Chemically derived graphene–metal oxide hybrids as electrodes for electrochemical energy storage: pre-graphenization or post-graphenization?†

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The introduction of a secondary phase is an efficient and effective way to improve the electrochemical performance of graphene towards energy storage applications. Two fundamental strategies including pre-graphenization and post-graphenization were widely employed for graphene-based hybrids. However, there is still an open question of which way is better. In this contribution, we investigated the differences in the structure and electrochemical properties of pre- and post-graphenized graphene–SnO2 hybrids. The pre-graphenization is realized by synthesis of thermally reduced graphene and subsequent impregnation of SnO2, while the post-graphenization is realized by introducing a Sn-containing phase onto GO sheets followed by chemical reduction. The pre-graphenization process provides a large amount of pores for ion diffusion, which is of benefit for loading of SnO2, fast ion diffusion for supercapacitors, and higher capacity for Li-ion batteries, but poor stability, while the post-graphenization process offers compact graphene and good interaction between the SnO2 and graphene, which provides stable structure for long term stability for supercapacitor and Li-ion battery use.

1. Introduction

Advanced energy storage and conversion is an important issue for a sustainable development of our society. Electrochemical energy storage devices, such as supercapacitors and batteries, are playing a core role in balancing the energy generated by engines, solar and wind power. Supercapacitors, or electrochemical capacitors, are energy storage devices that store charges electrostatically through the reversible adsorption/desorption of ions in the electrolyte onto active materials,1,2 while Li-ion batteries, which consist of two electrodes that are capable of reversibly hosting Li in ionic form,3 are widely used for consumer electronics, power management, and hybrid electric vehicles. However, the energy density or power density of the two systems still needs to be improved for demanding applications. Exploring advanced electrode materials is one of the most straightforward approaches to improve the efficiency of electrochemical energy storage systems.

The element carbon is a very flexible choice for building electrochemical energy storage devices.4 Graphite, hard carbon, glassy carbon, carbon black, mesocarbon microbead, activated carbon, and mesoporous carbon have been widely utilized in various energy storage systems.5 Carbon nanotubes have been applied as an electric conductive additive for Li-ion batteries.6 Graphene, the two-dimensional carbon crystal lattice with excellent electronic conductivity, optical transparency, mechanical strength, inherent flexibility, and huge theoretical surface area, has been considered a novel and portable nano-carbon component for electrodes of energy storage devices.7–9 However, the irreversible aggregation of graphene sheets always creates more void units and masks active sites for pseudo-capacitor or Li-intercalation. Thus, metal oxides (e.g. RuO2,10 MnO2,11 Co3O4,12 NiO,13 SnO2,14,15 Fe3O4 (ref. 17)), conductive polymers (e.g. PANI,18 PPY19) or nanocarbon (e.g. carbon nanotube20) are introduced as secondary phases that serve as “spacers” to avoid the re-stacking of graphene, provide pseudo-active centres for supercapacitors, or host storage materials for Li-ion batteries.
SnO$_2$ has become very attractive as the anode material for next-generation LiBs because of its high theoretical capacity of 790 mA h g$^{-1}$. The applications of graphene-based electrodes for supercapacitor and Li-ion battery use are also highlighted by recent reviews.$^8$

To develop graphene-based hybrid electrodes with superior performance in electrochemical energy storage, the selection of appropriate raw materials and the optimization of synthesis strategy are of great importance. Among various approaches for graphene production, the chemically derived graphene (CDG), which uses graphite, graphite oxide (GO) or other graphite derivatives as starting materials, can be produced in large scale, and provides further processability and abundant functions for industrial applications as well.$^7$ Up to now, the reduction of GO to CDGs is the most widely applied technique for the large scale preparation of graphene. During the preparation of graphene-based hybrids, as shown in Fig. 1, the current reported methods can be simply classified into two general strategies according to the processes of CDG synthesis: (1) pre-graphenization strategy: CDG is synthesized (such as thermally reduced graphene (TRG)) before the second component is introduced; (2) post-graphenization strategy: a composite composed of a CDG precursor (usually graphene oxide) and the second component is pre-prepared, followed by converting the precursor into chemical reduced graphene (CRG). Both of them have been widely used for graphene-based hybrid electrode fabrication, but it is still an open question as to which one is better.

To explore an advanced technique as well as reveal the chemical and material science for fabrication of graphene-based electrode materials, SnO$_2$, which is an important n-type semiconductor with a wide band gap ($E_g = 3.6$ eV) for many applications such as gas sensors, supercapacitors, and lithium-ion batteries (LiBs), is selected as the secondary component to the graphene supports by pre- or post-graphenization. Recently, SnO$_2$ has become very attractive as the anode material for the next-generation LiBs because of its high theoretical capacity of 790 mA h g$^{-1}$. As shown in Fig. 1, both pre-graphenization and post-graphenization process are carried out for SnO$_2$@graphene hybrid fabrication, and SnO$_2$@TRG and SnO$_2$@CRG electrodes are obtained and carefully characterized. Both the graphenes and their hybrids are evaluated for supercapacitors and Li-ion battery electrodes, so as to provide insightful materials chemistry towards development of advanced graphene-based electrodes.

2. Experimental

2.1 Pre-graphenization: SnO$_2$@TRG hybrids

The thermally reduced graphene was obtained by thermal expansion of GO powder under high vacuum. GO was prepared by a modified Hummers method. The as-prepared GO was put into a quartz tube that was sealed at one end and stoppered at the other end, through which the reactor was connected to the high vacuum pump. The tube was heated at a rate of 30 °C min$^{-1}$ under high vacuum (<3.0 Pa). At about 200 °C, an abrupt expansion was observed. To remove the abundant functional groups, the expanded GO was kept at 250 °C for 20 min and a high vacuum was maintained (below 5.0 Pa) during heat treatment. The as-prepared graphene sample was denoted as TRG. The SnO$_2$@TRG hybrids were prepared by a facile excessive impregnation of the above TRG. In a typical process, 500 mg of TRG was mixed with 500 mL of 0.1 M SnCl$_2$ aqueous solution (with 0.1 M HCl as pH adjuster) in an ice bath (−0 °C). The black mixture was kept in the ice bath with intensive stirring for 10 min, to realize moderate anchoring of Sn$^{2+}$ on the active sites of graphene. The product was isolated by vacuum filtration and rinsed copiously with water (5 × 100 mL) and ethanol (5 × 100 mL). Finally, the sample was air dried at 110 °C for 24 h to obtain SnO$_2$@TRG hybrids.

2.2 Post-graphenization: SnO$_2$@CRG hybrids

The CRG was prepared by a chemical reduction approach. In a typical procedure, GO (500 mg) was dispersed in 500 mL water followed by sonication (200 W) for 30 min to yield a homogeneous brown hydrosol of graphene oxide. The above hydrosol was mixed with 50 mL hydrazine monohydrate (NH$_2$–NH$_2$·H$_2$O, 100%) in a 1000 mL round-bottom flask, and heated in an oil bath at 100 °C under a water-cooled condenser for 24 h, during which the reduced GO gradually precipitated out as black solids. The product was isolated by vacuum filtration and washed thoroughly with water and ethanol to remove excessive metal salts. Finally, the sample was air dried in a watch glass at 110 °C for 24 h to obtain chemically reduced graphene. The SnO$_2$@CRG hybrids were prepared by pre-impregnation of graphene oxide followed by a similar chemical reduction approach. In a typical experimental, 500 mL of graphene oxide hydrosol (1.0 mg mL$^{-1}$) was pre-mixed with 250 mL of SnCl$_2$ aqueous solution (concentration of 0.32 mg mL$^{-1}$ with 0.10 M HCl as pH adjuster). The mixture was stirred in an ice bath for 10 min, and then moved to an oil bath over which 50 mL of 100% NH$_2$–NH$_2$·H$_2$O was added gradually. The solution was heated and kept at 100 °C with intensive stirring under a water-cooled condenser for 24 h. The as-prepared products of SnO$_2$@CRG hybrids are separated, washed and dried using the same method as mentioned above for CRG.

![Fig. 1 Illustration of the pre- and post-graphenization route for metal oxide–graphene hybrid fabrication.](image)
2.3 Sample characterization

The morphologies of the samples were characterized using a Hitachi S4800 scanning electron microscope (SEM) operated at 2.0 kV and a Philips CM200 LaB₆ transmission electron microscope (TEM) operated at 200.0 kV; the HRTEM images of the samples were collected on a FEI Cs-corrected Titan 80-300 microscope operated at 80.0 kV. Energy dispersive X-ray spectroscopy (EDS) analysis was performed using a Titan 80-300 apparatus with the analytical software INCA. The samples were ultrasonically dispersed in ethanol, and then a drop of the solution was deposited on a Lacey carbon film grid to be used for TEM characterization; X-ray diffraction (XRD) measurements were performed at room temperature (Cu Kα radiation, k = 0.15406 nm, D8 Advance, BRUKER/AXS, Germany); X-ray fluorescence (XRF) was employed to analyze the elemental composition of the samples. Before XRF testing, the sample was pre-grinded with wax in ethanol to form a slurry, and then pressed into a pellet with thickness of ca. 35 mm; Brunauer–Emmett–Teller (BET) specific surface areas and Barret–Joyner–Halenda (BJH) pore size distributions of the SnO₂–graphene hybrids were determined by N₂ physisorption at 77 K using a Micromeritics 2375 BET apparatus; X-ray photoelectron spectroscopy (XPS) was performed on the Thermo VG ESCA-LAB250 surface analysis system with parameters: Al Kα = 1486.6 eV, Power = 150 W (HV = 15 kV and I = 10 mA), spot size = 500 lm, pass energy 50.0 eV and energy step size 0.1 eV.

2.4 Supercapacitor performance measurements

The electrochemical properties of graphene–SnO₂ hybrids were measured in an aqueous system (electrolyte: 6.0 M KOH). A three-electrode system was employed in the measurement, whereby Ni foam coated with electrode materials served as the working electrode, a platinum foil electrode as counter electrode and a saturated hydrogen electrode (SHE) served as reference electrode. In order to prepare a working electrode, a mixture of our active material, carbon black, and poly(tetrafluoroethylene) with a weight ratio of 80 : 5 : 15 was ground together to form a homogeneous slurry. The slurry was squeezed into a film and then punched into pellets. The punched pellets with a piece of nickel foam on each side were pressed under 2.5 MPa and dried overnight at 110 °C. Each electrode was quantified to contain roughly 5.0 mg active materials. The electrodes were impregnated with electrolyte under vacuum for 1.0 h prior to the electrochemical evaluation. Cyclic voltammogram (CV) curves (scan rates varying from 3 to 500 mV s⁻¹) and electrochemical impedance spectroscopy (EIS) profiles were measured with a VSP BioLogic electrochemistry workstation. The electrochemical capacitances were both obtained from CV curves. The Nyquist plot was fitted by EC-Lab software.

2.5 Li-ion battery performance measurements

The performances of graphene-based hybrids as anode materials for lithium ion batteries were tested with CR2025 coin cells. A mixture of SnO₂@CRG nanocomposites or SnO₂@TRG, carbon black, and polyvinylidene fluoride at a weight ratio of 80 : 10 : 10 was pasted on pure Cu foil (99.6%, Goodfellow) to make the working electrode. A microporous polyethylene sheet (Celgard 2400) was used as separator. The electrolyte was 1.0 M LiPF₆ dissolved in a mixed solution of ethylene carbonate–dimethyl carbonate–ethylene methyl carbonate (1 : 1 : 1, by weight) obtained from Ube Industries Ltd. Pure lithium foil (Aldrich) was used as counter electrode. The cells were assembled in an Ar-filled glove box. The discharge and charge measurements were carried out at different current densities in the voltage range of 0–3.0 V on a Neware battery test system. The specific capacity of the SnO₂@graphene nanocomposites was calculated based on the mass of the anode materials (SnO₂ and graphene). Cyclic voltammogram measurements were performed on a Solartron 1470E electrochemical workstation at a scan rate of 0.1 mV s⁻¹.

3. Results and discussion

3.1 Pre-graphenization: structure of TRG and SnO₂@TRG hybrids

In the pre-graphenization process, the GO is thermally expanded and reduced into a fluffy black powder. As shown in Fig. 2a, the as-obtained TRGs have a hierarchically honeycomb-like morphology: the crumpled graphene sheets with many ripples and wrinkles are loosely stacked or folded with each other to construct a continuous and interconnected 3D macroscopic architecture, with a Brunauer–Emmett–Teller (BET) surface area of ~293 m² g⁻¹. The diameter of the macropores ranges from 100 to 300 nm (Fig. 2a and b). The TRG has a coarse edge, which can be attributed to the fast decomposition of oxygen-containing functional groups (such as carboxyl, carbonyl groups) during thermal exfoliation. After the impregnation and calcination process, the pre-graphenized SnO₂@TRG hybrid still holds a porous morphology with twisted and loosely packed graphene sheets. However, the regularity of the ordered honeycomb structure is lost gradually. As the basic building blocks, the
graphene sheets are larger than 1 μm in diameter, between which pores ranging from 20 to 100 nm are clearly identified (Fig. 2c). The microtexture of SnO₂@TRG was further examined by TEM. SnO₂ nanoparticles with sizes ranging between 3 and 5 nm with a density of ca. 4 × 10¹² cm⁻² are formed on the graphene sheets. Some of the SnO₂ particles are agglomerated into chain-like structures. A lattice with a d₁₀₀ space of ≈3.35 Å can be clearly demonstrated on the inserted figure of the high resolution TEM images (Fig. 2d), indicating a good crystallization of SnO₂.

The XPS results show that the atomic percentages of Sn, C, and O element are 1.71, 85.84, and 12.44 at%, respectively (Table 1). From the XPS scan of SnO₂@TRG (Fig. 3d), the Sn components present the typical 3d₅/₂ (485.6 eV) and 3d₃/₂ (494.0 eV) level with a gap of 8.4 eV and area ratio of ∼1.5, which further confirms the state of SnO₂ on TRG.

The other route for SnO₂@graphene hybrids is post-graphenization, in which the Sn⁴⁺ species are grafted onto the surface of GO in advance, and then the chemical transformation from graphene oxide into graphene is conducted by solution based chemical reduction. As shown in Fig. 4a, the CRG exhibits closely packed graphene agglomerates, in which the graphene sheets with high-density ripples and wrinkles are randomly crumpled (Fig. 4b). After SnO₂ addition, the post-graphenized SnO₂@CRG hybrid still holds a highly twisted structure (Fig. 4c), in which only micropores and mesopores are observed. SnO₂ nanoparticles with a density of ca. 3 × 10¹² cm⁻² and the increase in the intensity of the peak and shoulder at ≈26.6° is ascribed to a secondary re-stacking of graphene during impregnation and drying, and the amalgamation of the (002) line of graphite with the nearby (110) line of SnO₂. The crystalline size along the (110) lattice (L₁₁₀) of SnO₂ is estimated to be ≈3.8 nm according to the Scherrer equation, which is consistent with the TEM observation.

The N₂ adsorption–desorption isotherms are carried out to evaluate the change of pore structure for TRG before and after SnO₂ impregnation. As shown in Fig. 2c, both sorption isotherms exhibit the typical Type III isotherm with H₃ hysteresis loop according to IUPAC classification, showing materials characteristic of macropores (pore size >50 nm) and comprised of aggregates (loose assemblages) of plate-like particles forming slit-like mesopores (Fig. 3b). The specific BET surface area (S_BET), t-plot micropore surface area (pore size <2 nm) (S_micro), and total pore volume (V_p) of TRG and SnO₂@TRG are summarized in Table 1. After SnO₂ impregnation, the S_BET is slightly increased from 293 to 325 m² g⁻¹, while the V_p is decreased simultaneously from 1.62 to 1.26 cm³ g⁻¹, with a corresponding increase of S_micro from 6.9 to 12.8 m² g⁻¹. The BJH adsorption pore size distribution (Fig. 3c) indicates the key role of exterior meso- and macropores with relatively larger diameters (pore size >2 nm) in contributing the S_BET of TRG and SnO₂@TRG, however, the average diameter of the pore is decreasing after the introduction of SnO₂. The evolution of porous structure is attributable to the collapse of exterior macropores due to the capillary effect during solution based impregnation and the air drying process (Fig. 3c).

Furthermore, the XPS results show that the atomic percentages of Sn, C, and O element are 1.71, 85.84, and 12.44 at%, respectively (Table 1). From the XPS scan of SnO₂@TRG (Fig. 3d), the Sn components present the typical 3d₅/₂ (485.6 eV) and 3d₃/₂ (494.0 eV) level with a gap of 8.4 eV and area ratio of ∼1.5, which further confirms the state of SnO₂ on TRG.

### 3.2 Post-graphenization: structure of SnO₂@CRG hybrids

The post-graphenization process of SnO₂@graphene hybrids is post-graphenization, in which the Sn⁴⁺ species are grafted onto the surface of GO in advance, and then the chemical transformation from graphene oxide into graphene is conducted by solution based chemical reduction. As shown in Fig. 4a, the CRG exhibits closely packed graphene agglomerates, in which the graphene sheets with high-density ripples and wrinkles are randomly crumpled (Fig. 4b). After SnO₂ addition, the post-graphenized SnO₂@CRG hybrid still holds a highly twisted structure (Fig. 4c), in which only micropores and mesopores are observed. SnO₂ nanoparticles with a density of ca. 3 × 10¹² cm⁻² and

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### Table 1 Quantification results of BET, XRF and XPS on the TRG, SnO₂@TRG, CRG, and SnO₂@CRG samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_BET a (m² g⁻¹)</th>
<th>V_p a (m³ g⁻¹)</th>
<th>S_micro a (m² g⁻¹)</th>
<th>Bulk. Sn b (%)</th>
<th>Surf. Sn c (%)</th>
<th>Surf. C (%)</th>
<th>Surf. O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRG</td>
<td>293</td>
<td>1.62</td>
<td>6.9</td>
<td>0</td>
<td>0.00</td>
<td>89.70</td>
<td>10.30</td>
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<tr>
<td>SnO₂@TRG</td>
<td>325</td>
<td>1.26</td>
<td>12.8</td>
<td>3.86</td>
<td>1.71</td>
<td>85.84</td>
<td>12.44</td>
</tr>
<tr>
<td>CRG</td>
<td>666</td>
<td>0.60</td>
<td>69.9</td>
<td>0</td>
<td>0.00</td>
<td>88.43</td>
<td>11.57</td>
</tr>
<tr>
<td>SnO₂@CRG</td>
<td>818</td>
<td>1.09</td>
<td>NA</td>
<td>2.00</td>
<td>0.74</td>
<td>88.06</td>
<td>11.21</td>
</tr>
</tbody>
</table>

a Calculated by N₂ physisorption. b Obtained from XRF. c Quantified by XPS.
a diameter of 3.5–5.5 nm are uniformly distributed on the graphene sheets. The lattice of SnO$_2$ ($d_{110} \sim 3.35$ Å) can be clearly observed on the HRTEM images (Fig. 4d), which implies a high crystallization degree of the SnO$_2$ particles.

Comparing with the pre-graphenized TRG, CRG exhibits broader and stronger diffraction peaks of the graphite (002) and (101) lattice in the XRD pattern (Fig. 5a), indicating an over re-stacking and entanglement of graphenes within the macro-assembly. However, after introduction of only 2 wt% of Sn components, the graphite associated peaks are significantly minimised with the emersion of very weak SnO$_2$ peaks, due to the formation of SnO$_2$ nanocrystals which could further act as the isolation spacers between graphene. Thus, the BET surface area is extended from CRG (666 m$^2$ g$^{-1}$) to SnO$_2$@CRG (818 m$^2$ g$^{-1}$), as more closed pores may become opened ones which are accessible to the N$_2$ molecules (Table 1).

Furthermore, the N$_2$ sorption isotherms of both CRG and SnO$_2$@CRG, as shown in Fig. 5b, present a typical Type IV isotherm with apparent H$_2$ hysteresis loop, indicating the presence of ink-bottle pores between graphene sheets in the architecture. It is noteworthy that the curve of the N$_2$ sorption isotherm of CRG is apparently different from that of TRG (Fig. 3b and 5b) and there are no macropores in CRG (Fig. 5b). In addition, the $S_{BET}$ of CRG (666 m$^2$ g$^{-1}$) is higher than that of TRG (293 m$^2$ g$^{-1}$). These phenomena are mainly attributed to over re-stacking and entanglement of graphenes in CRG materials, generating more mesopores, and to inadequate exfoliation of graphite oxide in TRG. After SnO$_2$ introduction, the pore volume is increased from 0.60 to 1.09 cm$^3$ g$^{-1}$ and the vanishing micropore surface area in SnO$_2$@CRG is observed. The BJH adsorption pore size distribution of CRG and SnO$_2$@CRG exhibits the parabolic profile with peaks at ~4 and ~10 nm, respectively (Fig. 5c), which is distinct from pre-graphenized SnO$_2$@TRG samples.

As calculated from XPS, the surface contents of Sn, C, and O on SnO$_2$@CRG are determined to be 0.74, 88.06, and 11.21 at%, respectively (Table 1). The Sn3d fine scan spectrum exhibits the similar 3d$_{5/2}$ and 3d$_{3/2}$ line to SnO$_2$@TRG at 486.5, 495.0 eV with a gap of 8.5 eV, indicating the grafting of SnO$_2$ on CRG. However, the content of Sn in SnO$_2$@CRG is much less than that of SnO$_2$@TRG, as confirmed by XPS and XRF analysis (Table 1).

In the post-graphenization process, due to π–π interaction between graphene sheets, the reduced graphene oxide sheets are likely to be re-stacked into agglomerations in the solution based reduction procedure. Attributing to the removal of negatively charged functional groups, the electrostatic repulsion which keeps the graphene oxide hydrosol stable is decreased. The agglomeration became even more severe due to the capillary attraction effect, as water molecule spacers are spilled out from the graphene interlayer in the final drying process. However, the pre-introduced SnO$_2$ species on the basal plane of graphene oxide could act as the spacers between graphene so as to prevent the over-compact restacking and agglomeration of graphene during the “wet” process of reduction and drying.

### 3.3 Electrochemical performance

The SnO$_2$@TRG and SnO$_2$@CRG hybrids exhibit distinct microstructures (e.g. pore structure, particle loading state, composite interfacial property and functionalities) for their different origin of fabrication processes (pre-graphenization or post-graphenization). It would be interesting and meaningful to correlate these structural differences with their electrochemical performance as energy storage materials. Thus, SnO$_2$@TRG and SnO$_2$@CRG, with the bare sample TRG and CRG as references, are fabricated and evaluated as electrodes for supercapacitors and Li-ion batteries, respectively.
the scan rate increases, the value of CRG drops very fast with samples at different scan rates from 3.0 to 500 mV s\(^{-1}\).

The inner surface of CRG, which greatly contribute to the BET accessible to the electrolyte. Conversely, the inner surface of TRG is endowed with the active surface areas which are highly exposed to the electrolyte due to the open structure of TRG with numerous large pores could serve as the buffer pool to the electrolyte, thus providing a convenient path for ion diffusion between the graphene sheets and electrolyte. Therefore, the TRG electrode exhibits a relatively quicker response in charge/discharge cycling than CRG constructed by over compacted graphene sheets.

The TRG and CRG, after introduction of SnO\(_2\) nano-particles to form the hybrids of SnO\(_2\)@TRG and SnO\(_2\)@CRG, behave quite differently as supercapacitor electrodes. As shown in Fig. 6d, both the initial \(C_T\) at 3 mV s\(^{-1}\) and the capacitance retention at higher scan rates of SnO\(_2\)@CRG are improved significantly. However, the supercapacitor performance of the SnO\(_2\)@TRG electrode is not enhanced as expected, but rather decreased compared with the bare TRG. As a result, the SnO\(_2\)@CRG exhibits the highest \(C_T\) as a supercapacitor electrode among all the samples, with an initial \(C_T\) approaching 189.4 F g\(^{-1}\) and retention of 33.7% at 3.0 mV s\(^{-1}\). The controversial effects of SnO\(_2\) hybridization on supercapacitor performance are primarily dependent on the pre- or post-graphenization strategy induced structural difference of the resulting materials.

The GC curves at the current density of 1.0 A g\(^{-1}\) are shown in Fig. 7a. All samples exhibit the typical symmetrical charge–discharge patterns of a supercapacitor. In accordance with the capacitances calculated from CV curves, the SnO\(_2\)@CRG has the best performance on energy storage among the four samples (184.0 F g\(^{-1}\)).

To further confirm the double layer formation of the electrodes, AC impedance spectroscopy is employed to determine the internal components of the devices (Nyquist plots as shown in Fig. 7b). An equivalent circuit model (inset of Fig. 7b) is introduced to simulate the capacitive and resistive elements of the cells under analysis. These elements include the internal resistance of the graphene-based electrode \(R_i\), the capacitance and resistance due to contact interface \(C_{iR}\) and \(R_j\), a Warburg diffusion element attributable to the ion migration through the graphene \(C_W\), and the capacitance inside the pores \(C_p\). The fitting results are shown in Table 2.

In accordance with the synthesis strategy induced structural difference, the as-received SnO\(_2\)@graphene hybrids by either pre-graphenization or post-graphenization exhibit a decrease in internal resistance \(R_i\) due to the increase of charge carrier density in graphene lattice from the electron donor-SnO\(_2\) nanoparticles. As a result, SnO\(_2\)@CRG has the minimum \(R_i\) (0.51 Ω) among the four samples. However, the ion diffusion behavior shows distinct tendency upon SnO\(_2\) decoration by two different graphenization strategies. Compared with TRG (0.71 Ω), the Warburg diffusion resistance of SnO\(_2\)@TRG is increased to 2.48 Ω.

3.3.1 Supercapacitor. Cyclic voltammetry, electrochemical impedance spectrum, and galvanostatic charge/discharge (GC) techniques are employed to characterize the supercapacitor performance. As shown in Fig. 6a, at a very low scan rate of 3.0 mV s\(^{-1}\), the CV curve of each sample indicates a typical electric double-layer capacitor (EDLC) character. Among them, SnO\(_2\)@CRG exhibits a more prominent Faradic redox reaction behavior with relatively lower resistance. Fig. 6c shows the CV characteristics of SnO\(_2\)@CRG at different scanning rates, which maintain an EDLC behavior at the higher scan rates of over 200 mV s\(^{-1}\). The gravimetric capacitance \(C_F\) of each electrode at various scan rates is calculated from CV curves and presented in Fig. 6b, while the initial \(C_T\) and associated specific capacitance \(C_F\) at 3 mV s\(^{-1}\) is shown in Fig. 6d. It is found that the bare samples TRG and CRG exhibit quite a similar capacitance (162.1 F g\(^{-1}\) and 169.3 F g\(^{-1}\)).

However, as the scan rate increases, the value of CRG drops very fast with a final retention of 22.6% at 500 mV s\(^{-1}\), which is significantly lower compared with TRG (35.1% at 500 mV s\(^{-1}\)). This phenomenon is in accordance with microstructure and pore structure of thermal/chemical reduced graphene. On one hand, with the exterior porous structure of the assembly and residual surface oxygen functionalities on each basic building block, TRG is endowed with the active surface areas which are highly accessible to the electrolyte. Conversely, the inner surface of ink-bottle pores in CRG, which greatly contribute to the BET surface area, is very difficult to be wetted by the electrolyte. Therefore, though the BET area of TRG (293 m\(^2\) g\(^{-1}\)) is significantly smaller than that of CRG (666 m\(^2\) g\(^{-1}\)), the specific capacitance per BET area \(C_F\) of TRG (0.55 F m\(^{-2}\)) is remarkably higher than that of CRG (0.25 F m\(^{-2}\)).

On the other hand, the “open” structure of TRG with numerous large pores could serve as the buffer pool to the electrolyte, thus providing...
Table 2 Summary of internal components in electrodes

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_i$ (Ohm)</th>
<th>$R_e$ (Ohm)</th>
<th>$C_p$ (F g$^{-1}$)</th>
<th>$W$ (Ohm s$^{1/2}$)</th>
<th>$C_d$ (F g$^{-1}$)</th>
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<td>TRG</td>
<td>1.65</td>
<td>0.40</td>
<td>0.27</td>
<td>0.71</td>
<td>170.51</td>
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<td>CRG</td>
<td>1.50</td>
<td>0.36</td>
<td>0.12</td>
<td>0.45</td>
<td>226.07</td>
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<tr>
<td>SnO$_2$@CRG</td>
<td>0.51</td>
<td>0.36</td>
<td>0.09</td>
<td>0.36</td>
<td>232.53</td>
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</tbody>
</table>

0.74 Ω s$^{-1/2}$, which is ascribed to the collapse of some honeycomb-like structures during the impregnation and drying process. Conversely, the value for SnO$_2$@CRG (0.36 Ω s$^{-1/2}$) is smaller than that of CRG (0.45 Ω s$^{-1/2}$), which is attributed to the prominent “spacer” effect of SnO$_2$ nano-particles. Thereafter, from a viewpoint of thermodynamics, the mass transfer within the electro-chemical system is significantly promoted through: (i) improvement of charge transfer along the graphene lattice and between graphene by π–π interactions of delocalized electrons arising from both graphitic domains and SnO$_2$ electron donors; and (ii) optimization of the porous structure by preventing the re-stacking of graphene so as to offer a low resistance channel for ion diffusion. Thus, the PC-active SnO$_2$ species combining with the graphene surface inside the pores of SnO$_2$@CRG are highly accessible to the ions of electrolyte, so as to give rise to capacitance inside pores with a maximum value of as high as 232.53 F g$^{-1}$ among the four samples.

3.3.2 Li-ion battery. SnO$_2$ shows a high theoretical capacity of Li$^+$ intercalations–deintercalations (790 mA h g$^{-1}$), which makes it a promising anode material for Li-ion batteries. Fig. 8 shows the representative CVs of the sample. Specifically, two pairs of redox current peaks can be clearly observed. The first dominant pair (cathodic, anodic) shown at the potential ($V$) of (0.01, 0.7) can be attributed to the alloying (cathodic scan) and dealloying (anodic scan) processes. The first pair is much more pronounced than the second pair, marking its major contribution to the total capacity of the cell. The intensity of this pair of SnO$_2$@TRG is much higher than that of SnO$_2$@CRG, which is attributed to its loading amount of SnO$_2$ as shown in Table 1.

The cycling performances of SnO$_2$@TRG and SnO$_2$@CRG are demonstrated in Fig. 9. The discharge capacities in the 1st cycle are 1468 mA h g$^{-1}$ for SnO$_2$@TRG, and 978 mA h g$^{-1}$ for SnO$_2$@CRG. The formation of solid electrolyte interface (SEI) is the main reason that caused the large capacity and also the irreversible capacity loss. For the 2nd cycle, the discharge capacities are 857 mA h g$^{-1}$ for SnO$_2$@TRG, and 375 mA h g$^{-1}$ for SnO$_2$@CRG. The discharge capacities in the 6th cycle are 707 mA h g$^{-1}$ for SnO$_2$@TRG with a coulombic efficiency of 90%, and 366 mA h g$^{-1}$ for SnO$_2$@CRG with a coulombic efficiency of 94%. With higher current density during the galvanostatic discharge (Li insertion, voltage decreases)/charge (Li extraction, voltage increases) process, the discharge capacity further decreased. The discharge capacities in the 7th cycle (current density at 400 mA g$^{-1}$) are 580 mA h g$^{-1}$ for SnO$_2$@TRG, and 366 mA h g$^{-1}$ for SnO$_2$@CRG. Further increase of charge and discharge current to 800 mA g$^{-1}$ caused the drop of capacity of SnO$_2$@TRG and SnO$_2$@CRG to 286 and 206 mA h g$^{-1}$, respectively. Upon returning back to a low current density of 100 mA g$^{-1}$, the discharge capacities for SnO$_2$@TRG and SnO$_2$@CRG recovered to 540 and 271 mA h g$^{-1}$ at the 17th cycle. Comparing the performance of TRG and CRG (Fig. S1†), the addition of SnO$_2$ acted as spacer for the CRG sample, but a filler in the TGR pores. The graphene electrode afforded the main characteristics of Li storage for the current hybrid electrode. Compared with the CRG electrode, improved Li storage performance for SnO$_2$@CRG was presented; while the discharging capacity of SnO$_2$@TRG was not as high as that of pure TRG anode materials.

The cycling performances of SnO$_2$@graphene composite and pure graphene anode materials are presented in Fig. 10 and S2†, respectively. With a charge/discharge current density at 400 mA g$^{-1}$, SnO$_2$@TRG and SnO$_2$@CRG composites show discharge capacities of 204 and 196 mA h g$^{-1}$ even after 100 cycles (Fig. 10). A rapid capacity loss can be observed during the initial three cycles for SnO$_2$@CRG and CRG. In contrast, a gradual loss occurred on SnO$_2$@TRG and TRG. The higher initial discharge capacity of the SnO$_2$@TRG composite can be attributed to its loading amount of SnO$_2$ as shown in Table 1.
However, because of the unstable porous structure and complex surface chemistry, the high capacity of both SnO$_2$@TRG and TRG is not well maintained. This indicated that pre-graphenization provides huge surface area for more metal oxide anchoring, while such a porous TRG is not very stable. In contrast, the post-graphenization process provides more anchoring sites for the formation of a large number of small SnO$_2$ particles, and the as-obtained SnO$_2$@CRG shows a more stable behavior as an anode material.

4. Conclusions

To clarify the effect of pre- or post-graphenization for graphene-based hybrids, two kinds of SnO$_2$@graphene hybrids are explored with the same GO and Sn precursors. For the pre-graphenization strategy: the thermally reduced graphene is obtained before the second component (SnO$_2$) is introduced; for the post-graphenization strategy: a composite composed of graphene oxide and the second component (SnO$_2$) is pre-prepared, followed by converting the precursor into chemically reduced graphene. The SnO$_2$ nanoparticles with a loading of 6.3 wt% are distributed on porous TRG, while a loading of 3.3 wt% was determined on compacted CRG. When the SnO$_2$@graphene is used as a supercapacitor electrode, the SnO$_2$@CRG exhibits the highest $C_F$ as a supercapacitor electrode among all the samples with an initial $C_F$ approaching 189.4 F g$^{-1}$ and retention of 33.7% at 3.0 mV s$^{-1}$. The gravimetric capacitance of CRG drops very fast with a final retention of 22.6% at 500 mV s$^{-1}$, which is significantly lower compared with TRG (35.1% at 500 mV s$^{-1}$). When they are employed as Li-ion battery electrodes, the discharge capacities in the 1$^{st}$ cycle are 1468 and 978 mA h g$^{-1}$ for SnO$_2$@TRG and SnO$_2$@CRG, respectively. With higher current density during the galvanostatic discharge (Li insertion, voltage decreases)/charge (Li extraction, voltage increases) process, the discharge capacities of both SnO$_2$@TRG and SnO$_2$@CRG decreased gradually. Even after 100 cycles at 400 mA g$^{-1}$, a discharging capacity of 204 and 196 mA h g$^{-1}$ can still be retained for SnO$_2$@TRG and SnO$_2$@CRG, respectively. This suggested that the method of graphenization provides the hybrid with different structure and electrochemical performance. The pre-graphenization process provides a large amount of pores for ion diffusion, which is of benefit for loading of SnO$_2$, fast ion diffusion for supercapacitors, and higher capacity for Li-ion batteries, but poor stability, while the post-graphenization process offers compact graphene and good interaction between the SnO$_2$ and graphene, which provides stable structure for long term stability for supercapacitor and Li-ion battery use. The optimized graphenization method for graphene hybrids should be further explored to provide new insights into hybrid formation and advanced materials for energy storage.

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Notes and references