

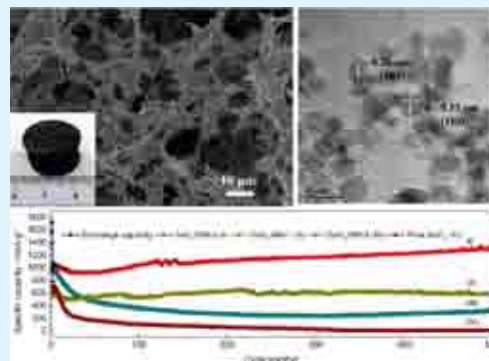
Solvothermal-Induced 3D Macroscopic SnO₂/Nitrogen-Doped Graphene Aerogels for High Capacity and Long-Life Lithium Storage

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Supporting Information

ABSTRACT: 3D macroscopic tin oxide/nitrogen-doped graphene frameworks (SnO₂/GN) were constructed by a novel solvothermal-induced self-assembly process, using SnO₂ colloid as precursor (crystal size of 3–7 nm). Solvothermal treatment played a key role as N,N-dimethylmethanamide (DMF) acted both as reducing reagent and nitrogen source, requiring no additional nitrogen-containing precursors or post-treatment. The SnO₂/GN exhibited a 3D hierarchical porous architecture with a large surface area (336 m²g⁻¹), which not only effectively prevented the agglomeration of SnO₂ but also facilitated fast ion and electron transport through 3D pathways. As a result, the optimized electrode with GN content of 44.23% exhibited superior rate capability (1126, 855, and 614 mAh g⁻¹ at 1000, 3000, and 6000 mA g⁻¹, respectively) and extraordinary prolonged cycling stability at high current densities (905 mAh g⁻¹ after 1000 cycles at 2000 mA g⁻¹). Electrochemical impedance spectroscopy (EIS) and morphological study demonstrated the enhanced electrochemical reactivity and good structural stability of the electrode.



KEYWORDS: tin oxide, solvothermal, nitrogen doping, graphene, aerogels, lithium ion batteries

INTRODUCTION

Lithium ion batteries (LIBs) are currently the dominant power source for portable electronic devices and viewed as the most promising candidate to electrical/hybrid vehicles.^{1,2} In order to store and transport energy more efficiently, many efforts have been devoted to explore various high-energy anode materials, such as SnO₂,^{3,4} Fe₂O₃,⁵ and Co₃O₄,⁶ for the next generation of rechargeable LIBs. However, the practical use of these materials is greatly hampered by the poor cycling performance arising from their low electronic conductivity, severe aggregation, and huge volume changes upon extended Li insertion/extraction. To address these problems, fabricating carbonaceous nanocomposites, especially graphene-based hybrid anodes, was proved to be an effective strategy.^{7–10} Graphene, with high conductivity and large specific surface area, can serve as an intriguing substrate to disperse electrochemically active materials, thus improving electrical conductivity and structural integrity of the electrode. To date, various graphene-based hybrid anodes have been developed. Although improved electrochemical performances have been achieved, some disadvantages for lithium storage still exist in these hybrids. For example, most of the previous works were focused on preparation of two-dimensional (2D) graphene-based composites in which nanoparticles anchored on the surface of graphene sheets (GS). In most cases, the 2D GS would easily reaggregate or restack during drying due to the van der Waals forces, which significantly reduced the accessible surface area and limited electron and ion transport.^{2,11,12} Furthermore, GS

usually possess a limited number of reactive sites, which result in a low specific capacity, large irreversible capacity, and fast capacity fade.^{13–15} Therefore, it is still a big challenge to further optimize their electrochemical performance.

To overcome these issues, it is believed that two strategies are feasible. The first one is to assemble 2D GS into macroscopic 3D architectures, which can effectively prevent restacking of graphene, providing resultant graphene-based composites with large specific surface area, porous structure, and fast electron transport kinetics due to the continuous graphene backbone.^{16–19} For example, Chen et al.²⁰ pioneered the capture of preprepared Fe₃O₄ into 3D graphene network under mild conditions (oil bath at 95 °C) with the aid of reducing agents (NaHSO₃). As claimed, the composite delivered a high capacity of 730 mAh g⁻¹ even at a current density of 1600 mA g⁻¹. Similarly, Cong et al. developed α -FeOOH/GS and magnetic Fe₃O₄/GS hydrogels under the synergistic effects of the reduction of GO by ferrous ions and in situ simultaneous deposition of nanoparticles on GS.²¹ Besides, MoS₂/GS,^{18,22} Fe₂O₃/GS,^{16,23} and TiO₂/GS²⁴ aerogels that were constructed by a hydrothermal method also demonstrated the effectiveness of macroscopic 3D architectures to the final lithium storage properties.

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Apart from the geometrical control, chemical doping, especially nitrogen-doping of GS, was another effective way to improve lithium storage performance.^{14,15,25–27} This is because nitrogen doping can modulate the electronic structure of graphene, create defects to decrease the energy barrier of lithium penetration, and enhance reactive sites.^{28,29} Very recently, a variety of transition metal oxides (e.g., TiO₂,^{30,31} MnO,³² Co₃O₄,³³ SnO₂,^{28,34,35} Fe₂O₃²⁹) composited with nitrogen-doped graphene (GN) have been designed as electrodes for LIBs. These hybrids exhibited significantly higher specific capacity than that of the metal oxide/GS counterpart. In this literature, either nitrogen-containing precursors (polypyrrole,²⁸ urea,^{35,36} ammonia,³³ N₂H₄³¹) have to be added during the compositing process or additional post-treatment (N₂H₄ vapor treatment,³⁴ annealing in NH₃ atmosphere^{30,32}) needs to be carried out for nitrogen-doping. For the former, the toxicity of the nitrogen source (N₂H₄, NH₃) should be considered, and the later often required rigorous conditions or special instruments. Therefore, it is still a challenge to prepare GN by a facile method. Considering that both nitrogen-doping of GS and 3D macroscopic frameworks can greatly improve lithium storage properties, it is highly demanded to develop graphene-based composites that combine the two characteristics together. However, to the best of our knowledge, little research has been done on this aspect.

In this study, we successfully constructed 3D macroscopic SnO₂/GN aerogels, comprising self-assembled nitrogen-doped graphene networks and ultrasmall SnO₂ nanocrystals (3–7 nm), via a novel solvothermal-induced self-assembly process using SnO₂ colloid sol as precursor. SnO₂ was selected as the research object because of its abundance and high theoretical capacity (782 mAh g⁻¹ based on conventional alloying mechanism, 1494 mAh g⁻¹ assuming that all Sn was oxidized to Sn⁴⁺).^{37,38} Here, solvothermal treatment played a key role as DMF acted both as reducing reagents and nitrogen sources, requiring no additional nitrogen-containing precursors or any post-treatment. The resulting macroscopic SnO₂/GN aerogels simultaneously possess high surface area (336 m² g⁻¹), hierarchical porous structure, and high electrical conductivity. Such unique features can facilitate the ultrafast diffusion of lithium ions/electrons within the electrode and, simultaneously, accommodate the volume change of SnO₂ during cycling. Moreover, nitrogen-doping of GS can modulate the electronic structure of graphene and further enhance the lithium storage properties. Benefitting from the combined N-doped property and 3D graphene frameworks, the SnO₂/GN exhibits excellent rate capability (1126, 855, and 614 mAh g⁻¹ at 1000, 3000, and 6000 mA g⁻¹, respectively) and outstanding long-term cyclic stability at high current densities (905 mAh g⁻¹ after 1000 cycles at 2000 mA g⁻¹). Importantly, the work described here can also be extended to prepare various metal oxide/GN aerogels, for the application in a broad range of LIBs, sensors, catalysts, and so on.

EXPERIMENTAL SECTION

Preparation of SnO₂ Nanocrystal Aqueous Dispersion. 1.0 g of SnCl₄·5H₂O was first dissolved in 50 mL of distilled water. The resulting solution was then hydrothermally treated at 120–180 °C for 12–28 h. The obtained white precipitate was washed repeatedly by centrifugation and redispersed in water to form an aqueous dispersion.

Synthesis of SnO₂/GS Hybrid Aerogels. In a typical synthesis, SnO₂ dispersion was added dropwise into graphene oxide (GO) dispersion (2 mg mL⁻¹), followed by ultrasonating for 30 min. The mixed suspension was centrifuged to remove H₂O and redispersed in

40 mL of DMF to form SnO₂/GO dispersion. Subsequently, SnO₂/GO dispersion in DMF was solvothermally treated at 120–200 °C for 6–16 h to reduce GO and induce self-assembly process to obtain a 3D SnO₂/GN monolith. Finally, the monolith was taken out, washed repeatedly with distilled water, and freeze-dried into an aerogel for further use. To obtain the optimal electrochemical performance, the various GN contents of 55.76%, 44.23%, and 18.62% were used. The samples were named as SnO₂/GN-1, SnO₂/GN-2, and SnO₂/GN-3, respectively. Detailed characterization was carried out on the optimized sample SnO₂/GN-2 hereafter.

Electrode Preparation. The electrodes were prepared by mixing 80 wt % active material, 10 wt % conducting carbon black, and 10 wt % polyvinylidene fluoride binder in N-methyl-2-pyrrolidone. The homogeneous slurries were then pasted on copper current collector and dried under vacuum at 110 °C for 12 h.

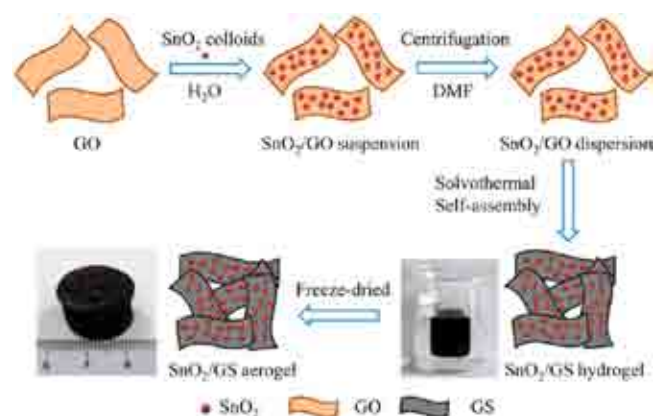
Material Characterization. The morphology of samples was characterized by the transmission electron microscope (JEM-2100F, JEOL, Tokyo, Japan). The field-emission scanning electron microscope (FE-SEM) analysis was performed on JSM-6700F at an acceleration voltage of 10.0 kV. X-ray diffraction (XRD) was carried out on D/max 2550 V X-ray diffraction-meter with Cu-K α irradiation at $\lambda = 1.5406$. Thermal gravimetric analysis (TGA) was conducted in air at a heating rate of 10 °C min⁻¹. X-ray photoelectron spectroscopy (XPS) analysis was conducted using twin anode gun, Mg K α (1253.6 eV) (Microlab 310F Scanning Auger Microprobe, VG SCIENTIFIC LTD). Conductivity was measured by a four-point probe method in the van der Pauw configuration with an Accent HL5500 system. N₂ adsorption/desorption isotherms were determined using a Micromeritics ASAP2010 Analyzer (USA).

Electrochemical Measurements. Cyclic voltammetry (CV) was carried out in a voltage range of 0–3.0 V with a scan rate of 0.5 mV s⁻¹. The electrochemical impedance spectroscopy (EIS) measurements were carried out with a PARSTAT 2273, using a sine wave of 10 mV over a frequency range of 100 kHz–0.1 Hz. The electrochemical properties of the electrodes were characterized at room temperature. Li foil was used as the counter electrode. 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 a glovebox with the concentrations of moisture and oxygen below 1 ppm. The batteries were measured using a CT2001 battery tester.

RESULTS AND DISCUSSION

The SnO₂/GN 3D macroscopic aerogels were fabricated by a solvothermal-induced self-assembly strategy developed in our group and a subsequent freeze-drying process (Scheme 1). Briefly, homogeneous SnO₂ colloids were prepared using a hydrothermal method.³⁹ As is well known from colloidal science,⁴⁰ metal oxide colloid has a tendency to adsorb cations.

Scheme 1. Schematic Illustration of Preparation of SnO₂/GN Aerogels



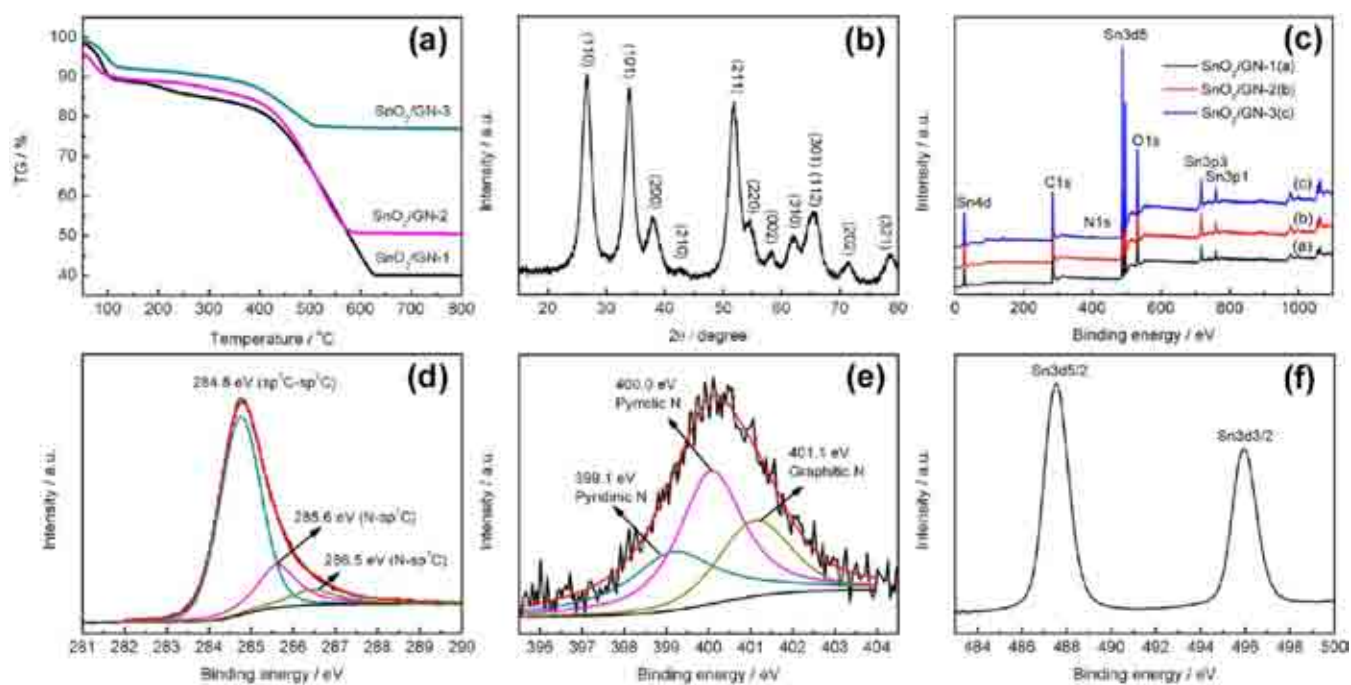


Figure 1. (a) TG curves and (b) XRD patterns of SnO₂/GN; (c) XPS spectra of SnO₂/GN; (d) XPS C1s spectrum of SnO₂/GN-2, which can be split into three peaks at 284.8, 285.8, and 286.5 eV; (e) XPS N1s spectrum of SnO₂/GN-2. The N1s peak can be split into three peaks at 399.1, 400.0, and 401.1 eV; (f) XPS Sn3d spectrum.

Here, the prepared SnO₂ was positively charged with a zeta potential of +34 mV, while GO was negatively charged (zeta potential was -56 mV) due to the presence of oxygen-containing functional groups.⁵ Driven by strong electrostatic attractive interaction, SnO₂ colloidal nanoparticles (see the Supporting Information, Figure S1), with a diameter of 3–7 nm, can uniformly and tightly anchor on the surface of GO when they were mixed together (Figure S2). Noteworthy, even after a long time of sonication, SnO₂ still strongly connected with GO, further demonstrating the strong interaction between them. Subsequently, solvothermal treatment in DMF was employed to induce the self-assembly process and achieve nitrogen-doping of GS, where DMF acted as both reducing reagent and nitrogen sources,^{41,42} requiring no additional nitrogen-containing precursors or any post-treatment. Specifically, GO was deeply reduced to GS with simultaneous incorporation of nitrogen species into the graphene lattice. Meanwhile, GN anchored with SnO₂ nanoparticles acted as a building block and self-assembled into a 3D monolith (Scheme 1) with an interconnected network, driven by π - π stacking interactions due to the decrease of oxygenated groups on graphene.^{21,24} Furthermore, the SnO₂ nanoparticles anchored on GN can serve as the space to effectively avoid aggregation of the GN during reduction process. Finally, the monolith was repeatedly exchanged with distilled water and freeze-dried to obtain aerogels. Notably, the content of SnO₂ in the as-prepared architectures was readily tunable by simply adjusting the ratio of SnO₂ to GO during the synthesis process. As shown in Figure 1a, the weight ratios of GN are 55.76%, 44.23%, and 18.62% for SnO₂/GN-1, SnO₂/GN-2, and SnO₂/GN-3, respectively, by getting rid of the weight loss of adsorption water. Detailed calculation can be found in Figure S3. The conductivity of SnO₂/GN-2 was measured to be 97 S m⁻¹. It means GN can serve as an efficient electrically conducting network for fast electronic transport, which will result in high

powder density of the electrode. XRD revealed that the peaks of SnO₂ in SnO₂/GN can be well indentified as a tetragonal rutile-like SnO₂ (Figure 1b, JCPDF 41-1445).

To confirm N-doping of graphene, X-ray photoemission spectroscopy (XPS) studies were carried out. The survey scan spectrum from XPS analysis showed the sample contained C, O, N, and Sn elements (Figure 1c). The atomic percentages of doped nitrogen in GN are 2.17%, 2.25%, and 2.22% for SnO₂/GN-1, SnO₂/GN-2, and SnO₂/GN-3, respectively. The C1s core level peak of SnO₂/GN-2 can be resolved into three components centered at 284.8, 285.6, and 286.5 eV, assigned to sp²C-sp²C, N-sp²C, and N-sp³C bonds,^{7,43} respectively (Figure 1d). Similarly, the N1s peak can also be resolved into three components centered at 399.1, 400.0, and 401.1 eV, representing pyridinic, pyrrolic, and graphitic type of N atoms doped in the graphene structure^{7,29} (Figure 1e). Nitrogen doping can introduce a large number of surface defects into graphene, which leads to the formation of a disordered carbon structure that enhances Li intercalation properties.^{32,43} Additionally, theoretical studies illustrated that the pyridinic N in carbon materials could apparently reduce the energy barrier for Li penetrating (about 1.44 eV, much lower than that of 10.5 eV for perfect GS).^{35,43,44} Since lithium storage is also a kinetic process, the existence of vacancies and electron deficiencies in pyridinic N will provide a feasible pathway for Li penetration into graphene layers, thus also contributing to the improvement of reversible capacity. In addition, the Sn3d_{5/2} (487.2 eV) and Sn3d_{3/2} (495.6 eV) peaks found in the XPS data (Figure 1f) further confirm the formation of SnO₂.

The morphology and structure of the resultant SnO₂/GN were characterized by FE-SEM and TEM (Figure 2). SEM images showed an interconnected, porous 3D graphene framework with continuous macropores in the micrometer size range (Figure 2a and b). Closer observation discloses that

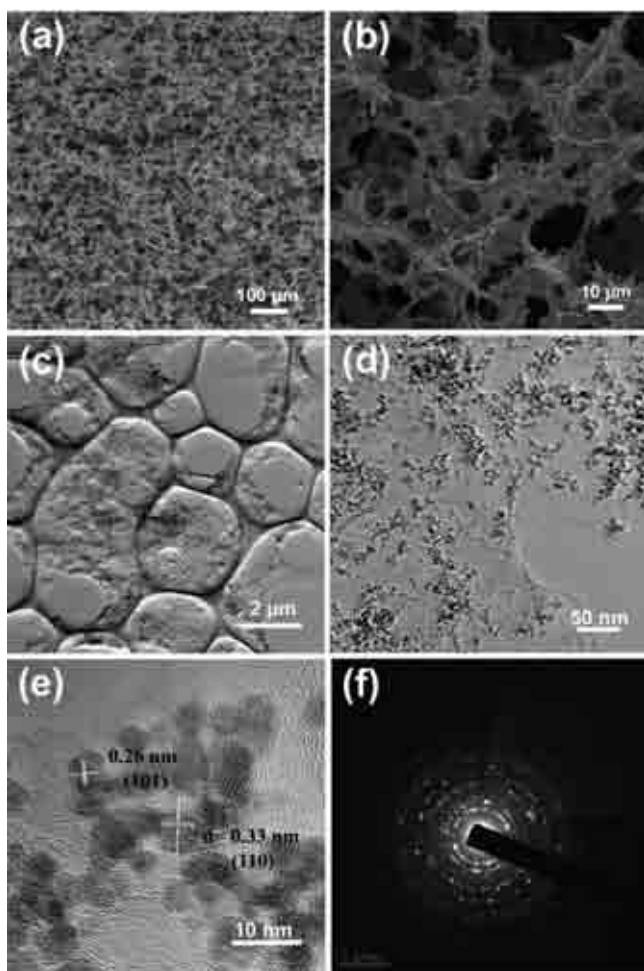


Figure 2. The morphology and nanostructure of the resultant SnO₂/GN-2: (a–b) SEM images, (c–d) TEM images, (e) HRTEM image, and (f) the corresponding SAED patterns.

SnO₂ nanoparticles, with a particle size of 3–7 nm, were homogeneously dispersed within the hybrid (Figure S4). The chemical composition was verified by energy dispersive spectroscopy (EDS) where elements Sn, O, and C were detected (Figure S5). A low-magnified TEM image of SnO₂/GN (Figure 2c) showed that the size of GN was about several micrometers, while the high-magnified TEM image further demonstrated that SnO₂ nanocrystals were homogeneously distributed on the surface of GN (Figure 2d), consistent well

with SEM images. The HRTEM image displayed that SnO₂ was highly crystalline with crystal lattice fringes of 0.33 and 0.26 nm (Figure 2e), corresponding to the (110) and (101) face of SnO₂, respectively. The corresponding selected area electron diffraction (SAED) pattern further demonstrated the high-quality single-crystalline nature of SnO₂.

The porous nature of SnO₂/GN-2 architecture was demonstrated by BET measurement (Figure 3). The adsorption-desorption isotherms exhibited a typical IV hysteresis loop at a relative pressure between 0.4 and 0.8, characteristic of pores with different pore sizes (Figure 3a). Remarkably, the specific surface area of SnO₂/GN-2 reached up to 336 m² g⁻¹, which was much higher than that of pure SnO₂ (176 m² g⁻¹). This result highlighted that the building up of 3D frameworks by solvothermal assembly was an effective way to achieve a high surface area for hybrid materials.^{16,22} BJH calculations disclosed the pore volume was 0.234 cm³ g⁻¹ with an average pore diameter of 3.7 nm (the inset in Figure 3a). The high porosity can provide not only more surface reaction sites but also sufficient buffer space to alleviate the volume expansion of SnO₂ during lithiation and delithiation and is therefore favorable for the electrochemical properties.^{2,25}

Coin cells with metallic Li counter electrode were assembled to evaluate the electrochemical performance of the electrode. Figure 4a exhibited the CV curves for the first five cycles of the SnO₂/GN-2 electrode. In the first cathodic scan, there are four reduction peaks at 1.27 V, 0.85 V, ~0.6 V, and ~0.1 V, respectively. The two at 1.27 and 0.85 V should be attributed to the reduction of SnO₂ to SnO (eq 1), the conversion of SnO to Sn (eq 2), respectively, accompanying with the formation of Li₂O.⁴⁵ The shoulder peak at ~0.6 V can be ascribed to the decomposition of the electrolyte on the surface of SnO₂ and GN, leading to the formation of the solid-electrolyte-interphase (SEI).³⁴ The fourth reduction peak around 0.1 V reflects Li–Sn alloying (eq 3) and the intercalation of lithium ion into GN (eq 4).^{45,46} In the first anodic process, the oxidation peak at 0.58 V was related to the dealloying of Li_xSn (eq 3). While another peak at 1.29 V was ascribed to partial transformation of Sn and Li₂O to SnO₂.^{34,38,47,48} This indicated that the commonly regarded irreversible conversion reaction, SnO₂ + 4Li⁺ + 4e⁻ → 2Li₂O + Sn, was partial reversible in SnO₂/GN composite (eqs 1 and 2). It was well known that the required activation energy for oxidation and solid-state double decomposition reactions decreased with decreasing particle size.^{37,49} Here, the reversible conversion reaction of SnO₂ may be due to the ultrasmall size of SnO₂.⁵⁰ In the subsequent cycles, the CV curves were almost

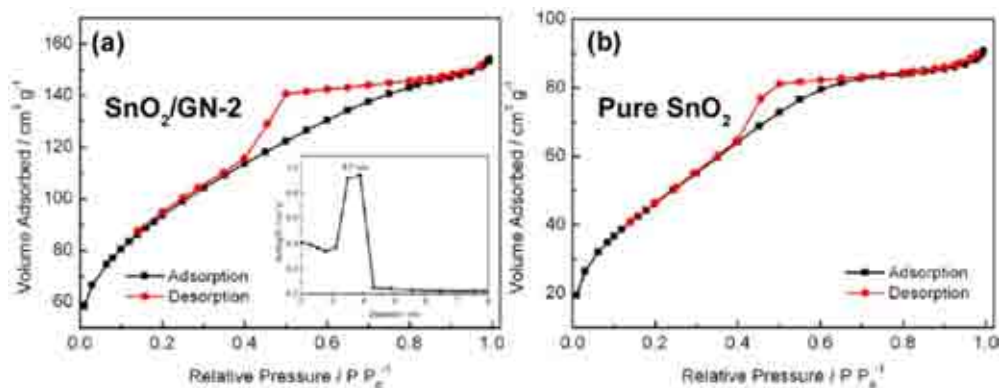


Figure 3. Nitrogen adsorption and desorption isotherms of SnO₂/GN-2 (a) and pure SnO₂ (b).

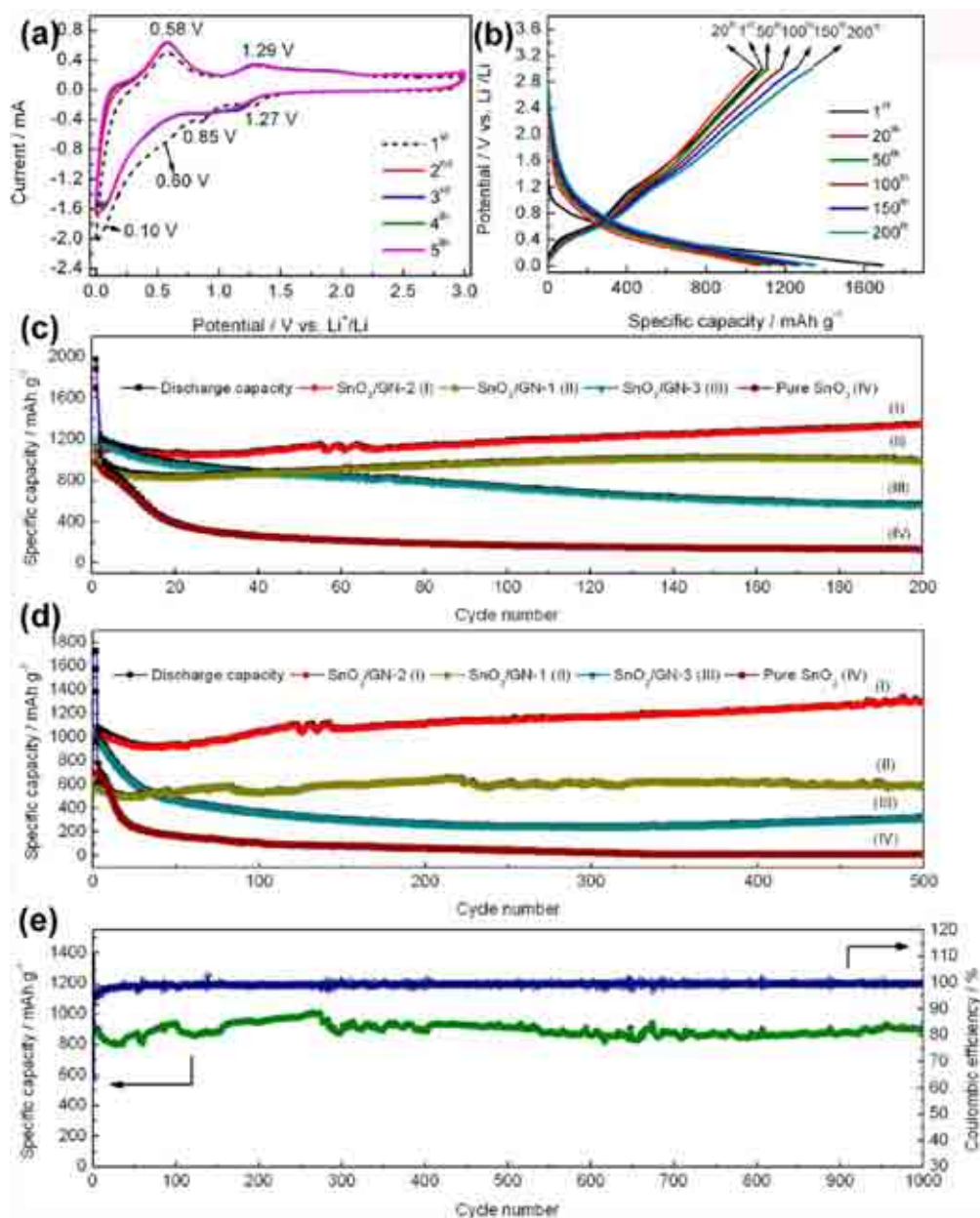


Figure 4. (a) Cyclic voltammograms for the first five cycles of SnO₂/GN-2 electrode; (b) charge-discharge profiles of SnO₂/GN-2 electrode at a current density of 500 mA g⁻¹; (c and d) comparative cycle performance of different electrodes at a current density of 500 and 1000 mA g⁻¹, respectively; (e) cycle performance of SnO₂/GN-2 electrode at a current density of 2000 mA g⁻¹. The capacity is based on the weight of the whole composite.

overlapped, implying an excellent reversibility of lithium insertion and extraction reactions. The whole process can be expressed as

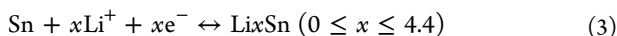
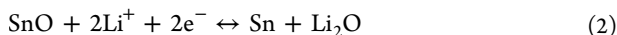
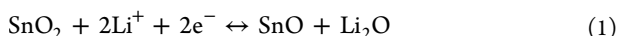


Figure 4b showed the representative charge/discharge curves of SnO₂/GN-2 at a current density of 500 mA g⁻¹ between 0.01–3.0 V vs Li⁺/Li. A voltage plateau ranging from 0.6 to 1.4 V was observed at the discharge step, while two plateaus at

~0.6 and 1.3 V existed in the charge curves. The charge/discharge curves were in good accordance with the CV profiles. The initial discharge and charge capacity were 1693 and 1083 mAh g⁻¹ (based on the total mass of SnO₂/GN hybrid material), respectively, corresponding to a coulombic efficiency (CE) of 64.0%. This performance is close to the theoretical capacity of SnO₂/GN-2^{51,52,34,53} ($C_{\text{theo.}} = C_{\text{SnO}_2,\text{theo.}} \times \%_{\text{SnO}_2} + C_{\text{GS,theo.}} \times \%_{\text{GS}} = 1494 \times 0.5577 + 774 \times 0.4423 = 1175.5 \text{ mAh g}^{-1}$). The ultrasmall size of SnO₂ nanocrystals, unique 3D porous architectures coupled with nitrogen-doping of graphene should contribute mostly to such high capacities. Specifically, on one hand, the SnO₂ in the GN matrix had a fine particle size (3–7 nm) and multiple electrical contacts with the carbon matrix, which endow the electrode superior electrochemical activities and large electrochemical interface lithium storage. On

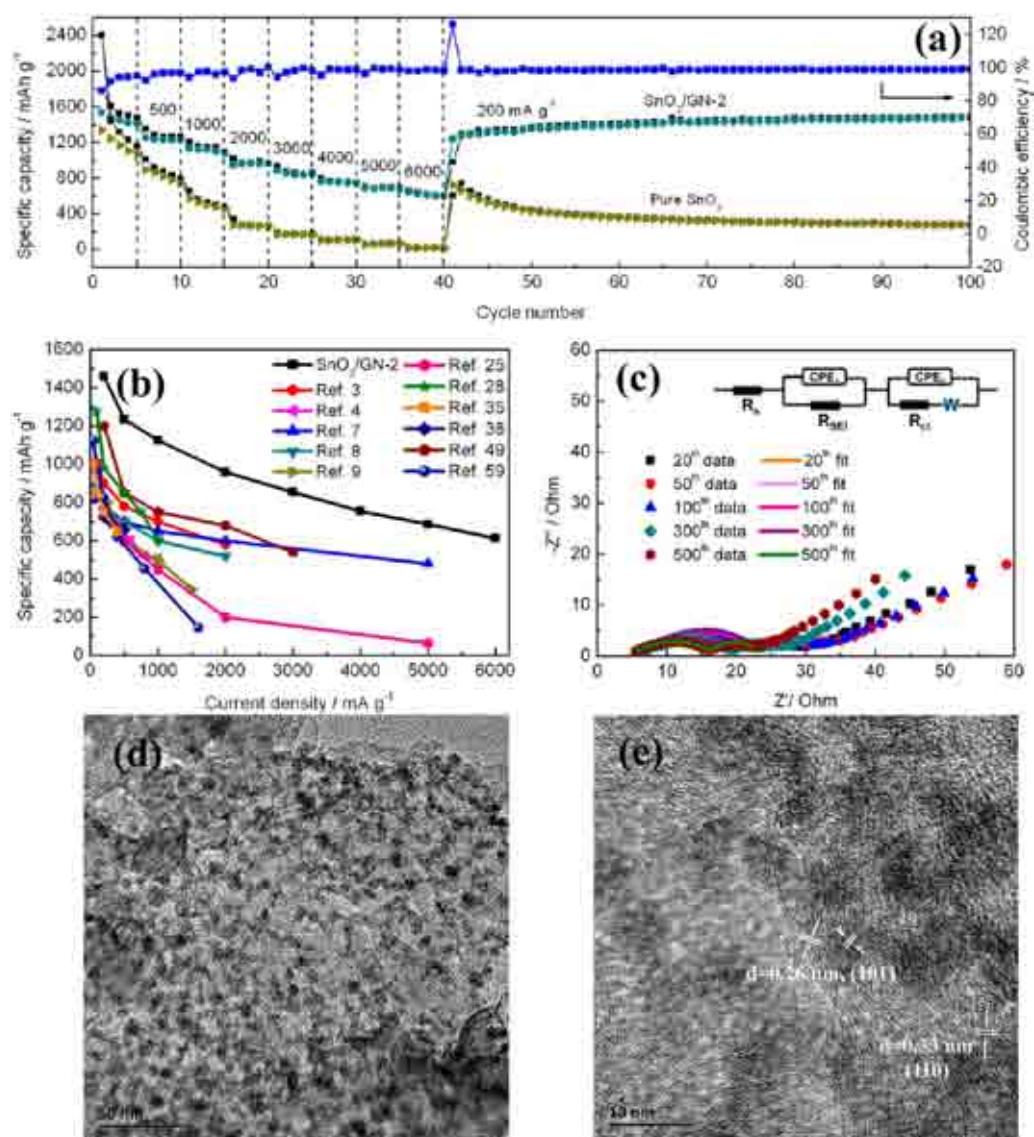


Figure 5. (a) The rate capability of SnO₂/GN-2 and pure SnO₂ electrode at different current densities (200–6000 mA g⁻¹); (b) Comparison of capacity at different current densities for SnO₂/GN-2 electrodes with those of reported SnO₂-based hybrid anodes; (c) Nyquist plots SnO₂/GN-2 after specific cycles. The inset in (c) represents the equivalent circuit model of the electrode. CPE is the constant phase element; (d and e) TEM and HRTEM images of SnO₂/GN-2 after cycling at 500 mA g⁻¹.

the other hand, the unique 3D porous architectures can facilitate fast ion and electron transport through 3D pathways and provide the electrode with abundant reactive sites.⁵⁴ Thirdly, graphene, especially nitrogen-doped graphene, with rich of sides and defects, can also greatly enhance the lithium storage capacity. Subsequently, the charge capacity slightly decreased during 20 cycles (1050 mA h g⁻¹) and then gradually increased in the following cycles and reached up to 1340 mA h g⁻¹ after 200 cycles (capacity retention of 134%). The higher performance of SnO₂/GN-2 than that of theoretical capacity can be attributed to the very small size with large electrochemical interface lithium storage,^{55,56} superior electrochemical activities, and also partial reversible reaction of the SEI.¹⁹ Similar phenomenon, that capacity decreased to some extent then gradually increased, has been commonly observed in metal oxide/carbon composites.^{2,37,49,57} Closer observation showed that the differences among the charge curves of different cycles mainly happened above 1.0 V (the oxidation of Sn). The slight decay of capacity during the first 20 cycles could be due to the

partial pulverization of original SnO₂ and in situ formed Sn. As demonstrated in previous reports, the particle size of SnO₂ and Sn will become smaller than original ones due to electrochemical milling effect after continuous cycling.^{37,53,58,59} Therefore, the reactivity of oxidation of Sn to SnO₂ will be enhanced due to the decreased particle size, which may result in the gradual increase in capacity after 20 cycles.

To understand the effect of the SnO₂/GN ratio on electrochemical performance, composites with different relative content of SnO₂ and GN were prepared (Figure 4c). The GN contents were 55.76%, 44.23%, and 18.62% for SnO₂/GN-1, SnO₂/GN-2, and SnO₂/GN-3 as determined by TG, respectively. For pure SnO₂, the capacity decayed severely and retained only 136 mA h g⁻¹ after 200 cycles, with the capacity retention of 14%. It should be pointed that although conversion reaction was also partially reversible during the first several cycles, the plateau above 1.0 V completely disappeared after 15 cycles (Figure S6). This may due to the high volume variation of Sn (>300%) and severe agglomeration, which leads

to the cracking and pulverization of the electrode, as well as a loss of electrical contact between active Sn and conductive additives or current collector.^{3,39} For SnO₂/GN-3, with the lowest amount of GN, serious capacity loss also occurred during cycling and retained only ~566 mAh g⁻¹ after 200 cycles. This is because such low content of GN was inadequate to well disperse SnO₂ nanocrystals, which would also result in pulverization and rapid capacity fading.² On the other hand, the lower conductivity may be another reason for the capacity decrease. In the case of SnO₂/GN-2, SnO₂ was tightly attached to GN and spatially separated, which helped to accommodate the volume change and prevent aggregation. Therefore, the specific capacity is the highest and cycling performance is much better than that of SnO₂/GN-3. Further increasing the content of GN in the hybrid (SnO₂/GN-1), although good cycling stability was also achieved (~100% capacity retention), the capacity (998 mAh g⁻¹) was much lower than that of SnO₂/GN-2. Here, SnO₂/GN-2 represented the highest specific capacity and the best cycling stability.

To further demonstrate the extraordinary cyclic stability of SnO₂/GN-2, the electrode was tested at a higher current density of 1000 mA g⁻¹ with a larger numbers of cycles (Figure 4d). Similarly, SnO₂/GN-2 exhibited the best cyclic performance: a capacity as high as 1305 mAh g⁻¹ was delivered after 500 cycles with a capacity retention of 136.7%. Even at an ultrahigh current density of 2000 mA g⁻¹, SnO₂/GN-2 still possessed a capacity up to 905 mAh g⁻¹ after 1000 cycles with a capacity retention of 102%, demonstrating an excellent prolonged cycling stability. Additionally, the average coulombic efficiency achieved nearly ~100% from the second cycle, indicating stabilization of SEI.^{1,6} Recently, Xu et al. reported a specific capacity of 1182 mAh g⁻¹ at a current density of 100 mA g⁻¹ for SnO₂ nanorods dispersed GN, which decreased to 803 mAh g⁻¹ after 100 cycles.³⁵ Wang et al. showed a specific capacity of 910 mAh g⁻¹ at 50 mA g⁻¹ for GN-SnO₂ sandwich paper.⁷ In another report, Ramaprabhu and co-workers synthesized SnO₂ nanoparticles dispersed GN, which delivered a capacity of 793 mAh g⁻¹ after 100 cycles at 90 mA g⁻¹.²⁸ Thus, the present SnO₂/GN aerogel exhibited a higher capacity and superior cyclic stability as compared to previously reported SnO₂/GN composites.

Besides high capacity and excellent cycling stability, SnO₂/GN also displayed superior rate capability. As shown in Figure 5a, the hybrid electrode delivered very high capacities of 1460, 1235, 1126, and 960 mAh g⁻¹ at 200, 500, 1000, and 2000 mA g⁻¹, respectively. Even at ultrahigh current density of 3000, 4000, 5000, and 6000 mA g⁻¹, the electrode still retained capacities up to 855, 755, 686, and 614 mAh g⁻¹, respectively. This rate performance was quite remarkable in that the capacity of 616 mAh g⁻¹ was achieved within ~6.0 min of charging or discharging time. Remarkably, the charge/discharge curves still maintained a kinetic feature at high current densities, indicating a facile charge transport process¹ (Figure S7). Noteworthy, few of the previously reported work have reported the rate performance under high current density of 6000 mA g⁻¹. Figure 5b reveals that the rate capability of SnO₂/GN-2 is higher than most of the reported SnO₂-based hybrid electrodes [SnO₂/GS (refs 3 and 8); SnO₂/GN (refs 7, 28, and 35); SnO₂/GS aerogel (ref 38); SnO₂@carbon (refs 4 and 59); GS/SnO₂/carbon (refs 25 and 49); SnO₂/GS/CNTs (ref 9)]. Importantly, a capacity of 1470 mAh g⁻¹ can be recovered in another 60 cycles when the current density returned to 200 mA g⁻¹. This further implied the stable structure of the hybrid and the excellent reversibility. As demonstrated in previous study,

the high rate performance was greatly dependent on the rapid ionic and electronic diffusion and transport. As for SnO₂/GN, the ultrasmall size of SnO₂ nanocrystals can dramatically shorten lithium diffusion length. The porous structure facilitated the penetration and diffusion of electrolyte, leading to fast lithium ion transport. Meanwhile, the interconnecting nitrogen-doped graphene network can provide 3D electron conducting channels within the electrode. In this way, both high speed electron and lithium ion pathways are satisfied. In contrast, pure SnO₂ exhibited poorer rate capability and cannot bear large current densities due to the inefficient ionic and electronic transport.

To explore the structural stability of the cycled electrode, we investigated the changes of morphology and structure of the electrode by using ex situ TEM technique. For pure SnO₂ electrode, Sn nanoparticles appear to aggregate into Sn clusters during cycling (Figure S8). These large Sn particles may not maintain their integrity due to the large volume change during cycling, resulting in poor capacity retention. In the case of SnO₂/GN electrode, it is clearly seen that the primary dispersibility was well preserved, demonstrating a good constraint on the aggregation of SnO₂ upon cycling (Figure 5d and e). The particles were pulverized into a smaller size of 3–5 nm, which is beneficial to lower the absolute volume change and achieve higher electrochemical reactivity, resulting in an enhanced capacity during cycling.^{59,60} In the HRTEM image, the nanoparticles showed a poor crystallinity; however, lattice fringes of SnO₂ can also be observed, which further confirms that the conversion reaction of SnO₂ to Sn and Li₂O is reversible.

Furthermore, AC impedance analysis was carried out to elucidate the charge and contact resistance of SnO₂/GN and pure SnO₂ at selected cycle numbers. The high frequency semicircle is associated with SEI film resistance (R_{SEI}), the middle frequency semicircle is linked to charge-transfer resistance through the electrode-electrolyte interface (R_{ct}), while the steep sloping line represents the lithium-diffusion process within electrodes.^{38,61,62} For pure SnO₂, R_{SEI} and R_{ct} increased dramatically with cycling, implying continuous growth of the SEI film and degraded charge transfer kinetics^{63,64} (Figure S9). In contrast, SnO₂/GN displayed a drastically smaller diameter of both semicircles than that of pure SnO₂ after the same cycles, benefitting from the highly conductive graphene network (Figure 5c). EIS fitting showed that R_{SEI} and R_{ct} decreased upon cycling (Table S1), demonstrating stable SEI and increased electron and lithium ion diffusion rate, which results from the reduced size of Sn and SnO₂ nanoparticles.^{49,65} Due to the excellent structural stability as well as facilitated transportation of electrons and lithium ions, SnO₂/GN exhibits both superior cycling and rate performances.

CONCLUSIONS

We have successfully constructed 3D macroscopic SnO₂/GN aerogels, comprising self-assembled nitrogen-doped graphene networks and ultrasmall SnO₂ nanocrystals (3–7 nm), via a novel solvothermal-induced self-assembly process using SnO₂ colloid sol as precursor. Such a unique architecture established by GN prevents the electrochemical aggregation of SnO₂ and ensures favorable transport kinetics for both electrons and lithium ions. Moreover, nitrogen-doping of GS can further modulate the electronic structure of graphene and further enhance the lithium storage properties. Benefitting from the

combined 3D graphene frameworks and nitrogen-doping effect, extraordinary rate capability and prolonged cyclic stability (905 mAh g⁻¹ after 1000 cycles at 2000 mA g⁻¹) were achieved. Morphological and EIS study demonstrated the persistent uniform distribution of SnO₂ and increased electrochemical reactivity of the electrode during cycling. We believe that the present synthetic route can be further extended to produce other graphene-based hybrid aerogels, for applications in catalysts, sensors, supercapacitors, and so on.

■ ASSOCIATED CONTENT

Supporting Information

Additional TEM, SEM, TG, EDS, CV, discharge–charge curves, EIS curves, and photograph of SnO₂ dispersion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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