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## ARTICLE

# Fe<sub>3</sub>O<sub>4</sub>/reduced graphene oxide with enhanced electrochemical performances towards lithium storage

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In this work, we reported the facile synthesis of the Fe<sub>3</sub>O<sub>4</sub>/reduced-graphene oxide (RGO) nanocomposites and their improved lithium storage capability. Fe<sub>3</sub>O<sub>4</sub>/RGO composites synthesized by a facile co-precipitate method exhibited outstanding electrochemical performance with good cycling stability. As an anode material for Lithium ion batteries (LIBs), the Fe<sub>3</sub>O<sub>4</sub>/RGO composites achieved a high reversible capacity of 1637 mA h g<sup>-1</sup> (0.1 A g<sup>-1</sup>) at the 10<sup>th</sup> cycle and still remained 1397 mA h g<sup>-1</sup> after 100 cycles. Moreover, the Fe<sub>3</sub>O<sub>4</sub>/RGO composites have excellent rate capability. Characterization results reveal that such large reversible capacity is attributed to the synergistic effect between Fe<sub>3</sub>O<sub>4</sub> and RGO, which the Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) with surface step atoms offer abundant electrochemical active sites for lithium storage and RGO acts as a volume buffer and electron conductor, and more importantly preserves the electrochemical active surfaces and avoids the aggregation of the Fe<sub>3</sub>O<sub>4</sub> NPs.

## 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.<sup>1-5</sup> 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<sup>-1</sup>) than the graphite (372 mA h g<sup>-1</sup>).<sup>6,7</sup> Among various available transition metal oxide anodes, Fe<sub>3</sub>O<sub>4</sub> with the theoretical capacities of 924 mA h g<sup>-1</sup>, has been considered as a promising candidate because of its nature abundance, inexpensive, and nontoxic.<sup>8-11</sup> Recent reports have shown that Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) exhibited much improved electrochemical performances than their bulk counterparts.<sup>12,13</sup> However, the severe volume expansions (> 200%) and agglomeration of Fe<sub>3</sub>O<sub>4</sub> NPs lead to serious capacity loss and poor cycling stability, which greatly hinder its practical application in LIBs.<sup>14</sup>

Combining Fe<sub>3</sub>O<sub>4</sub> 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.<sup>15,16</sup> Over the past few years, the integration of Fe<sub>3</sub>O<sub>4</sub> NPs with carbon materials such as carbon nanotubes<sup>17</sup>, activated carbon<sup>18</sup>, graphene<sup>19</sup>, carbon nanofibers<sup>20</sup>, etc. have been adopted to enhance the electrochemical performance of Fe<sub>3</sub>O<sub>4</sub>. In particular, graphene is widely regarded as a promising matrix to

host Fe<sub>3</sub>O<sub>4</sub> for its advantages of outstanding electron transport property, large surface area, superior mechanical strength and chemical stability,<sup>21</sup> which can provide a large electrode/electrolyte contact area, a short transport distance and fast diffusion rates for both lithium ions and electrons.<sup>15,22,23</sup> For example, Lian *et al.* developed Fe<sub>3</sub>O<sub>4</sub>/graphene nanocomposites by a gas/liquid interface reaction, and these composites exhibited a specific capacity of 1048 mA h g<sup>-1</sup> up to 90 cycles.<sup>24</sup> Ji *et al.* reported a kind of Fe<sub>3</sub>O<sub>4</sub>/reduced graphene oxide (RGO) composites with a high reversible capacity of more than 900 mA h g<sup>-1</sup> at 0.05C.<sup>25</sup> Similarly, Su *et al.* fabricated Fe<sub>3</sub>O<sub>4</sub>/graphene composites by homogeneously distributed Fe<sub>3</sub>O<sub>4</sub> 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<sup>-1</sup> at 100 mA g<sup>-1</sup>.<sup>26</sup> Despite these progresses, the design and synthesis of high-performance Fe<sub>3</sub>O<sub>4</sub>/graphene composites anodes are still desirable. On the other hand, little attention has paid to the influence of the surface microstructure of Fe<sub>3</sub>O<sub>4</sub> 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<sub>3</sub>O<sub>4</sub>/RGO composites for LIBs and investigation of the correlation between the detailed microstructure of the Fe<sub>3</sub>O<sub>4</sub>/RGO composites and their electrochemical performances. Fe<sub>3</sub>O<sub>4</sub>/RGO composites prepared by a coprecipitation method achieved a high reversible capacity of 1637 mA h g<sup>-1</sup> (0.1 A g<sup>-1</sup>) at the 10<sup>th</sup> cycle and remained 1397 mA h g<sup>-1</sup> after 100 cycles, which are substantially higher than the reported values.<sup>27-30</sup>

Characterization results reveal that such large reversible capacity is attributed to the nano-sized  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  NPs, and thus resulting in readily reaction between active material and electrolyte.

## Experimental

### Synthesis of $\text{Fe}_3\text{O}_4/\text{RGO}$ nanocomposites

All reagents used were of analytical grade and were used directly without any purification. GO powders were synthesized by a modified Hummers method<sup>31-33</sup> and RGO powders were obtained by reducing these GO powders in the  $\text{N}_2/\text{H}_4$  atmosphere at 85 °C for 12 h. The  $\text{Fe}_3\text{O}_4/\text{RGO}$  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  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and 0.2 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (Tianjin Shentai Chemical Reagent Co., Ltd.). The reaction mixture was heated at 50 °C under a  $\text{N}_2$  atmosphere. After the solution was sonicated for 10 min, 10 ml of 8 M  $\text{NH}_4\text{OH}$  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  $\text{Fe}_3\text{O}_4/\text{RGO}$  product was obtained by magnetic separation and washed with distilled water and ethanol and finally dried under vacuum at 80 °C. For comparison, bare  $\text{Fe}_3\text{O}_4$  NPs was prepared by the same chemical precipitation process without the presence of the RGO. The  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites with a higher mass loading of 0.81  $\text{mg cm}^{-2}$  were also synthesized by triple the mass of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  without changing other conditions.

### Electrochemical Measurements

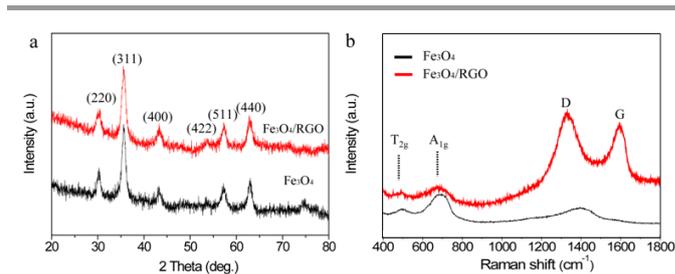
Active materials ( $\text{Fe}_3\text{O}_4/\text{RGO}$ , bare  $\text{Fe}_3\text{O}_4$ , RGO), acetylene black (as conductive agent), and polyvinylidene fluoride (PVDF as binder) in a weight ratio of 80:10:10 were dissolved in N-methylpyrrolidone (NMP) to form slurry. Then the slurry was coated onto a 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  $\text{LiPF}_6$  (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  $\text{Li}^+/\text{Li}$ ) by a battery testing system (LAND CT 2001A). All of the specific capacities were calculated on the basis of the total weight of  $\text{Fe}_3\text{O}_4/\text{RGO}$  (0.37  $\text{mg cm}^{-2}$ ),  $\text{Fe}_3\text{O}_4/\text{RGO}-2$  (0.81  $\text{mg cm}^{-2}$ ), bare  $\text{Fe}_3\text{O}_4$  (0.40  $\text{mg cm}^{-2}$ ), RGO (0.31  $\text{mg cm}^{-2}$ ).

### 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 G<sup>2</sup> F30), laser Micro-Raman Spectrometry (Renishaw inVia), photoelectron Spectroscopy (XPS, ESCALab250).

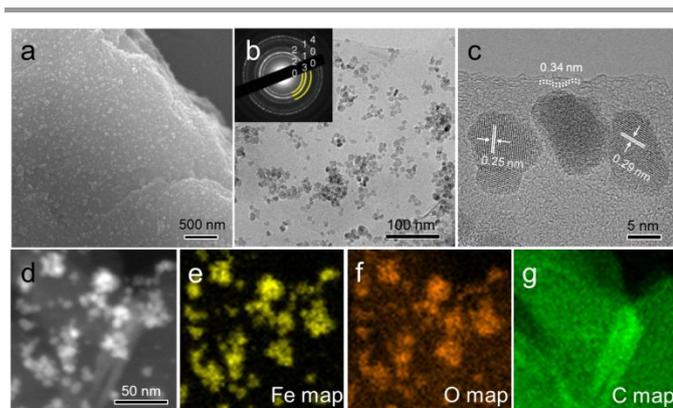
## Results and discussion

Fig. 1a shows the typical XRD patterns of the bare  $\text{Fe}_3\text{O}_4$  NPs and  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites. All the diffraction peaks in both bare  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4/\text{RGO}$  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  $\text{Fe}_3\text{O}_4$  NPs was very small. According to the Scherrer equation, the average size of  $\text{Fe}_3\text{O}_4$  NPs is calculated to be 9.8 nm for bare  $\text{Fe}_3\text{O}_4$  and 8.3 nm for  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites. Raman spectra of the bare  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites were collected in Fig. 1b. The characteristic Raman scattering peaks at 490 and 670  $\text{cm}^{-1}$ , corresponding to the  $\text{T}_{2g}$  and  $\text{A}_{1g}$  vibration modes of  $\text{Fe}_3\text{O}_4$ , were observed for both  $\text{Fe}_3\text{O}_4$  and the  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites.<sup>34,35</sup> The peaks at around 1336 and 1600  $\text{cm}^{-1}$  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  $\text{Fe}_3\text{O}_4/\text{RGO}$  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 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> 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  $\text{Fe}_3\text{O}_4$  instead of  $\text{Fe}_2\text{O}_3$  in the RGO matrix.<sup>36-38</sup> For carbon, the C1s XPS spectrum in Fig. S1c shows the low-oxygenated C at 284.8 eV, which reveals the efficient reduction of GO.<sup>9,39</sup>



**Fig. 1** (a) XRD patterns and (b) Raman spectra collected for bare  $\text{Fe}_3\text{O}_4$  NPs and  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites.

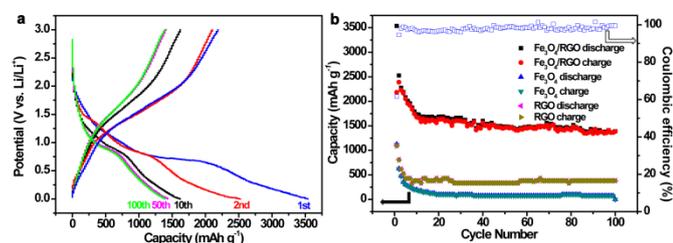
Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses were carried out to study the morphology and detailed microstructure of the  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites. SEM image reveals that a lot of  $\text{Fe}_3\text{O}_4$  NPs are densely and uniformly deposited on RGO surface (Fig. 2a). Fig. 2b displays a typical TEM image of the  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites. It is clearly seen that  $\text{Fe}_3\text{O}_4$  NPs with an average diameter of about 9-11 nm are homogeneously dispersed on the surface of RGO sheets, which is in accordance with SEM result. From the inset of Fig. 2b, the diffraction rings can be indexed to 220, 113 and 400 diffractions of fcc magnetite structure. The bright diffraction rings indicate that the  $\text{Fe}_3\text{O}_4$  NPs were well crystallized. Fig. 2c illustrates a high resolution TEM (HRTEM) image, showing the microstructure of RGO and  $\text{Fe}_3\text{O}_4$  NPs. The measured lattice fringes of 0.29 nm and 0.25 nm correspond to the interplanar distances of {220} and {113} plane of magnetite, respectively. Additionally, a characteristic inter-graphene spacing of 0.34 nm was also observed. As shown in Fig. 2d, small particles are easily visible when imaged in scanning TEM (STEM) mode with high-angle annular dark field (HAADF) detector. Moreover, the distributions of Fe, O and C are clearly presented by the STEM-EDS elemental maps (Fig. 2e, f and g),



**Fig. 2** (a) SEM and (b) TEM bright field image of  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites. Inset in (b) shows the corresponding SAED pattern of  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites. (c) HRTEM image and (d) HAADF-STEM image of  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites. (e-g) STEM-EDS elemental mapping of iron, oxygen, and carbon, respectively.

which indicate that the  $\text{Fe}_3\text{O}_4$  NPs are uniformly embedded on the RGO matrix. It is worth noting that the  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  NPs and RGO sheets.

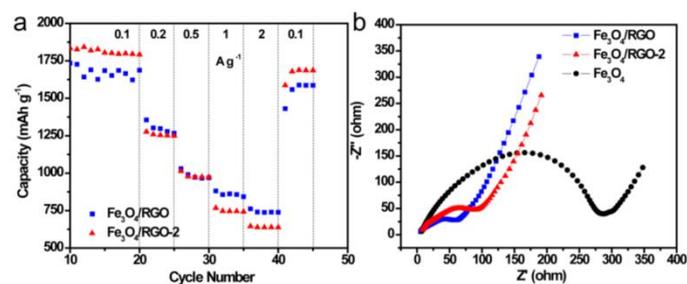
The electrochemical performances of the  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites were investigated using galvanostatic charge-discharge measurements. Fig. 3a presents the charge-discharge voltage profiles of the  $\text{Fe}_3\text{O}_4/\text{RGO}$  anode for 1<sup>st</sup>, 2<sup>nd</sup>, 10<sup>th</sup>, 50<sup>th</sup>, 100<sup>th</sup> at a current density of  $0.1 \text{ A g}^{-1}$  between 0.001 and  $3.00 \text{ V}$ . It can be seen that the  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites yielded a very high lithium storage capacity of  $3536.8 \text{ mA h g}^{-1}$  at the first discharge process, and obtained a reversible capacity of  $2189.6 \text{ mA h g}^{-1}$  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.<sup>26,40,41</sup> The discharge voltage plateau at around  $0.8 \text{ V}$  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  $\text{Fe}_3\text{O}_4/\text{RGO}$  anode at 2<sup>nd</sup>, 10<sup>th</sup>, 50<sup>th</sup>, 100<sup>th</sup> cycles are 2533.1, 1637.1, 1429.3,  $1397.3 \text{ mA h g}^{-1}$ , respectively. By contrast, the bare  $\text{Fe}_3\text{O}_4$  anode at 2<sup>nd</sup>, 10<sup>th</sup>, 50<sup>th</sup>, 100<sup>th</sup> cycles are 625, 200, 75,  $75 \text{ mA h g}^{-1}$ , respectively. Moreover, the presented capacities of the  $\text{Fe}_3\text{O}_4/\text{RGO}$  anode are also substantially higher than hollow- $\text{Fe}_3\text{O}_4/\text{graphene}$  anode (about  $1250 \text{ mA h g}^{-1}$  at  $0.1 \text{ A g}^{-1}$ ),<sup>27</sup>  $\text{Fe}_3\text{O}_4$  nanoparticle clusters anode (about  $850 \text{ mA h g}^{-1}$  at  $0.1 \text{ A g}^{-1}$ ),<sup>28</sup> nitrogen-doped  $\text{Fe}_3\text{O}_4/\text{graphene}$  anode (about  $1000 \text{ mA h g}^{-1}$  at  $0.1 \text{ A g}^{-1}$ ),<sup>29</sup> and  $\text{Fe}_3\text{O}_4\text{-CNT}$  composites (about



**Fig. 3** (a) Charge-discharge voltage profiles of  $\text{Fe}_3\text{O}_4/\text{RGO}$  anode at a current density of  $0.1 \text{ A g}^{-1}$ . (b) Cycling performances of  $\text{Fe}_3\text{O}_4/\text{RGO}$ , bare  $\text{Fe}_3\text{O}_4$ , and RGO anode charged and discharged at a current of  $0.1 \text{ A g}^{-1}$  up to 100 cycles.

$1400 \text{ mA h g}^{-1}$  at  $0.09 \text{ A g}^{-1}$ ).<sup>30</sup> In addition, the capacity of  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites has no obvious change after 50 cycles, indicating its excellent cycling stability. Fig. 3b compares the cycling performances of bare  $\text{Fe}_3\text{O}_4$ , RGO and  $\text{Fe}_3\text{O}_4/\text{RGO}$  electrodes at a current of  $0.1 \text{ A g}^{-1}$  during 100 cycles. Significantly, the  $\text{Fe}_3\text{O}_4/\text{RGO}$  electrode exhibited a much higher cycling capacity than the bare  $\text{Fe}_3\text{O}_4$  and RGO electrodes. For example, the  $\text{Fe}_3\text{O}_4/\text{RGO}$  electrode reached a high reversible capacity of  $1600 \text{ mA h g}^{-1}$  after 10 cycles while only  $197 \text{ mA h g}^{-1}$  for bare  $\text{Fe}_3\text{O}_4$  electrode and  $393 \text{ mA h g}^{-1}$  for RGO electrode. After 100 cycles, the  $\text{Fe}_3\text{O}_4/\text{RGO}$  electrode still retained  $1397.3 \text{ mA h g}^{-1}$  while the bare  $\text{Fe}_3\text{O}_4$  and RGO electrodes maintained about 75 and  $381$

$\text{mA h g}^{-1}$ . On the other hand, the coulombic efficiency of the  $\text{Fe}_3\text{O}_4/\text{RGO}$  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.<sup>42</sup> The enhanced electrochemical performance of  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites can be attributed to the synergistic effect between RGO and  $\text{Fe}_3\text{O}_4$  and the enhanced conductivity of  $\text{Fe}_3\text{O}_4/\text{RGO}$  electrode.

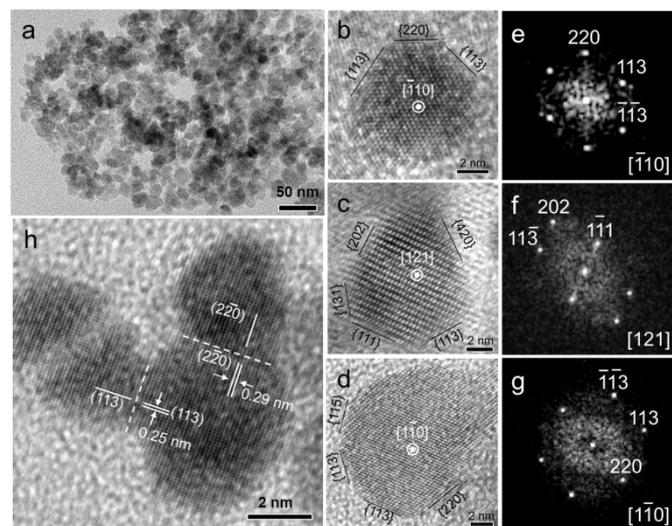


**Fig. 4** (a) Rate capability of the  $\text{Fe}_3\text{O}_4/\text{RGO}$  and  $\text{Fe}_3\text{O}_4/\text{RGO-2}$  electrodes at different current densities for 45 cycles. (b) Nyquist plots of  $\text{Fe}_3\text{O}_4/\text{RGO}$ ,  $\text{Fe}_3\text{O}_4/\text{RGO-2}$  and bare  $\text{Fe}_3\text{O}_4$  electrodes at fresh coin cells over the frequency range from  $100 \text{ kHz}$  to  $0.01 \text{ Hz}$ .

Rate performance is a key factor for successful practical application as anode electrode. The  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites also possessed a high rate capability. As shown in Fig. 4a, the  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites achieved very high capacities of 1637, 1266, 965, 839,  $721 \text{ mA h g}^{-1}$  at 0.1, 0.2, 0.5, 1 and  $2 \text{ A g}^{-1}$ , respectively. These values are much higher than those of the bare  $\text{Fe}_3\text{O}_4$  NPs (Fig. S2). Moreover, a capacity of  $1588 \text{ mA h g}^{-1}$  was still recoverable (only 3% loss of initial capacity) when the current rate was returned to  $0.1 \text{ A g}^{-1}$ . The excellent rate capability of  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites is considerably higher and comparable to the reported values for other  $\text{Fe}_3\text{O}_4/\text{carbon}$  materials composites, such as hollow- $\text{Fe}_3\text{O}_4/\text{graphene}$  sheet anode (about 40% from  $0.1\sim 2 \text{ A g}^{-1}$ ),<sup>27</sup> nitrogen-doped  $\text{Fe}_3\text{O}_4/\text{graphene}$  anode (about 61.6% from  $0.1\sim 1.6 \text{ A g}^{-1}$ ),<sup>29</sup> and  $\text{Fe}_3\text{O}_4\text{-CNT}$  composites (about 48.2% from  $0.09\sim 1.8 \text{ A g}^{-1}$ ).<sup>30</sup> Additionally, we have also studied the effect of the mass loading of  $\text{Fe}_3\text{O}_4$  on the rate capability of the  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites.  $\text{Fe}_3\text{O}_4/\text{RGO}$  composite with a high  $\text{Fe}_3\text{O}_4$  mass loading of  $0.81 \text{ mg cm}^{-2}$  (denoted as  $\text{Fe}_3\text{O}_4/\text{RGO-2}$ ) was obtained via increasing the amount of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  during synthesis process (Experimental section), and the typical TEM and HRTEM images are shown in Fig. S3. As shown in Fig. 4a, the  $\text{Fe}_3\text{O}_4/\text{RGO-2}$  can deliver capacities of 1834, 1251, 978, 742 and  $637 \text{ mA h g}^{-1}$  at 0.1, 0.2, 0.5, 1 and  $2 \text{ A g}^{-1}$ , respectively. The rate capability of  $\text{Fe}_3\text{O}_4/\text{RGO-2}$  from 0.1 to  $2 \text{ A g}^{-1}$  is about 35%, which is smaller than that of  $\text{Fe}_3\text{O}_4/\text{RGO}$  (about 44% from 0.1 to  $2 \text{ A g}^{-1}$ ). This decrease can be attributed to the increased resistance of  $\text{Fe}_3\text{O}_4/\text{RGO-2}$  arising

from the high mass loading of  $\text{Fe}_3\text{O}_4$ , which we will discuss in the following paragraph. As for the capacity did not significantly increase with the increased mass loading of  $\text{Fe}_3\text{O}_4$ , 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  $\text{Fe}_3\text{O}_4/\text{RGO}-2$  are still substantially higher than those of the bare  $\text{Fe}_3\text{O}_4$  NPs. All these results convincingly show that the incorporation of RGO could dramatically improve the capacity and cycling stability of  $\text{Fe}_3\text{O}_4$ .

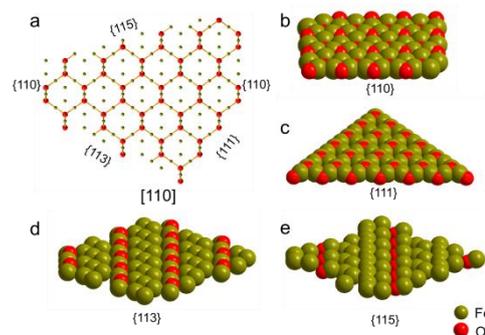
To gain an in-depth understanding of the enhanced electrochemical performance of  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites, electrochemical impedance spectroscopy (EIS) analysis was conducted on bare  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4/\text{RGO}$  and  $\text{Fe}_3\text{O}_4/\text{RGO}-2$  electrodes to investigate their electrochemical reaction kinetics. Fig. 4b shows the Nyquist plots of bare  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4/\text{RGO}$  and  $\text{Fe}_3\text{O}_4/\text{RGO}-2$  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,<sup>27,29</sup> 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  $\text{Fe}_3\text{O}_4/\text{RGO}$  and  $\text{Fe}_3\text{O}_4/\text{RGO}-2$  electrode are only 62 and 93  $\Omega$ , which are much smaller than that of bare  $\text{Fe}_3\text{O}_4$  electrode (284  $\Omega$ ), again confirming the enhanced conductivity of  $\text{Fe}_3\text{O}_4/\text{RGO}$  anodes. The larger charge-transfer resistance of  $\text{Fe}_3\text{O}_4/\text{RGO}-2$  than the  $\text{Fe}_3\text{O}_4/\text{RGO}$  is due to the increased mass loading of the  $\text{Fe}_3\text{O}_4$ . Additionally, the relatively more vertical slope also indicates the easier and faster diffusion of lithium ions within the  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites electrode.



**Fig. 5** (a) TEM images of bare  $\text{Fe}_3\text{O}_4$  nanoparticles. (b, c, d) HRTEM images of individual  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  NPs viewed along  $\langle 332 \rangle$ , showing the orientation attachment through coherent interfaces.

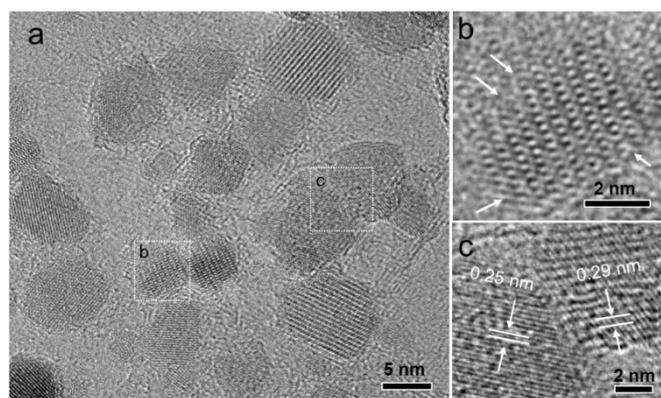
HRTEM investigation on the detailed microstructure of the  $\text{Fe}_3\text{O}_4$  NPs before and after integrating on RGO sheets were also carried out to further understand the origin of the superior electrochemical performances of the  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites. Fig. 5a shows the TEM images of typical bare  $\text{Fe}_3\text{O}_4$  NPs. It

can be seen that the as-synthesized  $\text{Fe}_3\text{O}_4$  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.<sup>43-46</sup> For magnetite  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  NPs are expected to stimulate the reversible conversion reaction by offering abundant surface step atoms that act as electrochemical active sites.<sup>18,47,48</sup> 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  $\text{Fe}_3\text{O}_4$  NPs would be favored,<sup>49,50</sup> 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  $\text{Fe}_3\text{O}_4$  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  $\langle 332 \rangle$  zone axis. Obviously, this HRTEM observation confirms that the adjacent  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  oriented along  $[110]$ , in which  $\{110\}$ ,  $\{111\}$ ,  $\{113\}$  and  $\{115\}$  facets are viewed edge-on. (b-e) Ball models of  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites. Separated  $\text{Fe}_3\text{O}_4$  NPs with different crystallographic orientation are uniformly dispersed on RGO. Most of the isolated  $\text{Fe}_3\text{O}_4$  NPs maintain their irregular shapes, suggesting that the step atoms on the high indexed exposed



**Fig. 7** (a) Typical HRTEM image of  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites, showing the uniformly-dispersed  $\text{Fe}_3\text{O}_4$  nanoparticles deposited on RGO. (b) Magnified HRTEM image of an individual  $\text{Fe}_3\text{O}_4$  nanoparticle, on which edges and corners can be observed, as indicated by white arrows. (c) HRTEM image of two  $\text{Fe}_3\text{O}_4$  NPs contacted by incoherent interface.

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  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  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.<sup>51,52</sup> Hence, combining properties of both high electrochemical activity and high conductivity, RGO sheets loaded by homogeneously dispersed  $\text{Fe}_3\text{O}_4$  NPs with active surfaces should be responsible for the superior electrochemical performances.

## Conclusions

In summary,  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites with superior electrochemical performances were successfully prepared by a simple coprecipitation method. The  $\text{Fe}_3\text{O}_4/\text{RGO}$  electrode exhibited substantially higher electrochemical performances than bare  $\text{Fe}_3\text{O}_4$  NPs and RGO electrodes. The  $\text{Fe}_3\text{O}_4/\text{RGO}$  composites delivered a high lithium storage capacity and good cycle stability of  $1637 \text{ mA h g}^{-1}$  at  $0.1 \text{ A g}^{-1}$  for the 10<sup>th</sup> cycle

and could remain  $1397 \text{ mA h g}^{-1}$  after 100 cycles. The improved capacities and excellent cycling stability are attributed to the synergistic effect between  $\text{Fe}_3\text{O}_4$  and RGO, which the  $\text{Fe}_3\text{O}_4$  NPs provide large portion of electrochemical active sites and the RGO substrate preserves the active surface of  $\text{Fe}_3\text{O}_4$  and acts as a conducting matrix as well as a volume buffer. These findings provide a new insight into the effect of  $\text{Fe}_3\text{O}_4$  NPs and RGO on the improvement of electrochemical performances.

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1. M. Armand and J. M. Tarascon, *Nature*, 2008, **451**, 652-657.
2. W. M. Zhang, X. L. Wu, J. S. Hu, Y. G. Guo and L. J. Wan, *Adv. Funct. Mater.*, 2008, **18**, 3941-3946.
3. B. Scrosati and J. Garche, *J. Power Sources*, 2010, **195**, 2419-2430.
4. G. L. Xu, Y. F. Xu, J. C. Fang, F. Fu, H. Sun, L. Huang, S. Yang and S. G. Sun, *ACS Appl. Mater. Inter.*, 2013, **5**, 6316-6323.
5. Y. Xie and C. Wu, *Dalton T.*, 2007, 5235-5240.
6. J. Jiang, Y. Li, J. Liu, X. Huang, C. Yuan and X. W. Lou, *Adv. Mater.*, 2012, **24**, 5166-5180.
7. Y. Liu and X. Zhang, *Electrochim. Acta*, 2009, **54**, 4180-4185.
8. S. Mitra, P. Poizot, A. Finke and J. M. Tarascon, *Adv. Funct. Mater.*, 2006, **16**, 2281-2287.
9. W. Chen, S. Li, C. Chen and L. Yan, *Adv. Mater.*, 2011, **23**, 5679-5683.
10. L. Wang, H. Ji, S. Wang, L. Kong and G. Yang, *Nanoscale*, 2013, **5**, 3793-3799.
11. R. Li, X. Ren, F. Zhang, C. Du and J. Liu, *Chem. Commun.*, 2012, **48**, 5010-5012.
12. P. L. Taberna, S. Mitra, P. Poizot, P. Simon and J. M. Tarascon, *Nat. Mater.*, 2006, **5**, 567-573.
13. C. Yang, J. Wu and Y. Hou, *Chem. Commun.*, 2011, **47**, 5130-5141.
14. Q. Q. Xiong, Y. Lu, X. L. Wang, C. D. Gu, Y. Q. Qiao and J. P. Tu, *J. Alloy. Comp.*, 2012, **536**, 219-225.
15. J. Hou, Y. Shao, M. W. Ellis, R. B. Moore and B. Yi, *Phys. Chem. Chem. Phys.*, 2011, **13**, 15384-15402.

16. J. Xiao, G. Xu, S. G. Sun and S. Yang, *Part. Part. Syst. Char.*, 2013, **30**, 893-904.
17. C. Ban, Z. Wu, D. T. Gillaspie, L. Chen, Y. Yan, J. L. Blackburn and A. C. Dillon, *Adv. Mater.*, 2010, **22**, E145-E149.
18. Z. M. Cui, L. Y. Jiang, W. G. Song and Y. G. Guo, *Chem. Mater.*, 2009, **21**, 1162-1166.
19. J. Z. Wang, C. Zhong, D. Wexler, N. H. Idris, Z. X. Wang, L. Q. Chen and H. K. Liu, *Chem-Eur. J.*, 2011, **17**, 661-667.
20. L. Wang, Y. Yu, P. C. Chen, D. W. Zhang and C. H. Chen, *J. Power Sources*, 2008, **183**, 717-723.
21. X. Lu, H. Dou, B. Gao, C. Yuan, S. Yang, L. Hao, L. Shen and X. Zhang, *Electrochim. Acta*, 2011, **56**, 5115-5121.
22. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666-669.
23. M. J. Allen, V. C. Tung and R. B. Kaner, *Chem. Rev.*, 2009, **110**, 132-145.
24. P. Lian, X. Zhu, H. Xiang, Z. Li, W. Yang and H. Wang, *Electrochim. Acta*, 2010, **56**, 834-840.
25. L. Ji, Z. Tan, T. R. Kuykendall, S. Aloni, S. Xun, E. Lin, V. Battaglia and Y. Zhang, *Phys. Chem. Chem. Phys.*, 2011, **13**, 7170-7177.
26. J. Su, M. Cao, L. Ren and C. Hu, *J. Phys. Chem. C*, 2011, **115**, 14469-14477.
27. R. Wang, C. Xu, J. Sun, L. Gao and C. Lin, *J. Mater. Chem. A*, 2013, **1**, 1794-1800.
28. S. H. Lee, S. H. Yu, J. E. Lee, A. Jin, D. J. Lee, N. Lee, H. Jo, K. Shin, T. Y. Ahn, Y. W. Kim, H. Choe, Y. E. Sung and T. Hyeon, *Nano Lett.*, 2013, **13**, 4249-4256.
29. Y. Chang, J. Li, B. Wang, H. Luo, H. He, Q. Song and L. Zhi, *J. Mater. Chem. A*, 2013, **1**, 14658-14665.
30. Y. Wu, Y. Wei, J. Wang, K. Jiang and S. Fan, *Nano Lett.*, 2013, **13**, 818-823.
31. X. Y. Peng, X. X. Liu, D. Diamond and K. T. Lau, *Carbon*, 2011, **49**, 3488-3496.
32. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339-1339.
33. Z. Wang, X. Zhou, J. Zhang, F. Boey and H. Zhang, *J. Phys. Chem. C*, 2009, **113**, 14071-14075.
34. O. N. Shebanova and P. Lazor, *J. Solid State Chem.*, 2003, **174**, 424-430.
35. P. R. Graves, C. Johnston and J. J. Campaniello, *Mater. Res. Bull.*, 1988, **23**, 1651-1660.
36. V. Chandra, J. Park, Y. Chun, J. W. Lee, I. C. Hwang and K. S. Kim, *ACS Nano*, 2010, **4**, 3979-3986.
37. D. Zhang, Z. Liu, S. Han, C. Li, B. Lei, M. P. Stewart, J. M. Tour and C. Zhou, *Nano Lett.*, 2004, **4**, 2151-2155.
38. T. Fujii, F. M. F. de Groot, G. A. Sawatzky, F. C. Voogt, T. Hibma and K. Okada, *Phys. Rev. B*, 1999, **59**, 3195-3202.
39. F. He, J. Fan, D. Ma, L. Zhang, C. Leung and H. L. Chan, *Carbon*, 2010, **48**, 3139-3144.
40. L. Wang, J. Liang, Y. Zhu, T. Mei, X. Zhang, Q. Yang and Y. Qian, *Nanoscale*, 2013, **5**, 3627-3631.
41. B. Jang, M. Park, O. B. Chae, S. Park, Y. Kim, S. M. Oh, Y. Piao and T. Hyeon, *J. Am. Chem. Soc.*, 2012, **134**, 15010-15015.
42. C. He, S. Wu, N. Zhao, C. Shi, E. Liu and J. Li, *ACS Nano*, 2013, **7**, 4459-4469.
43. J. Yin, Z. Yu, F. Gao, J. Wang, H. Pang and Q. Lu, *Angew. Chem. Int. Edit.*, 2010, **49**, 6328-6332.
44. H. B. Jiang, Q. Cuan, C. Z. Wen, J. Xing, D. Wu, X. Q. Gong, C. Li and H. G. Yang, *Angew. Chem. Int. Edit.*, 2011, **50**, 3764-3768.
45. Y. Sun and Y. Xia, *Science*, 2002, **298**, 2176-2179.
46. N. Tian, Z. Y. Zhou, S. G. Sun, Y. Ding and Z. L. Wang, *Science*, 2007, **316**, 732-735.
47. P. Poizot, S. Laruelle, S. Grugeon, L. Dupont and J. M. Tarascon, *Nature*, 2000, **407**, 496-499.
48. J. Jamnik and J. Maier, *Phys. Chem. Chem. Phys.*, 2003, **5**, 5215-5220.
49. J. W. Lee, T. Ahn, J. H. Kim, J. M. Ko and J. D. Kim, *Electrochim. Acta*, 2011, **56**, 4849-4857.
50. B. Jia and L. Gao, *J. Phys. Chem. C*, 2007, **112**, 666-671.
51. H. Wang, L. F. Cui, Y. Yang, H. Sanchez Casalongue, J. T. Robinson, Y. Liang, Y. Cui and H. Dai, *J. Am. Chem. Soc.*, 2010, **132**, 13978-13980.
52. H. Zhang, X. Yu, D. Guo, B. Qu, M. Zhang, Q. Li and T. Wang, *ACS Appl. Mater. Inter.*, 2013, **5**, 7335-7340.