Synthesis of rGO-Fe₃O₄-SnO₂-C Quaternary Hybrid Mesoporous Nanosheets as a High-performance Anode Material for Lithium Ion Batteries

Guoen Luo^a, Yuheng Lu^a, Songshan Zeng^b, Saibin Zhong^a, Xiaoyuan Yu^{a*}, Yueping Fang^a, Luyi Sun^{b*}

^aInstitute of Biomaterial, College of Materials and Energy, South China Agricultural University, Guangzhou 510642, China

^bInstitute of Materials Science, Department of Chemical & Biomolecular Engineering and Polymer Program, University of Connecticut, Storrs, Connecticut 06269, United States

Abstract: A quaternary hierarchical nanocomposite, rGO-Fe₃O₄-SnO₂-C, is rationally designed and synthesized via layer-by-layer constructions of reduced graphene oxide (rGO) flexible films, Fe₃O₄ nanoparticles, SnO₂ nanoparticles and an omnidirectional amorphous carbon layer. SEM and TEM **observations** show that the Fe₃O₄ and SnO₂ nanoparticles are uniformly dispersed on the rGO nanosheets and fully encapsulated by the outmost carbon **layers**, forming a sandwich-like buffering structure for excellent dimensional integrity. Furthermore, **nanopores** with an average size of 5.8 nm are fabricated within the quaternary hybrid nanosheets via a layer-by-layer packing of Fe₃O₄ and SnO₂ nanoparticles, which **possess the** different shapes and sizes. Galvanostatic charge/discharge measurements demonstrate that rGO-Fe₃O₄-SnO₂-C exhibits a reversible capacity of 868.6 mAh g⁻¹ after 100 cycles at **a current density of** 200 mA g⁻¹. Even at a current density of 2.0 A g⁻¹, it can be stably **operated during** the discharge/charge processes and deliver a reversible capacity of 414.7 mAh g⁻¹. The **excellent** electrochemical properties of rGO-Fe₃O₄-SnO₂-C can be attributed to the microstructural stability of the hybrid and the synergistic effects of the components inside the nanosheets.

Keywords: Ferroferric oxide; Tin oxide; Graphene; Nanosheets; Lithium ion batteries

*Corresponding authors

(X. Y. Yu) Tel: (86)134-1629-1988; Fax: 86-20-8528-5026; *E-mail*: yuxiaoyuan@scau.edu.cn

(L. Y. Sun) Tel: 860-486-6895; Fax: 860-486-4745; *E-mail*: luyi.sun@uconn.edu

1. Introduction

With the rapid development of portable electronics and hybrid electric vehicles, lithium-ion batteries (LIBs) have suffered from the limited gravimetric capacities of the electrode materials [1-3]. As for anode materials, a standard commercialized carbon-based material can deliver a gravimetric specific capacity of only about 372 mAh g⁻¹, which can not meet the urgent demand for high performance energy storage [4,5]. Transition metal oxides (TMOs), such as iron oxides [6,7], tin oxides [8,9], manganese oxides [10,11], and cobalt oxides [12,13], have attracted much attention as promising anode materials for the next generation of LIBs because of their advantages of high energy and power density [14,15]. For instance, Fe₃O₄ and SnO₂ exhibit the attractive theoretical capacities of 924 mAh g⁻¹ and 780 mAh g⁻¹, respectively, based on the following lithium storage mechanisms (eq 1, 2, and 3) [16, 17]:

However, most of the transition metal oxide electrode materials suffer from the Li-alloying agglomeration [18] and the growth of passivation layers [19] along with tremendous volume changes and stresses, and subsequent falling of the active materials from the electrode, resulting in the significant capacity fading during the lithiation/delithiation process [20,21]. So far, three main strategies have been widely used to improve the electrochemical performance of the transition metal oxide electrodes [22-24]: (I) Construction of mesoporous nanostructures, such as

nanoparticles (NPs) [25], nanospheres [26], nanotubes [27] and nanosheets [28], in order to keep the absolute small volume changes and stabilize the dimensional integrity and the microstructure of the overall material during cycling. For example, Liu et al. [29] synthesized the amorphous SnO₂ nano-membranes as anodes for LIBs, which demonstrated a long cycling life of 1000 cycles at 1600 mA g⁻¹ with a high reversible capacity of 854 mAh g⁻¹. (II) Fabrication of active/inactive composites, which involves intimately mixing two materials, one reacts with lithium whereas the other acts as an inactive confining buffer, such as Ag/Fe₃O₄ [30] and MnO₂@Fe₂O₃ [31]. It is reported that iron oxides and tin oxides can be combined as a relative active/inactive composite [32]. Due to the different lithium uptake/release potentials of the metal oxides, tin oxide NPs is effective to prevent the aggregation of iron oxide NPs during electrochemical cycling. (III) Buffering of the volume expansion/shrinkage from flexible materials, such as carbon [20,25-27] and polymer [33]. Carbon-based materials are the most widely used buffers for MO anodes thanks to their advantages of high conductivity, mechanical flexibility, chemical stability, and large surface area, which are effective to enhance the structural stability and electric conductivity of the electrode. It is worthy to mention that a new type of C₁-MO-C₂ (C₁: graphene nanosheets (GNs) [34,35], carbon nanofibers (CNFs) [36], carbon nanotubes (CNTs) [37]; C₂: amorphous nanocarbon) carbon-based sandwiched buffering structure has been developed in recent years. In this type of hybrid material, C₁ is defined as an efficient support or substrate carbon material to disperse MO particles well, C₂ is amorphous nanocarbon with good elasticity covering over the MO particles to effectively accommodate the strain of volume change and preventing MO particles from falling off from the substrate material. For instance, Huang et al. [38] reported the synthesis and electrochemical properties of rGO-SnO₂-C and rGO-Fe₂O₃-C. Except for the initial cycles, the rGO-MO-C type hybrids exhibited excellent cycling performances at various current densities. However, the reversible capacities of the anodes still need to be improved. Besides, it is very challenging to design approaches to simultaneously combine the support, MO NPs, and the carbon coating in one material system to synthesize C₁-MO-C₂ type hybrid materials.

In this work, based on the three aforementioned strategies, we designed a simple approach to

fabricate C_1 - MO_1 - MO_2 - C_2 type quaternary hybrid materials for high performance energy storage. As a result, rGO- Fe_3O_4 - SnO_2 -C hybrid nanosheets with numerous nano pores were synthesized using reduced graphene oxide as a substrate for layer-by-layer precipitation of Fe_3O_4 and SnO_2 nanoparticles, and finally encapsulated by omnidirectional amorphous nanocarbon. Compared to the typical C_1 - MO - C_2 material, in addition to the advanced sandwiched structure carbon buffering, Fe_3O_4 and SnO_2 was combined as a relative active/inactive electrochemical system in order to effectively prevent the aggregation and enhance the electronic conductivity of the anode material during the cycles. Besides, the nano pores inside the nanosheets are beneficial to accommodate the substantial volume changes of MO NPs and enhance the reversible capacity of the material. It can be speculated that this type of C_1 - MO_1 - MO_2 - C_2 hybrid material would overcome the drawbacks of MOs and thus obtain improved electrochemical performance as a promising anode material for high performance lithium ion batteries.

2. Experiment

2.1 Materials Preparation

The rGO- Fe_3O_4 - SnO_2 -C mesoporous hybrid nanosheets were synthesized via layer-by-layer *in situ* homogeneous precipitations of FeOOH and SnO_2 nanoparticles onto graphene oxide (GO) nanosheets, followed by a hydrothermal treatment of glucose for the construction of omnidirectional encapsulated amorphous carbon. GO was prepared from natural graphite flakes by a modified Hummers method [39, 40]. For the preparation of GO-FeOOH, 0.68 g $FeCl_3 \cdot 6H_2O$ was added to 250 mL of GO aqueous solution (containing 0.10 g GO, exfoliated by ultrasonication for 1 h) under constant mechanical stirring. After stirring for 0.5 h, the mixture was heated to 80 °C and kept for 12 h. After the GO-FeOOH mixture was cooled down, 0.53 g Na_2SnO_3 was added as a source of SnO_2 and sonicated for 0.5 h, then reacted at room temperature for 24 h under mechanical stirring. The resulting suspension GO-FeOOH- SnO_2 was collected by centrifugation, washed with deionized water, and then vacuum-dried at 50 °C for 24 h. For the carbon precursor coating process, 0.35 g glucose and 1.05 g urea was dissolved in 22 mL deionized water and 13 mL

ethanol until a clear solution was observed. Subsequently, 0.1 g GO-FeOOH-SnO₂ was added and dispersed by ultrasonication before transferring to a 50 mL Teflon autoclave, which was subsequently heated at 180 °C for 12 h. After cooling to room temperature, the suspension was harvested by centrifugation and then dried in a vacuum oven at 50 °C for 24 h, followed by heating in a tube furnace under N₂ at 450 °C for 3 h.

For comparison, rGO-Fe₃O₄-C was synthesized via the same carbon coating process with GO-FeOOH instead of GO-FeOOH-SnO₂ followed by heating under N₂ at 450 °C for 3 h. The rGO-Fe₃O₄-SnO₂ was obtained through an *in situ* transformation of GO-FeOOH-SnO₂ by the same heat treatment.

2.1 Characterization

The structure and morphology of the as-prepared samples were characterized by X-ray diffraction (XRD, D/Max-III X-ray diffractometer with Cu K α radiation), laser Raman spectroscopy (Renishaw in Via), scanning electron microscopy (SEM; JEOL JSM-6380LA), and transmission electron microscopy (TEM, Hitachi, H-800). Nitrogen adsorption-desorption isotherms were measured on a Gemini-2390 analyzer (Micromeritics Co., USA) at 77 K. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area, while the Barrett–Joyner–Halenda (BJH) method was used to derive pore-size distributions from the desorption branches of the isotherms. The total pore volumes, V_p, were estimated from the amount adsorbed at a relative pressure of P/P₀ = 0.95. In addition, thermogravimetric analysis (TGA) was carried out on a Netzsch TG 209 apparatus under an air flow at a rate of 30 mL min⁻¹ with a heating rate of 15 °C min⁻¹.

2.3 Electrochemical measurements

The working electrode was composed of the testing material (rGO-Fe₃O₄-C, rGO-Fe₃O₄-SnO₂ or rGO-Fe₃O₄-SnO₂-C), conductive carbon black and polyvinylidene fluoride (PVDF) in a mass ratio of 7:2:1. The CR2025 coin cells were assembled in a glove box filled with ultrapure argon, using lithium metal as the counter electrode, 1.0 mol/L LiPF₆ in ethylene carbonate/dimethyl carbonate (v/v=1:1) as electrolyte, and microporous polypropylene film

(Celgard 2400) as a separator. The cells were kept at room temperature for 24 hours before electrochemical testing. Galvanostatic charge/discharge tests were performed on a Neware battery test system at room temperature and various rates between cutoff potentials of 0.01 and 3.0 V (vs. Li/Li⁺). Electrochemical impedance spectroscopy measurements were performed in the frequency range from 10 mHz to 1 MHz by applying an alternating-current (ac) signal of 5 mV.

3. Results and discussion

The synthesis process of rGO-Fe₃O₄-SnO₂-C mesoporous hybrid nanosheets is illustrated in Scheme 1. First, Fe³⁺ cations from FeCl₃ were favorably binded onto GO sheets via electrostatic interactions and *in situ* hydrolyzed to immobilize FeOOH NPs onto the GO sheets. Second, as the remnant Fe³⁺ cations were adsorbed by FeOOH NPs, SnO₃²⁻ anions were concentrated on the surface of the GO-FeOOH nanosheets and hydrolyzed at room temperature to provide ultrafine SnO₂ NPs for a second homogeneous precipitation on the GO-FeOOH nanosheets. Finally, amorphous nanocarbon was formed among the metal oxide NPs on GO-FeOOH-SnO₂ by hydrothermal carbonization of glucose. During the heating process, the GO was *in situ* transformed into rGO and the FeOOH was transformed into Fe₃O₄ simultaneously to obtain rGO-Fe₃O₄-SnO₂-C mesoporous hybrid nanosheets.

Fig. 1 presents the SEM images of rGO-Fe₃O₄-C, rGO-Fe₃O₄-SnO₂ and rGO-Fe₃O₄-SnO₂-C composites. It is showed that all the samples exhibit a sheet-like structure because of using rGO as a substrate. However, the surface morphology of the samples is quite different. It is obvious that the metal oxide NPs of rGO-Fe₃O₄-SnO₂-C and rGO-Fe₃O₄-C have been successfully anchored onto both sides of the rGO nanosheets, while those of rGO-Fe₃O₄-SnO₂ have seriously self-aggregated from nanoscale into microscale probably due to the high temperature heat treatment. The much smoother surfaces of the two samples, especially rGO-Fe₃O₄-SnO₂-C hybrid nanosheets, indicates that the metal oxide NPs have been fully encapsulated by the amorphous nanocarbon layer to form a sandwiched hierarchical structure with the substrate of

rGO. On the other hand, by intimately mixing the Fe_3O_4 and SnO_2 NPs, the $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2\text{-C}$ nanosheets show a more packed arrangement and an excellent integrity to uniformly distribute metal oxide NPs on the surface of the rGO. Meanwhile, the average thickness of $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2\text{-C}$ nanosheets was increased slightly, which helps to keep them from severe stacking like $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2$. From the EDS analysis (Fig. S1), the mole ratio of Fe and Sn atoms in the $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2\text{-C}$ composite is ca. 2.6.

The TEM images of $\text{rGO-Fe}_3\text{O}_4\text{-C}$, $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2$ and $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2\text{-C}$ hybrids with different magnifications are shown in Fig. 2. After a strong ultrasonic treatment during preparation of the TEM samples, we can observe that the metal oxide NPs of $\text{rGO-Fe}_3\text{O}_4\text{-C}$ and $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2\text{-C}$ were firmly decorated on the surface of the rGO nanosheets, while those of $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2$ fell off, indicating that the coated carbon is effective to root the metal oxide NPs onto rGO nanosheets. At a higher magnification, it is found that the particles of the $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2\text{-C}$ hybrid nanosheets, in comparison to $\text{rGO-Fe}_3\text{O}_4\text{-C}$, are better-defined and the size distribution is narrowed into the range of 3–15 nm. Besides, the shapes of SnO_2 NPs and Fe_3O_4 NPs in the hybrid nanosheets are quite different and the size of SnO_2 NPs is much smaller than that of Fe_3O_4 NPs (3–5 nm for SnO_2 NPs and 10–15 nm for Fe_3O_4 NPs). The selected area electron diffraction (SEAD) image of $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2\text{-C}$ shows the multiple directional growth and low degree of crystallinity of the Fe_3O_4 and SnO_2 NPs in the hybrid. It is rational to infer that besides the ultrathin carbon layer, the intimate deposition of SnO_2 NPs was also beneficial to hinder the agglomeration of Fe_3O_4 NPs during the high temperature heat treatment, as the Fe_3O_4 NPs came from the decomposition and transformation of FeOOH with a tendency to get together. The efficient assembly of rGO flexible films, Fe_3O_4 and SnO_2 NPs, and amorphous carbon of the $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2\text{-C}$ hybrid nanosheets was achieved to enhance their interface contact and suppress the dissolution and agglomeration of particles, thereby promoting the structural stability and promising for high electrochemical activity.

To gain an insight into the internal structure of the composites, XRD experiments were carried out, as shown in Fig. 3a. The XRD patterns for $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2\text{-C}$ and $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2$

are quite similar, and all intensive peaks match well with the standard patterns of SnO₂ (JCPDS no. 41-1445) and Fe₃O₄ (JCPDS no. 65-3107), indicating that the crystal structure of SnO₂ and Fe₃O₄ remains intact after encapsulated by the carbon layer. No apparent diffraction peak at 26° corresponding to graphene was observed in the patterns of the samples. The characteristic peaks of Fe₃O₄ and SnO₂ for rGO-Fe₃O₄-SnO₂-C are considerably broadened, and the peak intensity is much weaker in comparison to rGO-Fe₃O₄-SnO₂, which therefore indicates that the MO NPs have a lower crystallinity (higher content of amorphous phase) and smaller particle size. In general, MOs with a low crystallinity is less likely to suffer structural collapse during charge/discharge processes as compared with the amorphous counterparts [41]. Because a lower degree of crystallinity is associated with a homogenous volume expansion and contraction, thus eliminating the existence of two phase regions and improving the cycling stability [42].

To quantify the contents of metal oxide NPs, carbon and rGO in the composites, thermogravimetric analysis (TGA) was carried out in air with a temperature range from room temperature to 800 °C, as shown in Fig. 3b. The miniscule weight loss that appeared below 150 °C was attributed to the evaporation of adsorbed water and the major weight loss from 300 to 600 °C indicated the combustion of rGO and carbon. It should be noted that the slight weight increase between 150 to 300 °C for rGO-Fe₃O₄-C was due to the oxidation of Fe₃O₄. It is shown that the weight ratio of rGO is calculated as 6.7% for rGO-Fe₃O₄-SnO₂. With further carbon coating, the total weight ratio of rGO and carbon for rGO-Fe₃O₄-SnO₂-C increased to ca. 27.7%, indicating that the total weight ratio of Fe₃O₄ and SnO₂ NPs was ca. 72.3%. Without the deposition of SnO₂ NPs, the weight ratio of rGO and carbon for rGO-Fe₃O₄-C was a little higher and reached ca. 33.3%, implying a thicker carbon layer for the Fe₃O₄ NPs of the sample.

Raman spectrum of rGO-Fe₃O₄-SnO₂-C is presented in Figure 3c. It shows a fairly strong D band in the vicinity of 1359 cm⁻¹ corresponding to the A_{1g} symmetry mode of carbon atoms and a sharp G band in the vicinity of 1596 cm⁻¹ corresponding to the E_{2g} mode of the sp² carbon atoms [43]. For further analysis, the Raman spectrum was separated into four bands by a multiple peak fit with a Voigt profile function. The fitting results are shown in Figure 3c and table 1. It is

reported that the 1598 cm^{-1} band (G band) is characteristic of the ideal graphitic lattice vibration mode and corresponds to the in-plane vibration of graphite; The 1360 cm^{-1} band (D band) corresponds to in-plane defects of sp^2 carbon; The 1523 cm^{-1} band (D3 band) is attributed to the defects outside the planes of aromatic layers, such as tetrahedral carbon; The 1230 cm^{-1} band (D4 band) is attributed to the stretching vibration of aliphatic carbon [44,45]. The high value of I_D/I_G indicates the disordered structure of amorphous nanocarbon and the defects inside rGO films, which can provide more active sides for lithium intercalation. On the other hand, the relative low value of $(A_{D3} + A_{D4}) / (A_D + A_G)$ indicates a high content of sp^2 carbon, which can improve the electronic conductivity of the anode material and thus provide better electronic contact for high power performance.

The surface area of the rGO- Fe_3O_4 -C and rGO- Fe_3O_4 - SnO_2 -C composites was characterized by nitrogen adsorption and desorption isotherms, as displayed in Fig. 4. the specific surface area of rGO- Fe_3O_4 - SnO_2 -C is $96.4\text{ m}^2\text{ g}^{-1}$, which was much higher than that of rGO- Fe_3O_4 -C ($38.9\text{ m}^2\text{ g}^{-1}$). Moreover, the pore size distribution calculated by the ~~Blavet~~–Halenda (BJH) method ranged from 2.0 to 100 nm (insets in Fig. 4). For the rGO- Fe_3O_4 -C composite, the average pore diameter is about 27.0 nm distributed from 2.5 nm to 70 nm. However, the average pore diameter of rGO- Fe_3O_4 - SnO_2 -C decreases to about 5.8 nm and the pore size distribution shifted to 2.5-20 nm. From the lower total carbon content, higher specific surface area, smaller pore size and narrower pore size distribution described above, it can be inferred that by precipitating two kinds of MO NPs in different shapes layer-by-layer, not only mesoporous nanocarbon but also numerous nano pores formed among the Fe_3O_4 and SnO_2 NPs inside the hybrid nanosheets, which is expected to be highly favorable for lithium ion diffusion and electron transfer, thus promising for further enhancing the electrochemical properties of the composite.

Lithium storage properties of the samples as an anode material for LIBs were investigated. Fig. 5 presents the initial discharge/charge curves and cycling performances of the as-prepared samples at a current density of 200 mA g^{-1} in the voltage window of 0.010–3.0 V. In the first

discharge process, all the samples display a voltage flat of about 0.68 V as shown in Fig. 5a, which could be attributed to the reduction of Fe_3O_4 . The $\text{rGO-Fe}_3\text{O}_4\text{-C}$, $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2$ and $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2\text{-C}$ hybrids deliver discharge specific capacities of 1668.9, 1927.6, and 1243.6 mA h g^{-1} with the coulombic efficiencies of 62.4%, 59.5% and 62.8%, respectively. Compared with that of $\text{rGO-Fe}_3\text{O}_4\text{-C}$ and $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2$, the low discharge capacity of $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2\text{-C}$ in the first cycle implies that the electrode did not fully uptake Li, as the electrolyte did not completely infiltrate the multi-layer mesoporous nanosheets before electrochemical activation. As shown in the SEM and TEM images, the Fe_3O_4 and SnO_2 nanoparticles were closely packed inside the nanosheets, which might be hard for charge transport and electrolyte penetration before electrochemical activation. The irreversible capacity loss in the first cycling process could be attributed to irreversible transformation from SnO_2 to Sn as illustrated in equ. 2 [46]. Besides, the formation of insulating Li_2O matrix and decomposition of electrolyte along with the formation of solid electrolyte interface (SEI) films are also responsible [47, 48], which prevent the fully uptake of Li into the negative electrodes. As the discharge/charge cycling carried on, the $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2$ exhibited a fast and continuous decay of the lithium storage capability along with the cycling, which delivered a discharge specific capacity of 581.3 mA h g^{-1} at the 100th cycle, with a capacity fading of 6.73 mA h g^{-1} per cycle on average. Without amorphous nanocarbon encapsulated, the cyclical volume changes of MO NPs can generate significant stresses in the electrode material, forming cracks and breakages in electrical conductive pathway. On the other hand, the $\text{rGO-Fe}_3\text{O}_4\text{-C}$ showed excellent cycling stability with almost no capacity fading after ten cycles of electrochemical activation. However, because of the low reversible discharge specific capacity of 661.1 mA h g^{-1} at the second cycle, it can only maintain a stable discharge specific capacity of 516.2 mA h g^{-1} even after a slight increase of 0.95 mAh g^{-1} per cycle on average since the 30th cycles. As for the $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2\text{-C}$, it displayed a medium high discharge capacity in the initial cycles and exhibited a slow and constant reversible capacity increase along with the cycling. As shown in Fig. 5c, it delivered discharge specific capacities of 1243.6, 819.8, 730.3, 746.2 and 868.6 mAh g^{-1} in the first, second, 10th, 50th and 100th cycle,

respectively, with a capacity increase of 1.54 mAh g^{-1} per cycle on average since the 10th cycle. Along with the electrochemical activation, the coulombic efficiency was effectively improved from 62.8% of the first cycle to 100.0% of the 100th cycle. The behaviors of capacity increase were also reported by other researchers in $\text{C}_1\text{-MO-C}_2$ systems due to the dramatical synergic effect of the components.^{35,38} The higher lithium storage properties of $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2\text{-C}$ hybrids could be attributed to the hierarchical sandwiched structure, which thoroughly encapsulates both Fe_3O_4 and SnO_2 NPs inside the nanosheets. The rGO nanosheets provided good electronic conductivity and buffering effect to some extent. The intact and robust protection by amorphous carbon could prevent the interlayer MO NPs from dropping off from the 2D networks during the discharge/charge processes. Meanwhile, the numerous nanopores produced by layer-by-layer packing of Fe_3O_4 and SnO_2 NPs provided greenways for the buffering of volume changes during cycling. In addition, the omnidirectional nanocarbon coating layer could inhibit the direct contact between MO NRs and electrolyte to reduce the amount of irreversible SEI films, leading to high coulombic efficiency.

The rate capability of the $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2\text{-C}$ mesoporous nanosheets was measured at various current densities as an important parameter for lithium ion batteries. As shown in Fig. 6a and 6b, the $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2\text{-C}$ delivered discharge specific capacities of 871.5, 739.1, 654.3, 576.0, 546.1, 503.3, 472.3 and 414.7 mAh g^{-1} at current densities of 100, 200, 400, 600, 800, 1000, 1500 and 2000 mA g^{-1} , respectively. The cycling performance of $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2\text{-C}$ showed excellent stability and similar capacity boosting effect was also observed even at high current densities. When the current density is decreased from 2000 to 100 mAh g^{-1} , the discharge capacity quickly increases back to 869.6 mAh g^{-1} as it returns to 100 mAh g^{-1} . As a consequence, the $\text{rGO-Fe}_3\text{O}_4\text{-SnO}_2\text{-C}$ nanosheets are promising for stable operation at various current densities.

To gain insight into the electrochemical reaction kinetics of different electrodes, electrochemical impedances of the samples were measured and the spectra are given in Fig. 7a and 7b in the form of the Nyquist plot. The impedance spectrum of each sample is comprised of one compressed semicircle in the high-frequency region and a straight line in the low frequency region.

The R_{ct} of rGO-Fe₃O₄-SnO₂ is smaller than that of rGO-Fe₃O₄-C as shown in Fig. 7a. It was reported that benefiting from the formation of metallic (Sn) nanograins on the surface of iron oxide NPs, which enhanced the electronic conductivity, the R_{ct} of iron oxide and tin oxide hybrids was found to be significantly reduced.³² However, the R_{ct} of rGO-Fe₃O₄-SnO₂-C is much lower than that of rGO-Fe₃O₄-SnO₂, indicating the omnidirectional nanocarbon is effective to enhanced the electronic conductivity of the entire hybrid material. In addition, the electrochemical impedance spectra of rGO-Fe₃O₄-SnO₂-C before and after cycles are given in Fig. 7b. The results show that the R_{ct} is as high as 2200 Ω before cycles. This is mainly because the poor conductivity of SnO₂ and the electrolyte had not infiltrated into the multi-layer nanosheets. However, it dramatically decreased to 27 Ω only after 3 cycles of electrochemical activation, indicating the formation of conductive metallic (M⁰) nanograins and the infiltration of electrolyte. The plot obtained after 100 cycles almost overlapped with the one obtained after 50 cycles, which implies the structural stability of the material during the reversible Li-ion uptake/release process. It is worth noting that the highly porous structure of the total electrode can also contribute to the improved electrochemical reaction kinetics by providing more active sites for Li storage and numerous channels for rapid electrolyte diffusion, resulting in not only better cyclability but enhanced rate capability as well. It should also be mentioned that although the formation of Sn nanograins could enhance the electronic conductivity of the samples, the amount of SnO₂ NPs should be controlled because it could also affect the cycling performance (Fig. S2). Finally, the TEM images of rGO-Fe₃O₄-SnO₂-C before and after 100 cycles of discharge/charge process at 200 mA g⁻¹ are shown in Fig. 7c and 7d. Except for the electrochemical agglomeration of the Fe₃O₄ and SnO₂ NPs and the formation of SEI films on the surface of the hybrid nanosheet, there is only marginal change in its microstructure even after charge and discharge for 100 cycles, indicating high structural stability of the electrode and accounting for the superior cyclability of the electrode.

4. Conclusions

In summary, rGO-Fe₃O₄-SnO₂-C quaternary hybrid nanosheets were successfully synthesized via layer-by-layer homogeneous precipitations followed by a solvothermal treatment. The rGO support, Fe₃O₄ and SnO₂ NPs, and amorphous carbon were uniformly simultaneously combined to form a sandwich-like buffering structure with nanopores in an average size of 5.8 nm. Due to the structural stability of the composites and the synergistic effects of the components inside the nanosheets, the rGO-Fe₃O₄-SnO₂-C nanosheets exhibited an improved capacity of 868.6 mAh g⁻¹ after 100 cycles at 200 mA g⁻¹ and excellent cycling stability with an increase of 1.54 mA h g⁻¹ per cycle since the 10th cycle. Furthermore, the composite showed excellent stability and capacity boosting effect even at high rates, delivering a reversible capacity of 414.7 mAh g⁻¹ at a current density of 2.0 A g⁻¹, demonstrating its potential as a promising hybrid material for high performance lithium ion batteries.

Acknowledgement

This research was financial supported by the Guangdong Natural Science Foundation (grant No. 9151064201000039), the Guangdong Science and Technology Planning Project (No. 2009B010900025), the National Natural Science Foundation of China (Nos. 51003034 and 21173088), the Key Academic Program of the 3rd phase ‘211 Project’ (No. 2009B010100001), the President of South China Agricultural University (No. K09140), the State Key Laboratory of Motor Vehicle Biofuel Technology (No. 2013025), and the Air Force Office of Scientific Research (No. FA9550-12-1-0159).

References

- [1] C. Capasso, O. Veneri, Experimental analysis on the performance of lithium based batteries for road full electric and hybrid vehicles, *Appl. Energ.* 136 (2014) 921.
- [2] R. Van Noorden, A better battery, *Nature* 507 (2014) 26.
- [3] A.L.M. Reddy, S.R. Gowda, M.M. Shaijumon, P.M. Ajayan, Hybrid nanostructures for energy storage applications, *Adv. Mater.* 24 (2012) 5045.
- [4] H.T. Zhang, X.Z. Sun, X. Zhang, H. Lin, W. Kai, Y. Ma, High-capacity nanocarbon anodes for lithium-ion batteries, *J. Alloys Comp.* 622 (2015) 783.
- [5] S.X. Wang, L.P. Yang, L.P. Stubbs, X. Li, C.B. He, Lignin-derived fused electrospun carbon fibrous mats as high performance anode materials for lithium ion batteries, *ACS Appl. Mater. Interfaces* 5 (2013) 12275.
- [6] L. Xiao, D.Q. Wu, S. Han, Y.S. Huang, S. Li, M.Z. He, F. Zhang, X.L. Feng, Self-assembled Fe_2O_3 /graphene aerogel with high lithium storage performance, *ACS Appl. Mater. Interfaces* 5 (2013) 3764.
- [7] L. Chen, H.Y. Xu, L.E. Li, F.F. Wu, J. Yang, Y.T. Qian, A comparative study of lithium-storage performances of hematite: nanotubes vs. nanorods, *J. Power Sources* 245 (2014) 429.
- [8] L. Noerochim, J.Z. Wang, S.L. Chou, D. Wexler, H.K. Liu, Free-standing single-walled carbon nanotube/ SnO_2 anode paper for flexible lithium-ion batteries, *Carbon* 50 (2012) 1289.
- [9] H.K. Zhang, H.H. Song, X.H. Chen, J.S. Zhou, H.J. Zhang, Preparation and electrochemical performance of SnO_2 @carbon nanotube core-shell structure composites as anode material for lithium-ion batteries, *Electrochim. Acta* 59 (2012) 160.
- [10] S. Luo, H.C. Wu, Y. Wu, K.L. Jiang, J.P. Wang, S.S. Fan, Mn_3O_4 nanoparticles anchored on continuous carbon nanotube network as superior anodes for lithium ion batteries, *J. Power Sources* 249 (2014) 463.
- [11] S.K. Park, A.H. Jin, S.H. Yu, J. Ha, B. Jang, S. Bong, S. Woo, Y.E. Sung, Y.Z. Piao, In situ hydrothermal synthesis of Mn_3O_4 nanoparticles on nitrogen-doped graphene as

- high-performance anode materials for lithium ion batteries, *Electrochim. Acta* 120 (2014) 452.
- [12] D.H. Ge, H.B. Geng, J.Q. Wang, J.W. Zheng, Y. Pan, X.Q. Cao, H.W. Gu, Porous nano-structured Co_3O_4 anode materials generated from coordination-driven self-assembled aggregates for advanced lithium ion batteries, *Nanoscale* 6 (2014) 9689.
- [13] Y.N. Huang, C.C. Chen, C.H. An, C.C. Xu, Y.N. Xu, Y.J. Wang, L.F. Jiao, H.T. Yuan, Synthesis of cobalt based complexes and conversion to Co_3O_4 nanoparticles as a high performance anode for lithium ion battery, *Electrochim. Acta* 145 (2014) 34.
- [14] J. Liu, X. W. Liu, Two-dimensional nanoarchitectures for lithium storage, *Adv. Mater.* 24 (2012) 4097.
- [15] H.B. Wu, J.S. Chen, H.H. Hng, X.W. Lou, Nanostructured metal oxide-based materials as advanced anodes for lithium-ion batteries, *Nanoscale* 4 (2012) 2526.
- [16] G.M. Zhou, D.W. Wang, F. Li, L.L. Zhang, N. Li, Z.S. Wu, L. Wen, G.Q. Lu, H.M. Cheng, Graphene-wrapped Fe_3O_4 anode material with improved reversible capacity and cyclic stability for lithium ion batteries, *Chem. Mater.* 22 (2010) 5306.
- [17] M.S. Park, Y.M. Kang, G.X. Wang, S.X. Dou, H.K. Liu, The effect of morphological modification on the electrochemical properties of SnO_2 nanomaterials, *Adv. Funct. Mater.* 18 (2008) 455.
- [18] I.A. Courtney, W.R. McKinnon, J.R. Dahn, On the aggregation of tin in SnO composite glasses caused by the reversible reaction with lithium, *J. Electrochem. Soc.* 146 (1999) 59.
- [19] S. Denis, E. Baudrin, M. Touboul, J.M. Tarascon, Synthesis and electrochemical properties of amorphous vanadates of general formula RVO_4 ($\text{R} = \text{In, Cr, Fe, Al, Y}$) vs. Li , *J. Electrochem. Soc.* 144 (1997) 4099 .
- [20] W.M. Zhang, X.L. Wu, J.S. Hu, Y.G. Guo, L.J. Wan, Carbon coated Fe_3O_4 nanospindles as a superior anode material for lithium-ion batteries, *Adv. Funct. Mater.* 18 (2008) 3941.
- [21] X.W. Lou, Y. Wang, C.L. Yuan, J.Y. Lee, L.A. Archer, A. template-free synthesis of SnO_2 hollow nanostructures with high lithium storage capacity, *Adv. Mater.* 18 (2006) 2325.

- [22] J.S. Chen, X.W. Lou, SnO₂-based nanomaterials: Synthesis and application in lithium-ion batteries, *Small* 9 (2013) 1877.
- [23] J. Jiang, Y.Y. Li, J.P. Liu, X.T. Huang, C.Z. Yuan, X.W. Lou, Recent advances in metal oxide-based electrode architecture design for electrochemical energy storage, *Adv. Mater.* 24 (2012) 5166.
- [24] A.S. Arico, P. Bruce, B. Scrosati, J.M. Tarascon, W. Van Schalkwijk, Nanostructured materials for advanced energy conversion and storage devices, *Nat. Mater.* 4 (2005) 366.
- [25] L. Pan, X.D. Zhu, X.M. Xie, Y.T. Liu, Smart hybridization of TiO₂ nanorods and Fe₃O₄ nanoparticles with pristine graphene nanosheets: hierarchically nanoengineered ternary heterostructures for high-Rate lithium storage, *Adv. Funct. Mater.* 25 (2015) 3341.
- [26] Y. Zhao, J.X. Li, C.X. Wu, Y.H. Ding, L.H. Guan, A yolk-shell Fe₃O₄@C composite as an anode material for high-Rate lithium batteries, *ChemPlusChem* 77 (2012) 748.
- [27] X.D. Zhu, K.X. Wang, D.J. Yan, S.R. Le, R.J. Ma, K.N. Sun, Y.T. Liu, Creating a synergistic interplay between tubular MoS₂ and particulate Fe₃O₄ for improved lithium storage, *Chem. Commun.* 51 (2015) 11888.
- [28] Y.T. Liu, X.D. Zhu, Z.Q. Duan, X.M. Xie, Flexible and robust MoS₂-graphene hybrid paper cross-linked by a polymer ligand: a high-performance anode material for thin film lithium-ion batteries, *Chem. Commun.* 49 (2013) 10305.
- [29] X.H. Liu, J. Zhang, W.P. Si, L.X. Xi, S. Oswald, C.L. Yan, O.G. Schmidt, High-rate amorphous SnO₂ nanomembrane anodes for Li-ion batteries with a long cycling life, *Nanoscale* 7 (2015) 282.
- [30] L. Pan, X.D. Zhu, X.M. Xie, Y.T. Liu, Delicate ternary heterostructures achieved by hierarchical co-assembly of Ag and Fe₃O₄ nanoparticles on MoS₂ nanosheets: morphological and compositional synergy in reversible lithium storage, *J. Mater. Chem. A* 3 (2015) 2726
- [31] X. Gu, L. Chen, Z.C. Ju, H.Y. Xu, J. Yang, Y.T. Qian, Controlled growth of porous α -Fe₂O₃ branches on β -MnO₂ nanorods for excellent performance in lithium-ion batteries, *Adv. Funct. Mater.* 23 (2013) 4049.

- [32] G.F. Xia, N. Li, D.Y. Li, R.P. Liu, C. Wang, Q. Li, X.J. Lu, J.S. Spendelow, J.L. Zhang, G. Wu, Graphene/Fe₂O₃/SnO₂ ternary nanocomposites as a high-performance anode for lithium ion batteries, *ACS Appl. Mater. Interfaces* 5 (2013) 8607.
- [33] L. Wang, D. Wang, Z.H. Dong, F.X. Zhang, J. Jin, Interface chemistry engineering for stable cycling of reduced GO/SnO₂ nanocomposites for lithium ion battery, *Nano Lett.* 13 (2013) 1711.
- [34] G. Wang, H. Wang, S.B. Cai, J.T. Bai, Z.Y. Ren, J.B. Bai, Synthesis and evaluation of carbon-coated Fe₂O₃ loaded on graphene nanosheets as an anode material for high performance lithium ion batteries, *J. Power Sources* 239 (2013) 37.
- [35] D.N. Wang, J.L. Yang, X.F. Li, D.S. Geng, R.Y. Li, M. Cai, T.K. Sham, X.L. Sun, Layer by layer assembly of sandwiched graphene/SnO₂ nanorod/carbon nanostructures with ultrahigh lithium ion storage properties, *Energy Environ. Sci.* 6 (2013) 2900.
- [36] M. Dirican, M. Yanilmaz, K. Fu, Y. Lu, H. Kizil, X.W. Zhang, Carbon-enhanced electrodeposited SnO₂/carbon nanofiber composites as anode for lithium-ion batteries, *J. Power Sources* 264 (2014) 240.
- [37] Z.Y. Wang, D.Y. Luan, S. Madhavi, Y. Hu, X.W. Lou, Assembling carbon-coated α -Fe₂O₃ hollow nanohorns on the CNT backbone for superior lithium storage capability, *Energy Environ. Sci.* 5 (2012) 5252.
- [38] X. Huang, J. Chen, H. Yu, R. Cai, S.J. Peng, Q.Y. Yan, H.H. Hng, Carbon buffered-transition metal oxide nanoparticle-graphene hybrid nanosheets as high-performance anode materials for lithium ion batteries, *J. Mater. Chem. A* 1 (2013) 6901.
- [39] W.S. Hummers, R.E. Offeman, Preparation of graphitic oxide, *J. Am. Chem. Soc.* 80 (1958) 1339.
- [40] D.C. Marcano, D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z.Z. Sun, A. Slesarev, L.B. Alemany, W. Lu, J.M. Tour, Improved synthesis of graphene oxide, *ACS Nano* 4 (2010) 4806.
- [41] X.F. Li, X.B. Meng, J. Liu, D.S. Geng, Y. Zhang, M.N. Banis, Y.L. Li, J.L. Yang, R.Y. Li,

- X.L. Sun, M. Cai, M.W. Verbrugge, Tin oxide with controlled morphology and crystallinity by atomic layer deposition onto graphene nanosheets for enhanced lithium storage, *Adv. Funct. Mater.* 22 (2012) 1647.
- [42] J.T. Yin, M. Wada, K. Yamamoto, Y. Kitano, S. Tanase, T. Sakai, Micrometer-scale amorphous Si thin-film electrodes fabricated by electron-beam deposition for Li-ion batteries, *J. Electrochem. Soc.* 153 (2006) A 472.
- [43] M.X. Chen, C.C. Zhang, X.C. Li, L. Zhang, Y.L. Ma, L. Zhang, X.Y. Xu, F.L. Xia, W. Wang, J.P. Gao, Wang W.; Gao J. P. A One-step method for reduction and self-assembling of graphene oxide into reduced graphene oxide aerogels, *J. Mater. Chem. A* 1 (2013) 2869.
- [44] C. Hu, S. Sedghi, A. Silvestre-Albero, G.G. Andersson, A. Sharma, P. Pendleton, F. Rodríguez-Reinoso, K. Kaneko, M.J. Biggs, Raman spectroscopy study of the transformation of the carbonaceous skeleton of a polymer-based nanoporous carbon along the thermal annealing pathway, *Carbon* 85 (2015) 147.
- [45] Y.W. Zhang, R. Wang, X.D. Lin, Z.H. Wang, J.Z. Liu, J.H. Zhou, K.F. Cen, Catalytic performance of different carbon materials for hydrogen production in sulfur-iodine thermochemical cycle, *Appl. Catal. B-Environ.* 166-167 (2015) 413.
- [46] I.A. Courtney, J.R. Dahn, Electrochemical and In Situ X-Ray Diffraction studies of the reaction of lithium with tin oxide composites, *J. Electrochem. Soc.* 144 (1997) 2045.
- [47] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.M. Tarascon, Searching for new anode materials for the Li-ion technology: Time to deviate from the usual path, *J. Power Sources* 97-98 (2001) 235.
- [48] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.M. Tarascon, Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries, *Nature* 407 (2000) 496.

Captions of Figures and Tables

Table 1 The fitting results and parameters of Raman spectrum of rGO-Fe₃O₄-SnO₂-C.

Scheme 1 Illustration of procedure for fabricating rGO-Fe₃O₄-SnO₂-C mesoporous hybrid nanosheets.

Fig. 1 SEM images of rGO-Fe₃O₄-C (a), rGO-Fe₃O₄-SnO₂ (b) and rGO-Fe₃O₄-SnO₂-C (c).

Fig. 2 TEM images of rGO-Fe₃O₄-C (a), rGO-Fe₃O₄-SnO₂ (b), rGO-Fe₃O₄-SnO₂-C (c) and SEAD image of rGO-Fe₃O₄-SnO₂-C (d).

Fig. 3 (a) XRD patterns of rGO-Fe₃O₄-C, rGO-Fe₃O₄-SnO₂ and rGO-Fe₃O₄-SnO₂-C; (b) TG curves of rGO-Fe₃O₄-C, rGO-Fe₃O₄-SnO₂ and rGO-Fe₃O₄-SnO₂-C; (c) Raman spectrum of rGO-Fe₃O₄-SnO₂-C.

Fig. 4 Nitrogen adsorption-desorption isotherm curves and pore-size distributions of rGO-Fe₃O₄-C (a) and rGO-Fe₃O₄-SnO₂-C (b)

Fig. 5 Electrochemical properties of the composites at the current density of 200 mA g⁻¹: (a) Initial discharge/charge curves of the samples; (b) Cycling performance of the samples; (c) Discharge/charge profiles of rGO-Fe₃O₄-SnO₂-C in the first, second, 10th, 50th and 100th cycles.

Fig. 6 (a) Rate performance of rGO-Fe₃O₄-SnO₂-C (I: 100, II: 200, III: 400, IV: 600, V: 800, VI: 1000, VII: 1500 and VIII: 2000 mA g⁻¹); (b) Discharge/charge profiles of rGO-Fe₃O₄-SnO₂-C at various rates.

Fig. 7 Nyquist plots of the three samples after 100 cycles (a) and the rGO-Fe₃O₄-SnO₂-C before and after cycles (b); TEM images of rGO-Fe₃O₄-SnO₂-C before (c) and after (d) 100 cycles of discharge/charge process at 200 mA g⁻¹.

Scheme 1

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7