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Fe$_3$O$_4$/reduced graphene oxide with enhanced electrochemical performances towards lithium storage

Chaolun Liang, $^{ab}$ Teng Zhai, $^a$ Wang Wang, $^a$ Jian Chen, $^b$ Wenxia Zhao, $^b$ Xihong Lu $^a$ and Yexiang Tong, $^{aa}$

In this work, we reported the facile synthesis of the Fe$_3$O$_4$/reduced-graphene oxide (RGO) nanocomposites and their improved lithium storage capability. Fe$_3$O$_4$/RGO composites were synthesized by a facile co-precipitation method and exhibited outstanding electrochemical performance with good cycling stability. As an anode material for Lithium ion batteries (LIBs), the Fe$_3$O$_4$/RGO composites achieved high reversible capacity of 1637 mA h g$^{-1}$ (0.1 A g$^{-1}$) at the 10$^{th}$ cycle and still remained 1397 mA h g$^{-1}$ after 100 cycles. Moreover, the Fe$_3$O$_4$/RGO composites have excellent rate capability. Characterization results revealed that such large reversible capacity is attributed to the synergistic effect between Fe$_3$O$_4$ and RGO, which allows for abundant electrochemical active sites for lithium storage and RGO acts as a volume buffer that suppresses the aggregation of the Fe$_3$O$_4$ nanoparticles (NPs). In this work, we focused on the development of Fe$_3$O$_4$/graphene nanocomposites by a gas/liquid interface reaction, and these composites exhibited a specific capacity of 1048 mA h g$^{-1}$ at 0.1 C. Ji et al. reported a kind of Fe$_3$O$_4$/reduced graphene oxide (RGO) composites with a high reversible capacity of more than 900 mA h g$^{-1}$ at 0.05C. Similarly, Su et al. fabricated Fe$_3$O$_4$/graphene composites by homogeneously distributed Fe$_3$O$_4$ NPs with a size of 7 nm onto the surface of graphene and found that they achieved a high reversible specific capacity of 1102 mA h g$^{-1}$ at 100 mA g$^{-1}$. Despite these progresses, the design and synthesis of high-performance Fe$_3$O$_4$/graphene composites are still desirable. On the other hand, little attention has paid to the influence of the surface microstructure of Fe$_3$O$_4$ NPs on this kind of composites, although which is of great importance to their electrochemical properties.

In this work, we focused on the development of high-performance Fe$_3$O$_4$/RGO composites for LIBs and investigated the correlation between the detailed microstructure of the Fe$_3$O$_4$/RGO composites and their electrochemical performances. Fe$_3$O$_4$/RGO composites prepared by a coprecipitation method achieved a high reversible capacity of 1637 mA h g$^{-1}$ (0.1 A g$^{-1}$) at the 10$^{th}$ cycle and remained 1397 mA h g$^{-1}$ after 100 cycles, which are substantially higher than the reported values.

**Introduction**

Nowadays, with the increasing demand of electric vehicle and portable electric equipment, rechargeable lithium ion batteries (LIBs) with high energy density, high power density, high rate capability and long-term stability are urgently required. In the past decade, transition metal oxides have been intensively investigated as anodes in LIBs because they have higher theoretical specific capacities (500~1000 mA h g$^{-1}$) than the graphite (372 mA h g$^{-1}$). Among various available transition metal oxide anodes, Fe$_3$O$_4$ with the theoretical capacities of 924 mA h g$^{-1}$, has been considered as a promising candidate because of its nature abundance, inexpensive, and nontoxic. Recent reports have shown that Fe$_3$O$_4$ nanoparticles (NPs) exhibited much improved electrochemical performances than their bulk counterparts. However, the severe volume expansions (>200%) and agglomeration of Fe$_3$O$_4$ NPs lead to serious capacity loss and poor cycling stability, which greatly hinders its practical application in LIBs.

Combining Fe$_3$O$_4$ NPs with carbon materials to form composites represents an effective strategy to overcome these drawbacks, because carbon materials can act as not only a volume buffer but also a barrier to suppress the aggregation of the active NPs during the charging/discharging process. Over the past few years, the integration of Fe$_3$O$_4$ NPs with carbon materials such as carbon nanotubes, activated carbon, graphene, carbon nanofibers, etc. have been adopted to enhance the electrochemical performance of Fe$_3$O$_4$. In particular, graphene is widely regarded as a promising matrix to host Fe$_3$O$_4$ for its advantages of outstanding electron transport property, large surface area, superior mechanical strength and chemical stability, which can provide a large electrode/electrolyte contact area, a short transport distance and fast diffusion rates for both lithium ions and electrons.

For example, Lian et al. developed Fe$_3$O$_4$/graphene nanocomposites by a gas/liquid interface reaction, and these composites exhibited a specific capacity of 1048 mA h g$^{-1}$ up to 90 cycles. Ji et al. reported a kind of Fe$_3$O$_4$/reduced graphene oxide (RGO) composites with a high reversible capacity of more than 900 mA h g$^{-1}$ at 0.05C. Similarly, Su et al. fabricated Fe$_3$O$_4$/graphene composites by homogeneously distributed Fe$_3$O$_4$ NPs with a size of 7 nm onto the surface of graphene and found that they achieved a high reversible specific capacity of 1102 mA h g$^{-1}$ at 100 mA g$^{-1}$. Despite these progresses, the design and synthesis of high-performance Fe$_3$O$_4$/graphene composites are still desirable. On the other hand, little attention has paid to the influence of the surface microstructure of Fe$_3$O$_4$ NPs on this kind of composites, although which is of great importance to their electrochemical properties.
Characterization results reveal that such large reversible capacity is attributed to the nano-sized Fe₃O₄ particles with surface step atoms which offering abundant electrochemical active sites for lithium storage. Moreover, more than acting as a volume buffer and electron conductor, RGO could also preserve the electrochemical active surfaces and avoid the aggregation of the Fe₃O₄ NPs, and thus resulting in readily reaction between active material and electrolyte.

**Experimental**

**Synthesis of Fe₃O₄/RGO nanocomposites**

All reagents used were of analytical grade and were used directly without any purification. GO powders were synthesized by a modified Hummers method and RGO powders were obtained by reducing these GO powders in the N₂/H₂ atmosphere at 85 °C for 12 h. The Fe₃O₄/RGO nanocomposites were prepared by a chemical precipitation process. For a typical synthesis, 200 ml distilled water dispersion containing 0.1 g graphene sheet was homogeneously mixed with 0.08 g FeCl₃·4H₂O and 0.2 g FeCl₂·6H₂O (Tianjin Shentai Chemical Reagent Co., Ltd.). The reaction mixture was heated at 50 °C under a N₂ atmosphere. After the solution was sonicated for 10 min, 10 ml of 8 M NH₄OH aqueous solution was added dropwise to precipitate ferric and ferrous salts. The reaction was carried out at 50 °C for 30 min under vigorous magnetic stirring. The Fe₃O₄/RGO product was obtained by magnetic separation and washed with distilled water and ethanol and finally dried under vacuum at 80 °C. For comparison, bare Fe₃O₄ NPs was prepared by the same chemical precipitation process without the presence of the RGO. The Fe₃O₄/RGO composites with a higher mass loading of 0.81 mg cm⁻² were also synthesized by triple the mass of FeCl₃·4H₂O and FeCl₂·6H₂O without changing other conditions.

**Electrochemical Measurements**

Active materials (Fe₃O₄/RGO, bare Fe₃O₄, RGO), acetylene black (as conductive agent), and polyvinylidene fluoride (PVDF as binder) in a weight ratio of 80:10:10 were dissolved in N-methylpyrrolidone (NMP) to form slurry. Then the slurry was coated onto a copper foil and treated in a vacuum oven at 100 °C for 12 h. The electrodes were pressed and cut into disks as anode. Coin cells (CR2032) were fabricated with as synthesized anode, lithium metal as counter electrode, Celgard 2400 as separator, and LiPF₆ (1 M) in ethylene carbonate / dimethyl carbonate / diethyl carbonate (EC/DMC/DEC, 1:1:1 vol%) as the electrolyte. The cell was assembled in an Ar-filled glove box. The rate capability and cycle life of the cells were tested in a potential window of 0.01–3 V (vs Li⁺/Li) by a battery testing system (LAND CT 2001A). All of the specific capacities were calculated on the basis of the total weight of Fe₃O₄/RGO (0.37 mg cm⁻²), Fe₃O₄/RGO-2 (0.81 mg cm⁻²), bare Fe₃O₄ (0.40 mg cm⁻²), RGO (0.31 mg cm⁻²).

**Material Characterization**

The morphology, microstructure, and compositions of the products were characterized by field-emission scanning electron microscopy (FE-SEM, JSM-6330F), X-ray diffractometry (XRD, D8 ADVANCE), transmission electron microscopy (TEM, JEM2010-HR, FEI Tecnai G² F30), laser Micro-Raman Spectrometry (Renshaw inVia), photoelectron Spectroscopy (XPS, ESCALab250).

**Results and discussion**

Fig. 1a shows the typical XRD patterns of the bare Fe₃O₄ NPs and Fe₃O₄/RGO composites. All the diffraction peaks in both bare Fe₃O₄ and Fe₃O₄/RGO samples can be well indexed to the face-centered cubic (fcc) magnetite (JCPDS No.65-3107). The broadened XRD peaks indicate that the size of the Fe₃O₄ NPs was very small. According to the Scherrer equation, the average size of Fe₃O₄ NPs is calculated to be 9.8 nm for bare Fe₃O₄ and 8.3 nm for Fe₃O₄/RGO composites. Raman spectra of the bare Fe₃O₄ and Fe₃O₄/RGO composites were collected t Fig. 1b. The characteristic Raman scattering peaks at 490 and 670 cm⁻¹, corresponding to the T₂g and A₁g vibration modes of Fe₃O₄, were observed for both Fe₃O₄ and the Fe₃O₄/RGO composites. The peaks at around 1336 and 1600 cm⁻¹ are assigned to the D and G-band from graphene, respectively. To further investigate the composition and surface oxidation state of the as-prepared composites, X-ray photoelectron spectroscopy (XPS) analyses were also performed to The XPS survey spectrum of the Fe₃O₄/RGO composites is shown in Fig. S1. Beside C, O and Fe signals, no any signals of impurity are detected, revealing that the product is highly pure. In the spectrum of Fe 2p (Fig. S1b), the peaks of Fe 2p3/2 and Fe 2p1/2 located at 711.12 and 724.65 eV correspond to the magnetite phase. In addition, the satellite peak at about 719.0 eV does not appear, indicating the formation of the Fe₃O₄ instead of Fe₃O₄ in the RGO matrix. For carbon, the Cls XPS spectrum in Fig. 1c shows the low-oxygenated C at 284.8 eV, which reveals the efficient reduction of GO.

![Fig. 1](image-url)
which indicate that the FeO$_4$ NPs are uniformly embedded on the RGO matrix. It is worth noting that the FeO$_3$ NPs are still strongly attached on the surface of RGO sheets even after ultrasonic treatment during the TEM sample preparation process, implying the strong interaction between FeO$_4$ NPs and RGO sheets.

The electrochemical performances of the FeO$_4$/RGO composites were investigated using galvanostatic charge-discharge measurements. Fig. 3a presents the charge–discharge voltage profiles of the FeO$_4$/RGO anode for 1$^{st}$, 2$^{nd}$, 10$^{th}$, 50$^{th}$, 100$^{th}$ at a current density of 0.1 A g$^{-1}$ between 0.001 and 3.00 V. It can be seen that the FeO$_4$/RGO composites yielded a very high lithium storage capacity of 3536.8 mA h g$^{-1}$ at the first discharge process, and obtained a reversible capacity of 2189.6 mA h g$^{-1}$ with an initial coulombic efficiency of 61.9%. The irreversible capacity loss is attributed to the inevitable formation of solid electrolyte interphase (SEI) and/or decomposition of electrolytes. The discharge voltage plateau at around 0.8 V in the first cycle, which is different from other cycles, again confirming the occurred irreversible reactions in the first cycle. The discharge capacities of the FeO$_4$/RGO anode at 2$^{nd}$, 10$^{th}$, 50$^{th}$, 100$^{th}$ cycles are 2533.1, 1637.1, 1429.3, 1397.3 mA h g$^{-1}$, respectively. By contrast, the bare Fe$_3$O$_4$ anode at 2$^{nd}$, 10$^{th}$, 50$^{th}$, 100$^{th}$ cycles are 625, 200, 75, 75 mA h g$^{-1}$, respectively. Moreover, the presented capacities of the FeO$_4$/RGO anode are also substantially higher than hollow–FeO$_4$/graphene anode (about 1250 mA h g$^{-1}$ at 0.1 A g$^{-1}$),$^{27}$ Fe$_3$O$_4$ nanoparticle clusters anode (about 850 mA h g$^{-1}$ at 0.1 A g$^{-1}$),$^{28}$ nitrogen-doped FeO$_4$/graphene anode (about 1000 mA h g$^{-1}$ at 0.1 A g$^{-1}$),$^{29}$ and FeO$_4$/CNT composites (about 1400 mA h g$^{-1}$ at 0.09 A g$^{-1}$).$^{30}$ In addition, the capacity of FeO$_4$/RGO composites has no obvious change after 50 cycles, indicating its excellent cycling stability. Fig. 3b compares the cycling performances of bare Fe$_3$O$_4$, RGO and FeO$_4$/RGO electrodes at a current of 0.1 A g$^{-1}$ during 100 cycles. Significantly, the FeO$_4$/RGO electrode exhibited a much higher cycling capacity than the bare Fe$_3$O$_4$ and RGO electrodes. For example, the FeO$_4$/RGO electrode reached a high reversible capacity of 1600 mA h g$^{-1}$ after 10 cycles while only 197 mA h g$^{-1}$ for bare Fe$_3$O$_4$ electrode and 393 mA h g$^{-1}$ for RGO electrode. After 100 cycles, the FeO$_4$/RGO electrode still retained 1397.3 mA h g$^{-1}$ while the bare Fe$_3$O$_4$ and RGO electrodes maintained about 75 and 381 mA h g$^{-1}$. On the other hand, the coulombic efficiency of the FeO$_4$/RGO electrode is almost 100% during the 100 cycles, suggesting the facile lithium insertion/extraction associated with efficient transport of ions and electrons within the electrodes.$^{42}$ The enhanced electrochemical performance of FeO$_4$/RGO composites can be attributed to the synergistic effect between RGO and FeO$_4$ and the enhanced conductivity of FeO$_4$/RGO electrode.

Rate performance is a key factor for successful practical application as anode electrode. The FeO$_4$/RGO composites also possessed a high rate capability. As shown in Fig. 4a, the FeO$_4$/RGO composites achieved very high capacities of 1637, 1266, 965, 839, 721 mA h g$^{-1}$ at 0.1, 0.2, 0.5, 1 and 2 A g$^{-1}$, respectively. These values are much higher than those of the bare FeO$_4$ NPs (Fig. S2). Moreover, a capacity of 1588 mA h g$^{-1}$ was still recoverable (only 3% loss of initial capacity) when the current rate was returned to 0.1 A g$^{-1}$. The excellent rate capability of FeO$_4$/RGO composites is considerably higher and comparable to the reported values for other FeO$_4$/carbon materials composites, such as hollow–FeO$_4$/graphene sheet anode (about 40% from 0.1–2 A g$^{-1}$),$^{27}$ nitrogen-doped FeO$_4$/graphene anode (about 61.6% from 0.1–1.6 A g$^{-1}$),$^{29}$ and FeO$_4$/CNT composites (about 48.2% from 0.09–1.8 A g$^{-1}$).$^{30}$ Additionally, we have also studied the effect of the mass loading of FeO$_4$ on the rate capability of the FeO$_4$/RGO composites. FeO$_4$/RGO composite with a high FeO$_4$ mass loading of 0.81 mg cm$^{-2}$ (denoted as FeO$_4$/RGO-2) was obtained via increasing the amount of FeCl$_2$·4H$_2$O and FeCl$_3$·6H$_2$O during synthesis process (Experimental section), and the typical TEM and HRTEM images are shown in Fig. S3. As shown in Fig. 4a, the FeO$_4$/RGO-2 can deliver capacities of 1834, 1251, 978, 742 and 637 mA h g$^{-1}$ at 0.1, 0.2, 0.5, 1 and 2 A g$^{-1}$, respectively. The rate capability of FeO$_4$/RGO-2 from 0.1 to 2 A g$^{-1}$ is about 35%, which is smaller than that of FeO$_4$/RGO (about 44% from 0.1 to 2 A g$^{-1}$). This decrease can be attributed to the increased resistance of FeO$_4$/RGO-2 arising from the addition of nitrogen-doped graphene.
from the high mass loading of Fe$_2$O$_4$, which we will discuss in the following paragraph. As for the capacity did not significantly increase with the increased mass loading of Fe$_2$O$_4$, it might be due to the fact that more NPs on the RGO would inevitably pack and aggregate more active NPs, as indicated by HRETM observation (Fig. S3). Nevertheless, the capacities of Fe$_2$O$_4$/RGO-2 are still substantially higher than those of the bare Fe$_2$O$_4$ NPs. All these results convincingly show that the incorporation of RGO could dramatically improve the capacity and cycling stability of Fe$_2$O$_4$.

To gain an in-depth understanding of the enhanced electrochemical performance of Fe$_2$O$_4$/RGO composites, electrochemical impedance spectroscopy (EIS) analysis was conducted on bare Fe$_2$O$_4$, Fe$_2$O$_4$/RGO and Fe$_2$O$_4$/RGO-2 electrodes to investigate their electrochemical reaction kinetics. Fig. 4b shows the Nyquist plots of bare Fe$_2$O$_4$, Fe$_2$O$_4$/RGO and Fe$_2$O$_4$/RGO-2 electrodes at fresh coin cells over the frequency range from 100 kHz to 0.01 Hz. All the electrodes present a semicircle in the middle-high frequency region and a sloped straight line in the low frequency region. The semicircle in the moderate high frequency region is assigned to the charge-transfer or electrochemical reaction resistance, while the sloped straight at low frequency is related to the diffusion of lithium ions in the active material. Obviously, the charge transfer resistance of Fe$_2$O$_4$/RGO and Fe$_2$O$_4$/RGO-2 electrode are only 62 and 93 Ω, which are much smaller than that of bare Fe$_2$O$_4$ electrode (284 Ω), again confirming the increased conductivity of Fe$_2$O$_4$/RGO anodes. The larger charge-transfer resistance of Fe$_2$O$_4$/RGO-2 than the Fe$_2$O$_4$/RGO is due to the increased mass loading of the Fe$_2$O$_4$. Additionally, the relatively more vertical slope also indicates the easier and faster diffusion of lithium ions within the Fe$_2$O$_4$/RGO composites electrode.

HRTEM investigation on the detailed microstructure of the Fe$_2$O$_4$ NPs before and after integrating on RGO sheets were also carried out to further understand the origin of the superior electrochemical performances of the Fe$_2$O$_4$/RGO composites. Fig. 5a shows the TEM images of typical bare Fe$_2$O$_4$ NPs. It can be seen that the as-synthesized Fe$_2$O$_4$ NPs existed in the form of irregular polyhedral shapes. HRTEM observation of about 100 randomly selected NPs was performed. Fig. 5b, c and d show some representative HRTEM images of the NPs along different projections. Fourier filtering was used to extract the information of lattice fringes. In order to index the exposed facets, distances and angles of diffractions in the reciprocal space were analyzed. HRTEM studies revealed that these particles are mainly defined by {220} (or equally {110}), {111} and {113} surface facets. In most cases, {113} facets can be frequently observed, while {115} exposed facets can also be seen on the spherical-like particle (as shown in Fig. 5d). In general, high-index surfaces offer a high density of atomic steps, dangling bonds and ledges that act as chemical active sites. 45-46 For magnetite Fe$_3$O$_4$ with inverse spinel fcc structure, the {113} and {115} surfaces are composed of low-coordinated surface step atoms (as shown in Fig 6), which can have a strong impact on the surface reactivity. Accordingly, the irregularly shaped Fe$_2$O$_4$ NPs are expected to stimulate the reversible conversion reaction by offering abundant surface step atoms that act as electrochemical active sites. 18,47,48 However, NPs with a large portion of surface atoms are both highly active and unstable. In order to reduce the high surface energy, the aggregation of the Fe$_2$O$_4$ NPs would be favored, especially during the charging and discharging process. More evidences for the aggregation tendency of NPs can be seen from the HRTEM image of three adjacent Fe$_2$O$_4$ NPs. As shown in Fig. 5h, distinct interfaces among the particles are observed. It can be seen that the bigger particle is connected with two smaller ones by the {113} and {220} facets, sharing the same crystallographic orientation of <332> zone axis. Obviously, this HRTEM observation confirms that the adjacent Fe$_2$O$_4$ NPs in a common crystallographic orientation tend to fuse together by a coherent interface to minimize surface free energies. Therefore, the orientation attachment of the irregularly shaped NPs results in the reduction of surface atoms and electrochemical reactivity sites, which deteriorate the specific capacity and cycle stability, as demonstrated in Fig. 3 and Fig. 4.

**Fig. 5** (a) TEM images of bare Fe$_2$O$_4$ nanoparticles. (b, c, d) HRTEM images of individual Fe$_2$O$_4$ nanoparticles with irregular shapes. (e, f, g) Fast Fourier Transform (FFT) pattern corresponding to (b), (c) and (d), respectively. (h) HRTEM image of three adjacent Fe$_2$O$_4$ NPs viewed along <332>, showing the orientation attachment through coherent interfaces.

HRTEM investigation on the detailed microstructure of the Fe$_2$O$_4$ NPs before and after integrating on RGO sheets were also carried out to further understand the origin of the superior electrochemical performances of the Fe$_2$O$_4$/RGO composites. Fig. 5a shows the TEM images of typical bare Fe$_2$O$_4$ NPs. It can be seen that the as-synthesized Fe$_2$O$_4$ NPs existed in the form of irregular polyhedral shapes. HRTEM observation of about 100 randomly selected NPs was performed. Fig. 5b, c and d show some representative HRTEM images of the NPs along different projections. Fourier filtering was used to extract the information of lattice fringes. In order to index the exposed facets, distances and angles of diffractions in the reciprocal space were analyzed. HRTEM studies revealed that these particles are mainly defined by {220} (or equally {110}), {111} and {113} surface facets. In most cases, {113} facets can be frequently observed, while {115} exposed facets can also be seen on the spherical-like particle (as shown in Fig. 5d). In general, high-index surfaces offer a high density of atomic steps, dangling bonds and ledges that act as chemical active sites. 45-46 For magnetite Fe$_3$O$_4$ with inverse spinel fcc structure, the {113} and {115} surfaces are composed of low-coordinated surface step atoms (as shown in Fig 6), which can have a strong impact on the surface reactivity. Accordingly, the irregularly shaped Fe$_2$O$_4$ NPs are expected to stimulate the reversible conversion reaction by offering abundant surface step atoms that act as electrochemical active sites. 18,47,48 However, NPs with a large portion of surface atoms are both highly active and unstable. In order to reduce the high surface energy, the aggregation of the Fe$_2$O$_4$ NPs would be favored, especially during the charging and discharging process. More evidences for the aggregation tendency of NPs can be seen from the HRTEM image of three adjacent Fe$_2$O$_4$ NPs. As shown in Fig. 5h, distinct interfaces among the particles are observed. It can be seen that the bigger particle is connected with two smaller ones by the {113} and {220} facets, sharing the same crystallographic orientation of <332> zone axis. Obviously, this HRTEM observation confirms that the adjacent Fe$_2$O$_4$ NPs in a common crystallographic orientation tend to fuse together by a coherent interface to minimize surface free energies. Therefore, the orientation attachment of the irregularly shaped NPs results in the reduction of surface atoms and electrochemical reactivity sites, which deteriorate the specific capacity and cycle stability, as demonstrated in Fig. 3 and Fig. 4.

**Fig. 6** (a) Atomic ball-stick model of magnetite Fe$_3$O$_4$ oriented along [110], in which {110}, {111}, {113} and {115} facets are viewed edge-on. (b-e) Ball models of Fe$_3$O$_4$ crystallography planes, showing the atomic arrangements on the {110}, {111}, {113} and {115} facets, respectively. Iron is colored green and oxygen is colored red. The {110} planes are flat with closely packed surface atoms. The {111} planes are composed of zigzag arranged atoms. The {113} and {115} planes are rough with low-coordinated step atoms.

Fig. 7 illustrates the structural features of the Fe$_3$O$_4$/RGO composites. Separated Fe$_3$O$_4$ NPs with different crystallographic orientation are uniformly dispersed on RGO. Most of the isolated Fe$_3$O$_4$ NPs maintain their irregular shapes, suggesting that the step atoms on the high indexed exposed
facets are preserved. As demonstrated in Fig. 7b, edges and corners that benefit the conversion reaction towards lithium storage can be observed on the surface of the isolated particle. Carbon layers attached to the surfaces of isolated particles can also be seen, which indicates that the highly active surfaces could be protected by RGO. The enlarged HRTEM image from square c in Fig. 7 reveals two particles contacted by {220} and {113} facets. The lattice mismatch between {220} and {113} is calculated to be 15.7%, implying that it is difficult for the contacting particles to merge together to form a secondary large particle. According to HRTEM observation of different areas in the copper grid (some typical images are shown in Fig. S4), no oriented attachment of Fe$_3$O$_4$ NPs through a coherent interface can be found, suggesting that the interaction between RGO and NPs are so strong that even the contacted NPs cannot rotate and align freely. Based on HRTEM analysis, it is indicated that the RGO is able to hinder the grain rotation and grain realignment that lead to orientation attachment, thus keeping the active materials apart from aggregation. Thereby, the Fe$_3$O$_4$ particles deposited on RGO were kept in a small dimension that benefits the electrode performances in two aspects: (1) the volume change during the charging and discharging processes could be accommodated. (2) A large portion of Fe$_3$O$_4$ NPs with electrochemical active surfaces maintain contact with the electrolyte, thus allowing readily access of ions and electrons to the active surfaces, which could contribute to the excellent rate performance. At the same time, RGO in the composites provides electron conductive channels among active particles as well as large electrode/electrolyte interfacial contact area as previously reported.$^{31,32}$ Hence, combining properties of both high electrochemical activity and high conductivity, RGO sheets loaded by homogeneously dispersed Fe$_3$O$_4$ NPs with active surfaces should be responsible for the superior electrochemical performances.

Conclusions

In summary, Fe$_3$O$_4$/RGO composites with superior electrochemical performances were successfully prepared by a simple coprecipitation method. The Fe$_3$O$_4$/RGO electrode exhibited substantially higher electrochemical performances than bare Fe$_3$O$_4$ NPs and RGO electrodes. The Fe$_3$O$_4$/RGO composites delivered a high lithium storage capacity and good cycle stability of 1637 mA h g$^{-1}$ at 0.1 A g$^{-1}$ for the 10$^{th}$ cycle and could remain 1397 mA h g$^{-1}$ after 100 cycles. The improved capacities and excellent cycling stability are attributed to the synergistic effect between Fe$_3$O$_4$ and RGO, which the Fe$_3$O$_4$ NPs provide large portion of electrochemical active sites and the RGO substrate preserves the active surface of Fe$_3$O$_4$ and acts as a conducting matrix as well as a volume buffer. These findings provide a new insight into the effect of Fe$_3$O$_4$ NPs and RGO on the improvement of electrochemical performances.

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Notes and references

$^{a}$ KLGHEI of Environment and Energy Chemistry, MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China. E-mail: chedhx@mail.sysu.edu.cn; luxx6@mail.sysu.edu.cn; Fax: +86-20-84112245; Tel: +86-20-84110071

$^{b}$ Instrumental Analysis and Research Centre, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China.

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