Accepted Manuscript

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PII: S0013-4686(17)32621-X

DOI: [10.1016/j.electacta.2017.12.061](https://doi.org/10.1016/j.electacta.2017.12.061)

Reference: EA 30849

To appear in: *Electrochimica Acta*

Received Date: 18 September 2017

Revised Date: 8 November 2017

Accepted Date: 9 December 2017

Please cite this article as: X. Ding, X. Huang, J. Jin, H. Ming, L. Wang, J. Ming, Sustainable solid-state strategy to hierarchical core-shell structured Fe_3O_4 @graphene towards a safer and green sodium ion full battery, *Electrochimica Acta* (2018), doi: 10.1016/j.electacta.2017.12.061.

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Graphics for

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**Sustainable solid-state strategy to hierarchical core-shell structured
Fe₃O₄@graphene towards a safer and green sodium ion full battery**

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Abstract

A sustainable solid-state strategy of SPEX milling is developed to coat metal oxide (*e.g.*, Fe_3O_4) with tunable layers of graphene, and a new hierarchical core-shell structured Fe_3O_4 @graphene composite is constructed. The presented green process can preserve the physicochemical properties of metal (oxide) nanocrystals well while conveniently modifying them with graphene carbon, which is unique from the conventional approaches carried out in the solution followed by high temperature calcinations/carbonization. This strategy is environmental-friendly, cost-effective and feasible to extend for preparing more metal (oxide)-graphene materials readily with controllable layers of graphene. In energy storage applications, as-prepared Fe_3O_4 @graphene only modified with 10 wt% of graphene can show greater capacity of 283 mAh g^{-1} at 100 mA g^{-1} with capacity retention of 84% over 100 cycles in sodium battery (*vs.* 17% of pristine Fe_3O_4). As an appealing nonflammable anode, a completely new full battery of Fe_3O_4 @graphite/ $\text{Na}_{2.4}\text{Fe}_{1.8}(\text{SO}_4)_3$ is assembled, and an impressive energy density beyond $300 \text{ Wh kg}_{\text{cathode}}^{-1}$ with a high working voltage of 3.2 V is attained. Such kind of green battery comprising from the earth-abundant elements (*i.e.*, Na, Fe, S and O) can demonstrate extremely long cycle ability over 500 cycles and robust rate capability even to 10 C (where 1 C define as $108 \text{ mA g}_{\text{cathode}}^{-1}$) which are rarely reported before.

Keywords: Sodium ion battery, oxide, carbon, anode, cathode.

1. Introduction

Carbon modification of metal (oxide) is of great interest in the fields of electrochemistry [1], catalysis [2], energy storage (*e.g.*, solar-photovoltaics [3], fuel cell [4], super capacitor [5] and rechargeable battery [6]) and materials science [7] because of the high electronic conductivity and stable physicochemical properties of carbon, which can largely enhance the electronic transfer ability and structural stability of composite, thereby giving rise to superior performance. To date, numerous metal oxide-C composite (*e.g.*, Si@SiO_x/C [8], Co₃O₄-C [9], Fe₃O₄-C [10]) with different morphologies (*e.g.*, spheres [11], fibers [12], tubes [13], arrays [14], films [15]) and structures (*e.g.*, hollow [16], core-shell [11], hierarchical [17], porosity [18]) are being widely prepared. Indeed, most materials demonstrate excellent performance particularly as anode in metal-ion (*e.g.*, Li⁺, Na⁺, Mg²⁺, Al³⁺) batteries application.

However, the strategies of carbon modification often suffers several intrinsic issues: (i) high-cost carbon such as carbon nanotubes (*e.g.*, SnO₂/CNTs [13], CuO/CNTs [19]) or graphene (oxide) (*e.g.*, NiO/GNRs [20], SnO₂-rGO [21]) were used. Besides, the procedures of acid treating, washing, separation from the raw graphite to the final graphene (oxide) remains difficile and challenging for their practical applications; (ii) complex multi-steps were involved when the traditional carbon coating method was applied [10, 22]. For example, the metal (oxide) powders need to be immersed in the solution of carbon precursor (*e.g.*, carbohydrate [10], resol [18], polyvinylidene fluoride [23]) first for a coating of precursor. And then, the solution removal, powders drying and carbonization in a harsh inert atmosphere are needed for the final carbon formation on metal (oxide), let alone the time-consuming optimization; (iii) Particularly, it is difficult to control a precise amount of carbon, because one part of carbon would be reacted with the metal oxide in the calcination (*i.e.*, C + MO_x → CO/CO₂ + MO_y, x < y) [18]. Simultaneously, the valence of the metal can be changed as the reduction of metal oxide, which can be aggravated further by the hydrogen atom (*i.e.*,

which is always originated from the organic precursor in thermal treatment) [24]. These disadvantages are inevitable even when the precursor of metal salt (*e.g.*, metal nitrate) were used instead of oxide powders, because the decomposed metal (oxide) nano-crystals are much easier to be de-oxidized [17, 23]. Therefore, it is significant to develop one simple, reliable and green strategy to coat carbon on the metal oxide.

Herein we introduce a clean, faster and more efficient strategy to coat metal oxide (*e.g.*, Fe₃O₄) with tunable layers of graphene without using any solvent, in which the low cost graphite is physically crushed to the graphene avoiding the acid treatment. This method is environmental-friendly and much easier to extend for preparing other kind of metal (oxide)-graphene composite. Based on this strategy, a new hierarchical core-shell structured Fe₃O₄@graphene is prepared, in which the Fe₃O₄ nanocrystals were encapsulated within the layers of graphene. The Fe₃O₄@graphene exhibits greater sodium storage capability, and a green sodium ion full battery of Fe₃O₄@graphene/Na_{2.4}Fe_{1.8}(SO₄)₃ is further introduced. The battery has the characteristics of low-cost and sustainability. It demonstrates a high energy density of 300 Wh kg_{cathode}⁻¹ and cycle performance more than 500 cycles at 0.1 C with an impressive capacity retention of 70% and an appealing voltage of 3.2 V. The presented synthetic strategy provides a convenient way to construct metal (oxide)@graphene materials, and also the high performance of sodium ion full battery with the concept of using earth rich elements can stimulate more researches in energy storages to develop sustainable batteries towards commercialization.

2. Experimental details

2.1 Materials synthesis

Commercial graphite powder, Fe₃O₄ particles prepared from hydrothermal method [10], and the milling ball were placed into a 50 mL SPEX milling chamber (Retsch™ MM 400 Mixer Mill, Fisher Scientific). The mixture was milled at the frequency of 20 Hz for 4 h and then

the Fe_3O_4 @graphene composite was obtained. The mass ratio of graphite and Fe_3O_4 in raw materials was controlled at 1:9 and 2:8 respectively for parallel experiment. The sufficient milling time and frequency (*i.e.*, rate) are necessary to crush the graphite and then make them anchor on the surface of Fe_3O_4 particles. The $\text{Na}_{2.4}\text{Fe}_{1.8}(\text{SO}_4)_3$ was synthesized accordingly [25, 26]. The precursors of Na_2SO_4 and dehydrated FeSO_4 and the solvent of acetone with the molar ratio of 2:3:7 was ball milled for 6 h and then calcined at 350 °C for 24 h under steady Ar flow, finally giving rise to the product of $\text{Na}_{2.4}\text{Fe}_{1.8}(\text{SO}_4)_3$. Note that the $\text{Na}_{2.4}\text{Fe}_{1.8}(\text{SO}_4)_3$ is sensitive to the moisture, thus all the synthetic procedures and electrode preparations need to avoid the contact with moisture.

2.2 Materials characterization

The structure and morphology of Fe_3O_4 particles, Fe_3O_4 @graphene and the electrode were carried out by scanning electron microscope (SEM) on a XL30 ESEM microscope with a beam energy of 20 kV. The layers of graphene and Fe_3O_4 crystalline structure in Fe_3O_4 @graphene were observed by the high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) using a JEOL-2100F microscope operated at 200 kV. Crystallographic information was further acquired from the X-ray diffraction pattern (XRD) measured on a Bruker D8 GADDS diffractometer using $\text{Co K}\alpha$ radiation. The mass percent of graphene in the Fe_3O_4 @graphene was analyzed by thermogravimetric analysis (TGA) (Pyris Diamond TG/DTA) within the temperature of 50-900 °C under O_2 atmosphere with a heating rate of 10 °C min^{-1} . The surface area and porosity of materials were determined by a Quantachrome Autosorb-1-MP automated gas adsorption system using nitrogen as the adsorbate at liquid nitrogen temperature (77 K). The samples were outgassed under vacuum for 24 h at 100 °C. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, and the pore diameters were obtained from the desorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) method. The

monochromatized Al-K α X-ray source was used for the XPS analysis operated at 12 kV and 20 mA.

2.3 Electrode preparation

The active material of Fe₃O₄@graphene, conductive carbon of acetylene black (AB), and binders of poly(acrylic acid)/carboxymethyl cellulose with the mass ratio of 8:1:1 is mixed homogeneously in water to form a slurry and then casted on copper foil [27, 28]. After a vacuum drying overnight at 100 °C, the electrode is punched into Ø16 mm circular electrode and assembled into a 2032-type coin cell in glove box. The cell consists of electrode | glass fiber | sodium-metal using the electrolyte of 1.0 M NaPF₆ in ethylene carbonate/diethyl carbonate (w/w, 1/1). The electrode of Na_{2.4}Fe_{1.8}(SO₄)₃ is prepared in the glove box. The Na_{2.4}Fe_{1.8}(SO₄)₃, AB and PVDF in the mass ratio of 8:1:1 is mixed in the N-methylpyrrolidone and then casted on the aluminum foil. The electrode is dried in vacuum at 120 °C. Before assembling the full battery in coin cell, the Fe₃O₄@graphene electrode is sodiated first to compensate the irreversibility, and the sodiation process is similar as the lithiation in recent literature [29], in which the Fe₃O₄@graphene electrode contacts with the electrolyte-wetted sodium foil for the reaction. The mass ratio of Na_{2.4}Fe_{1.8}(SO₄)₃ cathode and Fe₃O₄@graphene anode is controlled around 2.3:1, and the optimal voltage maintains at 1.2-4.2 V as principled in recent researches [30].

2.4 Electrochemical measurement

The galvanostatic charge-discharge was conducted by the *TOSCAT-3100*, and the cyclic voltammetry (CV) was performed using *VMP-3* within the voltage of 0.01-3.0 V under the scanning rate of 0.1 mV s⁻¹. The electrochemical impedance spectroscopy (EIS) was conducted over a frequency range 200 kHz-10 mHz. Note that the unit of current density and capacity is based on the mass of Fe₃O₄@graphene anode if there is no specific description. The sheet resistance (R) of Fe₃O₄@graphene and pristine Fe₃O₄ particles were tested by the

semi auto 4-point probe system (Advanced Instrument Technology, square area $A = 1 \times 1$ mm²), under which the powders was pressed into the tablet with the thickness of 1 mm (L). The electric conductivity (σ) of samples were calculated from the equation of $\sigma = L/RA$.

3. Results and Discussion

3.1 Features of strategy and materials

Figure 1a demonstrates the schematic of solid-state SPEX milling, in which the graphite can be peeled off to the graphene layers under a high energy crush and then coat on the surface of collapsed Fe₃O₄ nanocrystals through Van der Waals forces, forming a hierarchical core-shell Fe₃O₄@graphene (Figure S1), as confirmed by the morphologic changes in SEM images (Figure 1b-g). The Fe₃O₄@graphene has a highly dense structure and the dispersed Fe₃O₄ nanocrystals were connected by the graphene. The thickness of graphene can be controlled with varying the amount of raw graphite. For example, the tunable thickness of graphene from ~1.5 nm (*i.e.*, 4.4 layers of graphene in theory) to ~7.2 nm (*i.e.*, 22 layers of graphitic layers in theory) were confirmed under the HRTEM images (Figure 1h-i) when the graphite amount was changed from 10 wt% to 20 wt%. Note that the calculated number of graphene (*i.e.*, interlayer space, 0.34 nm) are accordance well with the observed 3-5 layers and 20-25 layers in Figure 1h-i.

The TGA results show that the coated graphene is about 10 wt% and 20 wt%, which is in good agreement with the mass ratio of raw graphite (Figure 2a). Comparative XRD patterns in Figure 2b confirms the preservation of crystalline structure of Fe₃O₄ (JCPDS#88-0866) after the graphene coating, which can be further observed in HRTEM and SAED (Figure 1h-i). The only difference is the reduced particle size hinted by the increased peak width and noise-signal ratio. Note that the hierarchical core-shell structured Fe₃O₄@graphene is quite different from the traditional individual core-shell particles (*e.g.*, Fe₃O₄@C [10], SnO₂@C [11], C@TiO₂ [31]) and wires (*e.g.*, TiO₂@C [32], Fe₂O₃-C [33]), it has a low surface area

(*e.g.*, 11.9 and 4.1 m² g⁻¹ with 10 wt% and 20 wt% graphene respectively) due to the aggregation of Fe₃O₄ nano-crystals and connection of graphene, as measured by BET (Figure 2b) and demonstrated in TEM (Figure 1h-i). But, the composite still has a moderate pore volume around 0.03 cm³ g⁻¹ with the pore size of 1.9 nm (*vs.* 20.1 m² g⁻¹, 0.07 cm³ g⁻¹ of Fe₃O₄ particles with the porosity of 6.7 nm, Figure 2c). Note that not all material need a high surface area, such as electrode in battery, a low surface area with a moderate pore volume are critical for easier electrode preparation, higher energy density and less interfacial side-reactions [34]. After the re-construction of Fe₃O₄ and graphene, the valence of iron still belongs to Fe₃O₄ (*i.e.*, the Fe2p_{2/3} (2p_{1/2}), the binding energies of 710.7 eV (723.6 eV) and 712.0 eV (725.1 eV) are well assigned to Fe²⁺ and Fe³⁺ respectively) [35], further demonstrating the feasibility of this method to protect the oxide from de-oxidation (Figure 2d). Benefiting from the high electronic conductivity of adjacent graphene layers, the resistance of pristine Fe₃O₄ decreases from 1.02 MΩ/sq. to 964.9 Ω/sq. and 217.7 Ω/sq. for the sample of Fe₃O₄@graphene (10 wt%) and Fe₃O₄@graphene (20%) respectively. Based on above characterizations, it is reliable to extend this strategy for preparing other kinds of hierarchical metal (oxide)@graphene composite.

3.2 Sodium storage capacity

Recently, iron oxide is intensively investigated as an appealing anode in lithium and sodium ion battery due to its abundant reserves, low-cost, non-flammability and higher capacity (*e.g.*, ~926 mAh g⁻¹ *vs.* Li/Li⁺, Na/Na⁺) [36] over the commercial graphite (*i.e.*, 372 mAh g⁻¹ *vs.* Li/Li⁺) and hard carbon (*e.g.*, 220 mAh g⁻¹ *vs.* Na/Na⁺) [37]. Prompted by these advantages, the new hierarchical core-shell structured Fe₃O₄@graphene was evaluated as anode in the sodium ion battery. Comparing to the pristine Fe₃O₄ particles, the Fe₃O₄@graphene with 10 wt.% graphene demonstrates higher capacity with improved stability. As shown in Figure 3a-b, an average capacity of 206 mAh g⁻¹ in initial 100 cycles at a relative high current density

of 100 mA g⁻¹ was obtained, and it is much higher than 50 mAh g⁻¹ of Fe₃O₄ particles. The capacity of Fe₃O₄@graphene can maintain at 190 mAh g⁻¹ with the capacity retention of 84% (vs. the 5th cycle), which is much improved comparing to 18% of the pristine Fe₃O₄ (from 83 mAh g⁻¹ at the 5th cycle to 15 mAh g⁻¹) (Figure 3b). The capacity and stability of Fe₃O₄ is much improved compared to those results reported before [36, 38], even it can't achieve that high in lithium ion batteries due to the larger radius of Na⁺ than Li⁺ which has difficulty in ionic diffusion for the conversion reaction ($2x\text{Na}^+ + \text{Fe}_3\text{O}_4 + 2xe^- \rightarrow x\text{Na}_2\text{O} \cdot \text{Fe}_3\text{O}_{4-x}$). Although the irreversibility of Fe₃O₄@graphene in the first cycle is larger than that of pristine Fe₃O₄ particles due to the aggravating side-reactions resulted from the more active sites of graphene and Fe₃O₄ nanocrystals generated in the milling, the irreversibility can be easily compensated by the sodiation as discussed later. Note that the capacity of pristine Fe₃O₄ increases in initial cycles, which is also observed in lithium battery when the oxide were used as anode [18]; while this phenomenon disappears in the composite of Fe₃O₄@graphene. The comparative results show that reducing the particle size and carbon modification are necessary for higher oxide utilization and storage capacity, because the diffusion of sodium ions into the inner structure of Fe₃O₄ particles can be much easier [27]. As a result, the capacities of 233, 160, 117, 82 mAh g⁻¹ are obtained for the Fe₃O₄@graphene under the current densities of 100, 250, 500 and 800 mA g⁻¹ respectively; meanwhile it can recover to 201 mAh g⁻¹, demonstrating its robust rate capability (Figure 3b-c). By contrast, the low capacities of 81, 72, 64 and 54 mAh g⁻¹ are delivered under the same variation of current densities for the pristine Fe₃O₄ (Figure 3b-c).

3.3 Electrochemical and electrode Analysis

The improved performance is mainly ascribed to the positive effect of graphene, as confirmed by the comparative CV, EIS, and *ex-situ* SEM analysis. According to the Randles-Sevcik equation of $i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C_i v^{1/2}$ at 298 K (where i_p , n , A , D , C_i and v are peak

current, electron stoichiometry, electrode area, diffusion coefficient, concentration of lithium and scan rate respectively) [39, 40], the i_p of Fe_3O_4 @graphene are always higher than those of pristine Fe_3O_4 (Figure 4), demonstrating faster electrons transfer reaction. This is consistence with the higher capacity of 283 mAh g^{-1} comparing to 103 mAh g^{-1} of pristine Fe_3O_4 . The low resistance and high sodium ion diffusion rate of Fe_3O_4 @graphene are observed directly in the high and low frequency parts of EIS (Figure 4). In detail, The circuit model $R_{el}(RQ)_{ct}(RQ)_{pf}Q$ type is used for the non-linear least-square fitting the Nyquist plots. The R_{el} , $(RQ)_{ct}$ and $(RQ)_{pf}$ are ascribed to the electrolyte resistance, charge-transfer resistance, passivation film formation processes respectively and the low-frequency Q element accounts for Na^+ diffusion [41]. The charge-transfer resistance for Fe_3O_4 @graphene in the 1st and 20th cycles are 132 and 82.6Ω , which are lower than 157 and 100Ω of Fe_3O_4 particles (Figure 4a-b). The lower resistance of Fe_3O_4 @graphene is further confirmed by its higher electronic conductivity of $1.04 \times 10^{-2} \text{ S cm}^{-1}$ than $9.80 \times 10^{-6} \text{ S cm}^{-1}$ of pristine Fe_3O_4 ($\sigma = L/RA$). The interconnected graphene layers not only enhances the electronic conductivity but also is positive to form a uniform solid electrolyte layer for buffering the electrode variation. As demonstrated in Figure 5a-c, the solid electrode interface (SEI) layer formed on Fe_3O_4 electrode is imperfect and easy to decompose during charge/discharge process, and thus the protection ability is very limited. By contrast, a smooth, dense and fully covered SEI layer is observed on the Fe_3O_4 @graphene electrode surface (Figure 5d-f), which is helpful to maintain the stability of electrode as cycling, as demonstrated previously in lithium ion batteries [42].

3.4 Sustainable sodium ion full battery

The sodium ion battery attracts more attention recently because of the rich abundance and low-cost of elemental sodium, but its lower potential (*i.e.*, $\sim 0.3 \text{ V vs. Li/Li}^+$), limited energy density and inferior cycling performance unlike that of lithium ion battery needs to be fully

addressed. Herein, a high energy, stable and green sodium ion full battery comprising of Fe_3O_4 @graphene/ $\text{Na}_{2.4}\text{Fe}_{1.8}(\text{SO}_4)_3$ is introduced. This battery consists of rich and low-cost elements in earth and it has the sustainable and safer characteristics because the non-flammable electrode are used. The mass ratio of cathode/anode keeps around 2.3/1, and the optimized voltage window is fixed at 1.2-4.2 V based on the (dis-)charge curves of $\text{Na}_{2.4}\text{Fe}_{1.8}(\text{SO}_4)_3$ and sodiated Fe_3O_4 @graphene (Figure 6a-c), according to the principles in previous literature [30, 43]. The schematic model of presented sodium ion full battery is illustrated in Figure 6.

The full battery of Fe_3O_4 @graphene/ $\text{Na}_{2.4}\text{Fe}_{1.8}(\text{SO}_4)_3$ demonstrates a high working voltage of 3.2 V and an impressive cycle ability over 500 cycles with capacity retention of 70% under the rate of 0.1 C (Figure 7a-b, where define $1\text{C} = 108\text{ mA g}_{\text{cathode}}^{-1}$). Note that the initial capacity is as high as $102\text{ mAh g}_{\text{cathode}}^{-1}$, and also the capacity can achieve $93\text{ mAh g}_{\text{cathode}}^{-1}$ at the rate of 0.5 C with capacity retention of 82% over 200 cycles. Except the extremely durable cycle ability, the robust rate capability is more impressive. For example, average capacities of 102, 97, 93, 87, 77, 66 and $49\text{ mAh g}_{\text{cathode}}^{-1}$ are obtained under the rates of 0.1, 0.25, 0.5, 1.0, 2.5, 5.0 and 10 C respectively, where the capacity can recover to $100\text{ mAh g}_{\text{cathode}}^{-1}$ when the battery cycles back to 0.1 C, fully demonstrating the superior stability of battery (Figure 7c-d). Besides, the energy density of battery calculated by integrating the discharge curves versus cathode is as high as 300, 270, 251, 230, 190, 150 and $96\text{ Wh kg}_{\text{cathode}}^{-1}$ under the same rate variation, which are comparable and even better than most reported sodium ion full batteries before [43-53], particularly under the current densities below $500\text{ mA g}_{\text{cathode}}^{-1}$, as summarized in Figure S2. Furthermore, the practical energy density of sodium ion battery is calculated to be about $90\text{ Wh kg}_{\text{battery}}^{-1}$ based on the referee of current lithium ion batteries (Table S1). Note that another important features of such battery are the lowest cost elements used, more reliable and the concept of green configuration with

sustainable characteristics (Figure S2). Finally, the superior performance should be ascribed to the improved properties of Fe_3O_4 @graphene and specific crystalline structure of $\text{Na}_{2.4}\text{Fe}_{1.8}(\text{SO}_4)_3$, in which isolated edge-sharing Fe_2O_{10} dimers are in turn bridged together by SO_4 tetrahedral units strictly by corner-sharing mode, thereby forming a three-dimensional framework with large tunnels along c axis (Figure 6c).

4. Conclusions

A sustainable, convenient and extendable solid-state strategy is introduced to modify metal oxide with tunable layers of graphene without using any solvent/harmful chemicals and also avoiding the complex carbonization process and/or the high-cost precursors. In this way, a precise coating of graphene is finely controlled and the physicochemical properties of metal oxide are also preserved, where hierarchical core-shell structured metal (oxide)@graphene composite materials can be further constructed. As-prepared Fe_3O_4 @graphene only with 10 wt.% graphene demonstrates a high sodium storage capacity of 283 mAh g^{-1} at 100 mA g^{-1} with capacity retention of 84% over 100 cycles (vs. 17% of pristine oxide). Besides, a completely new full battery of Fe_3O_4 @graphite/ $\text{Na}_{2.4}\text{Fe}_{1.8}(\text{SO}_4)_3$, comprising the rich earth-reserved elements of Na, Fe, S and O is presented. An impressive energy density over $300 \text{ Wh kg}_{\text{cathode}}^{-1}$ and a high work voltage of 3.2 V are further demonstrated. The extremely stable cycle ability over 500 cycles and rather robust rate capability even to 10 C, as well as the concept of sustainability and green chemistry in battery can attract great attention in energy and environmental science.

Acknowledgements

This work was supported by the construct program of the key discipline in Hunan province (Applied Chemistry), Hunan Provincial Natural Science Foundation of China (2016JJ3094), Scientific Research Fund of Hunan Provincial Education Department (15C0933, 16C1082)

1 and Startup Foundation for Doctors of Hunan University of Arts and Science. J. Ming is
2 grateful for the support from the King Abdullah University of Science & Technology
3 (Kingdom of Saudi Arabia). H. Ming is grateful for the support from the the Natural Science
4 Foundation of China (NSFC: 21703285).

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Figure 1. (a) Schematic process to prepare hierarchical Fe_3O_4 @graphene composite. SEM images of (b) pristine Fe_3O_4 particles, (c) bulk graphite, (d) Fe_3O_4 @graphene (10 wt.%). (e-f) Elemental distribution of Fe and C in Fe_3O_4 @graphene. (g) Superimposed color of Fe and C elemental distribution as marked by the white frame in the left corner of (f). HRTEM of Fe_3O_4 @graphene with different percent of graphene (h) 10 wt.% and (i) 20 wt.%. Inset of (h) is the SAED of Fe_3O_4 @graphene (10 wt.%).

Figure 2. (a) TGA, (b) XRD, (c) BET and (d) XPS of pristine Fe_3O_4 particles and Fe_3O_4 @graphene. Inset of (c) is their pore size distribution.

Figure 3. (a) Typical charge-discharge curves, (b) cycle performance, (c) rate curves and (d) rate capabilities of Fe_3O_4 @graphene and pristine Fe_3O_4 particles electrode.

Figure 4. Comparative CV and EIS of Fe_3O_4 @graphene and pristine Fe_3O_4 particles (a) before discharge and (b) after 20th cycle discharge-charge .

Figure 5. Comparative pristine, discharged and charged electrode of (a-c) pristine Fe_3O_4 and (b-f) Fe_3O_4 @graphene electrode at the 20th cycle. The scale bar is 500 nm.

Figure 6. (a) Typical voltage vs. capacity profile of $\text{Na}_{2.4}\text{Fe}_{1.8}(\text{SO}_4)_3$ and sodiated Fe_3O_4 @graphene. (b) Schematic drawing of sodium ion full battery and (c) crystalline structure of $\text{Na}_{2.4}\text{Fe}_{1.8}(\text{SO}_4)_3$ and Fe_3O_4 .

Figure 7. (a) Typical voltage vs. capacity profiles from the 1st to 500th cycles, (b) cycle performance under different rates, (c) rate curves and (d) capability of Fe_3O_4 @graphene/ $\text{Na}_{2.4}\text{Fe}_{1.8}(\text{SO}_4)_3$ full battery.

1 **Figure 1**

1 **Figure 2**

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7 **Figure 5**

1 **Figure 6** 6 **Figure 7**

Highlights

1. A sustainable solid-state strategy is developed to coat metal (oxide) with graphene carbon.
2. A new hierarchical core-shell structured Fe_3O_4 @graphene composite is constructed.
3. As-prepared Fe_3O_4 @graphene demonstrates greater sodium storage capability.
4. Sodium ion battery of Fe_3O_4 @graphene/ $\text{Na}_{2.4}\text{Fe}_{1.8}(\text{SO}_4)_3$ with higher energy is configured.
5. The concept of green battery comprising from the earth-abundant elements is introduced.