compared with Fe₃O₄ electrode. The superior electrochemical responses of Fe₃O₄/GS composite disks assure the advantages of: (1) electrostatic self-assembly between high storage-capacity materials with GO sheets, and (2) the incorporation of GS in the Fe₃O₄/GS composite for high capacity LIB application.

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Conflicts of Interest

The authors declare no conflict of interest.

References


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