A general strategy toward graphene@metal oxide core–shell nanostructures for high-performance lithium storage†

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Received 18th July 2011, Accepted 9th August 2011
DOI: 10.1039/c1ee02168k

We demonstrate a simple, efficient, yet versatile method for the realization of core–shell assembly of graphene around various metal oxide (MO) nanostructures, including nanowires (NWs) and nanoparticles (NPs). The process is driven by (i) the ring-opening reaction between the epoxy groups and amine groups in graphene oxide (GO) platelets and amine-modified MO nanostructures, respectively, and (ii) electrostatic interaction between these two components. Nearly every single NW or NP is observed to be wrapped by graphene. To the best of our knowledge, this is the first report that substrate-supported MO NWs are fully coated with a graphene shell. As an example of the functional properties of these compound materials, the graphene@α-Fe2O3 core–shell NPs are investigated as the lithium-ion battery (LIB) electrode, which show a high reversible capacity, improved cycling stability, and excellent rate capability with respect to the pristine α-Fe2O3. The superior performance of the composite electrode is presumably attributed to the effectiveness of the graphene shell in preventing the aggregation, buffering the volume change, maintaining the integrity of NPs, as well as improving the conductivity of the electrode.

Introduction

Engineering of hybrid nanostructures has attracted tremendous attention due to its diverse functionalities integrated in a single object. Graphene is an up-and-coming carbon material comprised of monolayered hexagonal sp2 hybridized carbons. Together with atomic thickness, the two-dimensional conjugated chemical structure endows graphene with a host of attractive properties, such as large specific surface area, excellent electrical conductivity, good mechanical flexibility and strong thermal/chemical stability. It thus has been considered as an ideal reinforcing component for hybrids.
or composites. Hitherto, graphene has been blended with various organic and inorganic components to form functional composites. The incorporation of graphene into the composites can provide them with the unique functions of graphene and also possibly induce intriguing properties inherited from the synergistic effect. As a result, various graphene-based hybrid nanostructures have emerged in diverse areas such as catalysis, sensors, optoelectronics, and energy conversion and storage devices.

Of these, the lithium-ion battery (LIB) indeed benefits greatly from the introduction of graphene as a component of its electrode. It is known that transition metal oxides (MOs), albeit regarded as promising anode materials with high theoretical capacity (∼500 to 1000 mA h g⁻¹, compared with 372 mA h g⁻¹ for conventional graphite), still suffer from the problems of poor electrical conductivity and unsatisfactory cycling stability. The emergence of graphene provides new hope to alleviate these problems. A variety of transition MOs have been coupled with graphene and, as expected, demonstrated superior electrochemical performance. In general, graphene sheets (GS) in the as-obtained composites can (1) function as conductive channels; (2) provide an elastic buffer space to accommodate the volume change during repeated lithium uptake and removal reactions; and (3) prevent the aggregation of MO nanoparticles (NPs) and the cracking or crumbling of electrode material upon cycling. Consequently, the conductivity and integrity of the composite electrode can be effectively improved compared with the pristine MO electrode. Although tremendous efforts have been devoted to coupling graphene with MOs, current research accomplishments are mainly focused on graphene/MO NP composites; there are few reports on integrating one dimensional (1D) nanostructure with graphene, in spite of its promising applications especially in energy storage and conversion devices. Furthermore, a versatile method for coupling graphene with MO nanostructures of different dimensions is lacking.

Herein, we describe a simple and general strategy to wrap graphene onto different MO nanostructures including nanowires (NWs) and NPs. The fabrication procedure consists of three steps: pre-modification of MOs with amine groups, coating of a graphene oxide (GO) layer, and finally conversion of the GO shell to graphene. Of note, all steps are accomplished by simply immersing the pre-grown MO nanostructures into corresponding functional solutions at room temperature. Strikingly, the GS wrapping occurs along the entire length of individual MO NWs and the main body of every MO NPs. As a proof-of-concept demonstration of the application of such graphene-based core–shell nanostructures, graphene-wrapped α-Fe₂O₃ NPs are tested as the LIB anode. Compared with pristine α-Fe₂O₃, significantly improved specific capacity, rate capability, and cycling stability have been demonstrated. This can be attributed to the enhanced electron transport efficiency and structural integrity of the NPs arising from the graphene encapsulation.

### Experimental

#### 1. GO preparation

GO was prepared by a modified Hummers method. Firstly, 2 g of graphite powder and 1.5 g of NaNO₃ were added into 150 mL of 98% H₂SO₄ solution in a flask immersed in an ice bath. With the stirring still in progress, 9 g of KMnO₄ was added slowly, little by little, to the mixture to prevent a sudden accumulation of heat that is evolved. After that the mixture was stirred for 5 days at room temperature. Then, 10 mL of 30% H₂O₂ was added into the solution in order to completely react with the remaining KMnO₄, leading to a bright yellow solution. To purify the graphene oxide, the resulting mixture was washed by 3% H₂SO₄ and H₂O until the pH value of the solution was approximately 5–6. GO powder was obtained after freeze drying the suspension.

#### 2. Synthesis of graphene@metal oxide core–shell nanostructures

##### 2.1 Synthesis of SnO₂, CuO, and CoO NWs.

The SnO₂ NWs on a stainless steel (SS) substrate and oriented CuO NWs on a copper substrate were prepared via a standard chemical-vapor-deposition (CVD) method and a simple vapour–solid reaction method, respectively, according to our previous work. CoO NWs on Ti foil were also prepared through a two-step method reported previously.

##### 2.2 Synthesis of α-Fe₂O₃ NPs.

Different from the above approaches, the method for synthesizing α-Fe₂O₃ NPs is firstly reported here. In a typical procedure, 0.417 g of FeSO₄·7H₂O and 0.4 g of sodium citrate were dissolved in 30 mL of distilled water. After complete dissolution, the mixture was sealed into a Teflon-lined autoclave and maintained at 180 °C for 8 h. After it was cooled down to room temperature, the precipitation was collected and washed with distilled water and ethanol. The α-Fe₂O₃ NPs were obtained by annealing the as-collected precursor at 450 °C for 2 h in air.

##### 2.3 Preparation of graphene@metal oxide nanostructures.

Wrapping GS onto the surfaces of MO nanostructures was achieved by immersing the pre-formed MOs sequentially into the following three solutions for varied durations at room temperature.

1. Poly(allylamine hydrochloride) (PAH) solution (1 g L⁻¹), 1 h.
2. GO dispersion (0.2 g L⁻¹), 5 h.
3. Hydrazine (N₂H₄, 98%) 0.5 h.

For NW samples, all these steps can be accomplished by simply dipping the pre-grown substrate-supported MO NWs into corresponding solutions. While for α-Fe₂O₃ NPs, each step needs to be assisted with magnetic stirring to ensure a homogeneous mixture and centrifugation to separate the NPs.

#### 3. Characterization

Powder X-ray diffraction (XRD) analysis was performed using a D8 Advanced diffractometer with Cu Kα line. Transmission electron microscopy (TEM) images were recorded by a JEOL JEM-2010 transmission electron microscope with an accelerating voltage of 200 kV. Field-emission scanning electron microscopy (FESEM) analysis was conducted with a JEOL JSM-6700F electron microscope. Raman spectra and images were obtained by a WITec CRM200 confocal microscope Raman system with a piezocrystal controlled scanning stage. The excitation light is a 532 nm laser. The laser spot size is estimated to be 500 nm. Atomic force microscopy (AFM) was carried out using a Digital
Nanoscope V in the tapping mode. An etched silicon tip was used as a probe for imaging the samples. Thermogravimetry analyses (TGA, Q500) were carried out in the temperature range of 40 to 700 °C at a heating rate of 10 °C min⁻¹ in air. The surface area of graphene@α-Fe₂O₃ NPs was measured using Brunauer–Emmett–Teller (BET) (Quantachrome Instruments, Autosorb AS-6B). The Fourier-transformed infrared (FT-IR) spectroscopy was performed using potassium bromide (KBr) pellet in transmission mode on a NEXUS 670 FT-IR spectrometer.

4. Electrochemical measurement

The graphene@α-Fe₂O₃ and pristine α-Fe₂O₃ NPs were dried at 150 °C for 30 min under Ar atmosphere. Then, 80 wt% active material (graphene/α-Fe₂O₃ or α-Fe₂O₃), 10 wt% acetylene black (Super-P), and 10 wt% polyvinylidene fluoride (PVDF) binder were mixed into N-methyl-2-pyrrolidinone (NMP). The obtained slurry was coated onto Cu foil disks to form working electrodes, which were then dried in vacuum at 50 °C for 12 h to remove the solvent. Electrochemical measurements were performed using a two-electrode CR2032 (3 V) coin-type cells with lithium foil as counter and reference electrodes under ambient temperature. The electrolyte was 1 M LiPF₆ in a 50 : 50 (w/w) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Cell assembly was carried out in an argon-filled glovebox with both moisture and oxygen contents below 1.0 ppm. Cyclic voltammetry (CV, 0.005–3 V, 0.5 mV s⁻¹) was performed using an electrochemical workstation (CHI 760D).

Results and discussion

1. Wrapping graphene on MO NWs

Fig. 1 shows a typical formation procedure and the proposed functionalization mechanism of the graphene@MO core–shell NWs. To achieve the coating of GS, pre-synthesized MO NWs are just dipped sequentially into poly(allylamine hydrochloride) (PAH) solution, GO dispersion, and hydrazine (N₂H₄) solution for 1 h, 5 h, and 0.5 h, respectively (Fig. 1a). PAH solution here is used to modify the MO NWs by grafting onto their surface, providing them with amine end groups. Subsequent impregnation into GO dispersion makes the GO platelets spontaneously assemble onto the surface of PAH-modified NWs. This process occurs likely through two interactions: (i) the ring-opening reaction between the amine groups in the functionalized MO NWs and the epoxy groups in the GO platelets; and (2) electrostatic interaction between the positively charged amine-modified MO NWs and negatively charged GO platelets. Abundant amine groups in the PAH-modified NWs are able to cross-link the GO platelets via the epoxy groups of two or more platelets, stitching them together (Fig. 1b). In conjunction with the electrostatic interaction, such a chemical cross-linking results eventually in the marvellous core–shell assembly between the NWs and GO platelets. The resulting GO@MO NWs are then subjected to the N₂H₄ solution aiming at transforming GO into graphene (Fig. 1c). As shown in the scheme, in addition to the ones wrapped on the surface of the NWs, there should also be some GO platelets (and subsequent GS) stretching across the NWs (indicated by the red dashed arrows).

Three typical MO NWs, namely, SnO₂, CuO, and CoO NWs, are adopted to verify the feasibility and versatility of our protocol in achieving graphene@MO core–shell NWs. Corresponding XRD patterns of these NWs are shown in Fig. S1†. The thickness of the GO platelet in the dispersion is measured to be ~1 nm, indicating the monolayered structure (Fig. S2†). We firstly test this concept with the SnO₂ NWs grown on stainless steel (SS) substrates via a CVD method. No obvious change is noticed before and after GS coating under low-magnification scanning electron microscope (SEM) observation (Fig. S3a and b†). However, Raman characterization indeed manifests the presence of GO and graphene at corresponding steps (Fig. S3c†). Fig. 2a displays a representative SEM image of the graphene@SnO₂ NWs. At first glance, the SnO₂ NWs are just randomly interspersed rather than discernibly coated with GS (indicated by the red dashed circles). The strong Raman signals of the D and G bands of graphitic material were thus initially thought to stem from these randomly distributed GS (inset in Fig. 2a). However, careful observation enables us to grab a clear view of the core–shell structure (Fig. 2b). Another interesting observation of the graphene shell tearing up from one end of a SnO₂ NW reveals that GS are indeed tightly attached onto the SnO₂ NWs (Fig. 2c). A high-magnification transmission electron microscope (TEM) image further reveals the core–shell structure (Fig. 2d). The thickness of the graphene shell is approximately in the range from 1 to 3 nm (Fig. 2d). More straightforward evidence of the complete graphene wrapping around the NWs is imparted by the Raman mapping results of the D and G bands of graphene for randomly chosen single NWs (Fig. 2e and f, and S4†).

CuO NWs obtained from directly heating the copper foil in air represent another type of NWs following the vapour–solid growth mechanism. Unlike the case for SnO₂ NWs, after a series of immersions in different solutions, the tips of CuO NWs are prone to bind together due primarily to the capillary force (Fig. 3a and b). Further inspection under high-magnification SEM shows the presence of GS intertwining between the CuO NWs (Fig. 3c). Although the core–shell structure is not easily discernible under SEM (Fig. 3d and e), TEM observation can still identify the continuous graphene shell (Fig. 3f). The complete coverage of the GS is evidenced by Raman mapping of different single graphene@CuO NWs as well (Fig. 3g and h, and S5†). Apart from solid SnO₂ and CuO NWs, porous CoO NWs on Ti foil via thermal-decomposition are adopted to further prove the applicability of our method to porous NWs. The results resemble the cases for SnO₂ and CuO NWs, revealing the core–shell structure and continuous GS coating along entire individual NW (Fig. S6†).

II. Wrapping graphene on MO NPs

In addition to MO NWs, this strategy can also be easily extended to MO NPs. Here, α-Fe₂O₃ NPs obtained from thermal-decomposition of a Fe-containing precursor are employed to demonstrate the efficiency and adaptability of this approach. It can be seen that the precursor NPs are composed of sub-nanoparticles and are fairly uniform in size and shape with diameters of around 150 nm (Fig. 4a–c). Remarkably, these precursor NPs are stacked in a highly ordered way (Fig. S7†), which arises...
possibly from the self-assembly process of sub-nanoparticles. As the reaction system is free of any surfactants and other organic molecules, the citrate ligands are believed to act as the stabilizer of such a self-assembled structure. After annealing, the Fe-containing precursors are transformed to $\alpha$-Fe$_2$O$_3$ with “rose-like” morphology (Fig. 4d and e and S8†). Despite the phase and shape transitions, the resulting $\alpha$-Fe$_2$O$_3$ “nano-roses” still show high uniformity (Fig. S9†). However, the highly ordered stacking mode is destroyed probably due to the decomposition of citrate ligands. TEM characterization further discloses the porous structure of these $\alpha$-Fe$_2$O$_3$ “nano-roses”, which is likely caused by the removal of CO$_2$, CO, and H$_2$O gases and lattice contraction during annealing (Fig. 4f). Following the same procedures for wrapping graphene on MO NWs but conducted in beakers aided by magnetic stirring, GS can also be successfully wrapped around the surfaces of $\alpha$-Fe$_2$O$_3$ “nano-roses” (Fig. 4g–i). The Fourier-transformed infrared (FT-IR) spectra show that the epoxy C–O stretch at 1220 cm$^{-1}$ presented in GO ligands.
disappeared for GO@α-Fe₂O₃, which is probably interpreted as evidence of the ring-opening reaction between the epoxy groups in GO and the amine groups in PAH-modified α-Fe₂O₃ NPs (see details in Fig. S10†). The resulting graphene-encapsulated α-Fe₂O₃ “nano-roses” (G@α-Fe₂O₃) exhibit crinkled and rough textures, which are associated with the presence of flexible and ultrathin GS. In addition to wrapping on individual NPs, in some cases GS appear to interconnect neighboring NPs (Fig. 4g–i).

For quantifying the amount of graphene in the G@α-Fe₂O₃ composite, thermogravimetric analysis (TGA) was carried out in air. The result reveals that the weight fraction of graphene is as low as 2.8% (Fig. 5a), which is much lower than those of previously reported graphene/MO composites. Herein, the weight loss at the temperature below 100 °C is attributed to the evaporation of moisture. Moreover, the nitrogen isotherm adsorption–desorption curve together with the pore size distribution of G@α-Fe₂O₃ is given in Fig. 5b, disclosing that the BET specific surface area is around 79.5 m² g⁻¹ and the main pore size is about 20 nm.

III Electrochemical performance of G@α-Fe₂O₃ toward lithium storage

To demonstrate the effectiveness of the graphene-based compound nanostructure in improving the lithium storage performance, the electrochemical properties of G@α-Fe₂O₃ as the anode were
investigated by galvanostatic charge–discharge measurements. The voltage–capacity trace of pristine α-Fe₂O₃ NPs was also recorded for comparison. Fig. 6a displays the first discharge/charge voltage profiles of α-Fe₂O₃ and G@α-Fe₂O₃ electrodes in the voltage window of 0.005–3.0 V at a rate of 200 mA g⁻¹ (C/5, 1 C is defined as 1007 mA g⁻¹), showing the well-known signature of conversion reactions of iron oxides.¹¹,¹⁸,²¹ Specifically, the voltage decreases steeply to ca. 1.65 V, and then followed by a small slope (marked as 1). When the voltage continues to decrease to ca. 1.05 V, the second slope appears (marked as 2), which delivers a capacity of ca. 250 mA h g⁻¹. A long plateau is clearly observed when the voltage decreases to ca. 0.85 V (marked as 3), delivering a capacity of ca. 850 mA h g⁻¹. Thereafter, the voltage gradually decreases to the cut-off value. In general, the voltage slopes at ca. 1.65 V and 0.85 V are ascribed to the lithium intercalation and the reduction reaction of α-Fe₂O₃ to metallic Fe, respectively. Recently, the slope at ca. 1.05 V is attributed to the formation of an intermediate cubic phase Li₂Fe₂O₃.¹⁹,²⁰ The above processes are summarized into the following three lithiation steps:

\[
\alpha\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Li}_x\text{Fe}_2\text{O}_3 \rightarrow \text{cubic Li}_x\text{Fe}_2\text{O}_3 \leftrightarrow \text{Fe} + \text{Li}_2\text{O}
\]

While the electrochemical reaction pathways are the same, the cyclic performances of the G@α-Fe₂O₃ composite and pristine α-Fe₂O₃ are distinctly different (Fig. 6b). Apparently, the G@α-Fe₂O₃ composite delivers a much higher capacity than bare α-Fe₂O₃ throughout the cycling. In the first cycle, the discharge capacity of the α-Fe₂O₃ particle electrode is about 1179 mA h g⁻¹; the excess capacity compared with the theoretical value (≈1007 mA h g⁻¹) seems to derive from electrolyte decomposition in the low-potential region and the subsequent formation of an organic layer on the surface of the particles.⁸⁶ However, the capacity decreases to 290 mA h g⁻¹ after 100 cycles with only about 25% retention. In contrast, the α-Fe₂O₃ NPs, after being wrapped by graphene, show much improved cycling stability. From the 48th cycle, the capacity of the G@α-Fe₂O₃ composite starts to increase and reaches ~781 mA h g⁻¹ at the 100th cycle, which is much higher than that of bare α-Fe₂O₃ NPs. The initial discharge capacity is 1338 mA h g⁻¹; therefore 58% of the reversible capacity can be maintained over 100 cycles at a current density of 200 mA g⁻¹. One interesting phenomenon is that both electrodes exhibit an increasing trend of the capacity after certain cycles. This has also been observed in other transition-MO based cells and is possibly attributed to some long-term activation processes during charge–discharge cycling.¹¹,²¹

To better understand the advantage of the G@α-Fe₂O₃ composite in lithium storage, the discharge capacities under adjoining cycles of different rates were compared for both G@α-Fe₂O₃ and bare α-Fe₂O₃ electrodes (Fig. 6c). Note that, with respect to the reference α-Fe₂O₃, the specific capacity of G@α-Fe₂O₃ is substantially increased at all investigated charge–discharge rates from C/5 to 10 C. For example, the specific capacity of G@α-Fe₂O₃ at a rate of 5 C is as high as 269 mA h g⁻¹, 34 times higher than that of bare α-Fe₂O₃ (8 mA h g⁻¹). Moreover, the G@α-Fe₂O₃ electrode can still deliver a high capacity of 143 mA h g⁻¹ at a rate of 10 C, whilst the bare α-Fe₂O₃ cannot store charges any more. Importantly, after the high rate measurements, the specific capacities of both electrodes at C/5 are able to recover to almost the initial values, implying their good reversibility.

The increased specific capacity, good cycling stability, and enhanced high-rate capability of the G@α-Fe₂O₃ composite are attributed to its unique structure. As can be seen from the above results, the composite electrode has a high weight fraction of electrochemically active α-Fe₂O₃, large specific surface area, and ultrathin graphene shells as both buffer matrix and conducting pathways, which are all crucial factors accounting for the superior electrochemical properties. The former two characteristics are propitious to reach high specific capacity of the G@α-Fe₂O₃ composite. It is well-known that one advantage of transition-metal oxides over carbon-based materials in lithium storage is their high theoretical specific capacity. Hence, a large content of α-Fe₂O₃ could give rise to a high specific capacity. The large specific surface area, obviously, is highly favourable for LIB to achieve high specific capacity as it can provide more electrochemically active sites for Li⁺ insertion/extraction. In addition to these two features, the GS contribute more to the improved cycling stability and excellent rate capability for the following reasons. On one hand, the presence of GS can suppress the aggregation, buffer the volume change of α-Fe₂O₃ NPs, and maintain the electrical contact between α-Fe₂O₃ NPs and current...
collector as well during the cycling, thereby resulting in better cyclic stability with respect to the bare \( \alpha \)-Fe\(_2\)O\(_3\) NPs. On the other hand, graphene can facilitate electron transfer from wrapped porous \( \alpha \)-Fe\(_2\)O\(_3\) NPs within the whole electrode. Compared with bare \( \alpha \)-Fe\(_2\)O\(_3\) NPs, the conductive GS matrix in the composite electrode can act as “highways” for electron transportation between \( \alpha \)-Fe\(_2\)O\(_3\) NPs, which decreases the inner resistance, thus leading to a better rate capability. It needs to be pointed out that the graphene shell obtained from chemical reduction of GO contains a lot of defects and can thereby access the Li\(^+\) diffusion through these defective sites. To confirm the good conductivity of the composite electrode, Fig. 7 compares the Nyquist plots of G@\( \alpha \)-Fe\(_2\)O\(_3\) and \( \alpha \)-Fe\(_2\)O\(_3\) NPs. Apparently, the G@\( \alpha \)-Fe\(_2\)O\(_3\) electrode possesses a much lower resistance than the \( \alpha \)-Fe\(_2\)O\(_3\) electrode (~90 vs. ~199 \( \Omega \)), thus suggesting that the composite electrode possesses lower contact and charge-transfer impedances. As a result, Li\(^+\) diffusion and electron transfer are expedited at high cycling rates for the G@\( \alpha \)-Fe\(_2\)O\(_3\) electrode.

**Conclusions**

A general strategy is developed based on the ring-opening reaction between epoxy groups and amine groups and electrostatic interaction to achieve the self-assembled wrapping of graphene sheets around various metal oxide NWs and NPs. Raman mapping reveals the full coverage of an entire NW by graphene. The effectiveness of the graphene shell in preventing the aggregation, buffering the volume change, preserving the integrity of NPs, as well as serving as the conducting matrix possibly accounts for superior electrochemical performance of the composite electrode with respect to pristine metal oxide. We expect this protocol will open up a new pathway for the realization of various graphene-based hybrid materials for diverse applications.

**Acknowledgements**

This work is supported by the Singapore National Research Foundation under NRF RF Award No. NRF-RF2010-07 and MOE Tier 2 MOE 2009-T2-1-037.

**Notes and references**

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