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Hierarchical TiO₂–SnO₂–graphene aerogels for enhanced lithium storage†

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Three-dimensional (3D) TiO₂–SnO₂–graphene aerogels (TTGs) were built up from the graphene oxide nanosheets supported with both TiO₂ and SnO₂ nanoparticles (NPs) via a facile hydrothermal assembly process. The resulting TTGs exhibit a 3D hierarchical porous architecture with uniform distribution of SnO₂ and TiO₂ NPs on the graphene surface, which not only effectively prevents the agglomeration of SnO₂ NPs, but also facilitates the fast ion/electron transport in 3D pathways. As the anode materials in lithium ion batteries (LIBs), TTGs manifest a high reversible capacity of 750 mA h g^{−1} at 0.1 A g^{−1} for 100 cycles. Even at a high current density of 1 A g^{−1}, a reversible capacity of 470 mA h g^{−1} can still be achieved from the TTG based LIB anode over 150 cycles.

Introduction

As the power supply of portable electronic devices and electric vehicles, rechargeable lithium ion batteries (LIBs) have become more and more crucial for our daily life in the past decade. The electrode materials are of great importance for the electrochemical performance of LIBs including capacity and rate capability, which thus have been the main focus of materials scientists.^{1–6} Owing to the high theoretical capacity (782 mA h g^{−1}), natural abundance, low cost and environmental friendliness, tin oxide (SnO₂) is regarded as an excellent candidate for advanced LIB anodes. However, the distinct disadvantages of SnO₂ such as the low electronic conductivity and the high volume variation (up to 250%) induced by the alloying reaction with lithium (Li_xSn, 0 ≤ x ≤ 4.4) inevitably retard its practical applications.^{7–10} The hybridization of SnO₂ with graphene as a carbon matrix is one of the most appealing solutions to improve the electrode performance of SnO₂ since the intriguing electron transfer ability

of graphene can efficiently enhance the conductivity of the whole electrode and its outstanding mechanical stability can absorb the volume expansion of the electrode materials.^{11–13} Especially, the construction of three-dimensional (3D) SnO₂–graphene aerogels (SnO₂–GAs) with macroporous architectures can generate an interconnected graphene network to facilitate the penetration of electrolytes, the transportation of charge carriers and the accommodation of the electrode volume changes, which is therefore an impactful strategy to gain high performance LIB electrodes with a highly reversible capacity and excellent rate performance.^{14–17} Nevertheless, due to the lack of effective protection against the contact and the aggregation of the inner-plane SnO₂ NPs on their macropore walls, these 3D monoliths still suffer from certain capacity fading at the ultrahigh current density.^{18–20}

In this work, we report a novel approach to fabricating ternary hybrids with both titanium dioxide (TiO₂) and SnO₂ NPs immobilized on graphene aerogels (TTGs) via a mild hydrothermal assembly process. The condensed packing of TiO₂ and SnO₂ NPs with the size of 3–5 nm in the monolithic TTG leads to hierarchical porous structures with meso-macropores and a high BET surface area of 190 m² g^{−1}, which can effectively buffer the excessive volume change during the lithiation–delithiation process. As the anode in LIBs, TTG exhibits an excellent capacity of 750 mA h g^{−1} for 100 cycles at 0.1 A g^{−1} and 470 mA h g^{−1} at a high current density of 1 A g^{−1}. Moreover, a high reversible capacity of 230 mA h g^{−1} can be still achieved even at 5.0 A g^{−1}, which outperforms those of previously reported hybrids of TiO₂–SnO₂, TiO₂–SnO₂–carbon and TiO₂–SnO₂–GN.^{21–25}

Experimental section

All the chemical reagents were purchased from Sigma-Aldrich and used directly without further purification.

Synthesis of TTG

Graphene oxide (GO) was synthesized from natural graphite flakes using a modified Hummers method.²⁶ Tin chloride

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† Electronic supplementary information (ESI) available: Photoimages and additional SEM, XRD, TGA and pore size distribution details. See DOI: 10.1039/c4cp04887c

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($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 510 mg) was first dissolved into 70 ml dimethylformamide (DMF) suspension of GO (1.25 mg ml^{-1}). After adding 10 ml deionized (DI) water, the mixture was magnetically stirred for 2 h at 80°C . Then 440 mg $\text{Ti}(\text{OBu})_4$ was added and the resulting suspension was further stirred for 12 h at 80°C . After that, the as-prepared GO nanosheets decorated with both TiO_2 and SnO_2 NPs were dispersed in DI water (10 ml) in a cylindrical vial (15 ml), which was then transferred into a 80 ml Teflon-lined stainless-steel autoclave, sealed tightly, and heated at 180°C for 12 h. Finally, the as-prepared sample was freeze-dried overnight to produce TTG as a black monolith. In control experiments, a SnO_2 -graphene aerogel (TG) was prepared using a similar procedure without adding $\text{Ti}(\text{OBu})_4$. Moreover, by dipping TG in 50 ml HCl (1 mol l^{-1}) with 440 mg $\text{Ti}(\text{OBu})_4$ at 50°C and stirring for 12 h, TiO_2 NPs could be physically adsorbed on the macropore-wall of TG and the resulting sample was named PTTG.

Characterization

Scanning electron microscopy (SEM) images were acquired using a NOVA NanoSEM 230 (FEI, USA) microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images, SAED patterns, elemental maps were obtained using a JEM-2100 microscope (JEOL Ltd, Japan). X-ray diffraction (XRD) measurements were carried out on a D/max-2500 X-ray diffractometer (Rigaku Corporation, Japan) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.1542 \text{ nm}$). Thermogravimetric (TGA) analysis was monitored on a Q5000IR apparatus (TA Instruments, USA), with a heating rate of $20^\circ\text{C min}^{-1}$ in air.

Electrochemical measurements

Electrochemical experiments were performed in 2016 coin-type cells. The working electrodes were prepared by mixing the hybrids (TTGs), carbon black (Super-P), and poly(vinyl difluoride) (PVDF) at a weight ratio of 80 : 10 : 10 and pasted onto pure Cu foil (99.6%). The loading mass of active material (TTG, TG or PTTG) in each cell is $0.50\text{--}0.70 \text{ mg cm}^{-2}$. Pure Li foil was used as the counter electrode. The electrolyte, which consisted of a solution of 1 M LiPF_6 in ethylene carbonate/dimethyl carbonate (DMC) (1 : 1 v/v), was obtained from Ube Industries Ltd. The cells were assembled in an Ar-filled glove box with the concentrations of moisture and oxygen below 1 ppm. The electrochemical performance was tested at various rates in the voltage range of 0.01–3.0 V.

Results and discussion

The fabrication procedure of TTG is illustrated in Fig. 1. As the basic building blocks of the macroporous hybrid, 2D graphene nanosheets decorated with TiO_2 and SnO_2 NPs were first obtained by a stepwise hydrolysis of Sn^{4+} and Ti^{4+} in the presence of GO.^{21,27,28} Consequently, the hydrothermal treatment of the suspension of the nanosheets containing TiO_2 and SnO_2 NPs resulted in a TTG monolith with hierarchical porous frameworks. During the hydrothermal process, the *in situ* reduction of GO can decrease the oxygen content and improve the conductivity of the hybrid.^{20,28} In controlled experiments, the hybrid of SnO_2 and graphene aerogels

Fig. 1 Schematic illustration of the fabrication process for TTG: (1) the stepwise hydrolysis of Sn^{4+} and Ti^{4+} to form GO loaded with TiO_2 and SnO_2 NPs; (2) the hydrothermal treatment of the hybrid nanosheets from step (1) led to the graphene hydrogel containing TiO_2 and SnO_2 NPs; (3) TTG was obtained as a black monolith after the freeze drying of the hydrogel from step (2).

(TGs) and the mixture of TG and TiO_2 NPs (PTTGs) were also prepared to compare with TTGs.

The morphology and microstructure of the samples were first examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Fig. 2 and Fig. S1, ESI†). The cross-section of TTG exhibits a typical macroporous structure with pore sizes in the range of 10–50 μm (Fig. 2a and b). The high resolution SEM images of TTG further disclose that TiO_2 and SnO_2 NPs are uniformly loaded on both sides of the graphene sheets without obvious aggregation (Fig. 2c). Elemental mapping images of TTG confirm the homogeneous distributions of both Sn and Ti elements on the graphene sheets (Fig. 2d). In contrast, the obvious agglomeration of TiO_2 NPs can be easily observed on the surface of PTTGs (Fig. S1, ESI†). The TEM image demonstrates that the graphene sheets in TTG are homogeneously covered with TiO_2 and SnO_2 NPs with the size of around 3–5 nm (Fig. 2e). The high-resolution TEM (HRTEM) image further reveals that the crystal lattice fringes of TiO_2 and SnO_2 NPs are 0.33 and 0.26 nm (Fig. 2f), respectively, corresponding to the (110) and (101) planes of rutile SnO_2 (JPCDS No. 41-1445) and rutile TiO_2 (JPCDS No. 21-1276) (Fig. S2, ESI†).^{23,29}

Fig. 2 (a)–(c) SEM images of TTG, and (d) element mapping images of TTG; (e) and (f) TEM images of TTG.

Thermogravimetric analysis (TGA) was used to determine the chemical composition of TG, TTG and PTTG. As shown in Fig. S3 (ESI†), the TiO₂ content in TTG is around 41.6 wt%, while PTTG only has a weight content of 23.3 wt% for TiO₂ NPs. The almost doubled loading ratio of TiO₂ NPs in TTG suggests that our per-growth strategy provides a better opportunity to bind NPs on the wall-surface of graphene aerogels than the physical adsorption process.

The porosity of TG, TTG and PTTG was investigated by nitrogen physisorption measurements (Fig. S4, ESI†). The adsorption-desorption isotherm of TTG exhibits the typical type IV nitrogen adsorption branch, suggesting the existence of mesoporous structures in the hybrid (Fig. S4a, ESI†).^{27,30} And the pore size distribution calculated by the Barret-Joyner-Halenda (BJH) method indicates that the diameters of the mesopores range from 1.5 to 10.0 nm (Fig. S4b, ESI†), which should originate from the interval spaces among TiO₂ and SnO₂ NPs.²¹ The Brunauer-Emmett-Teller (BET) surface areas and total pore volumes of the samples are calculated to be 190 m² g⁻¹ and 0.197 cm³ g⁻¹ for TTGs, which are much higher than those of TGs (67 m² g⁻¹ and 0.072 cm³ g⁻¹). Nevertheless, PTTG has the highest BET surface area of 218 m² g⁻¹, which might be owing to the agglomeration of TiO₂ NPs on the macropore wall of graphene aerogels (Fig. S1, ESI†).^{31,32}

The electrochemical activity of TG and TTG was first studied by cyclic voltammetry (CV) at a scan rate of 0.1 mV s⁻¹ in the voltage range of 0.0–3.0 V. As shown in Fig. 3a and b, the CV profiles of both samples are very close to those of the reported SnO₂-based composites.^{33,34} As indicated in Fig. 3b, the irreversible small cathodic peak at ~0.75 V in the first cycle can be assigned to the partial reversible reduction of SnO₂ NPs by Li⁺ (eqn (1)) and the decomposition of the electrolyte on the surface of SnO₂ NPs, leading to the generation of a solid electrolyte interface (SEI).^{35–37} Two strong cathodic peaks at 0.18 and 0.95 V can be assigned to the formation of Li₂O (eqn (1)) and Li_{4.4}Sn alloys (eqn (2)),³⁸ respectively. During the charging process, the strong anode peak at 0.50 V and the broad peak at 1.24 V correspond to the phase

transition from the Li_xSn alloy to Sn and partially reversible to SnO₂.³⁹ Furthermore, there is no obvious peak between 1.5 and 3.0 V, which is associated with Li ions trapped in TiO₂,^{30,40} demonstrating that TiO₂ has little contribution to the lithium storage ability of TTG.⁹

The charge-discharge cycling performance of the TTG, TG and PTTG based electrodes under a current density of 0.1 A g⁻¹ at 0.01–3.0 V vs. Li⁺/Li is compared in Fig. 4a. The first charge and discharge capacities of the TTG electrode are 1250 and 890 mA h g⁻¹ with a Coulombic efficiency (CE) of 71%. And the capacity of the TTG electrode can be stabilized at 750 mA h g⁻¹ for 100 cycles without obvious loss of capacity. More importantly, TTG exhibits a superior cycling capacity (Fig. 4b) of ca. 470 mA h g⁻¹ for over 150 cycles at a high charging-discharging rate of 1 A g⁻¹. In contrast, the TG and PTTG based electrodes only deliver a reversible capacity of 600 and 380 mA h g⁻¹ at a current density of 0.1 A g⁻¹ after 100 cycles. In Fig. 4c, TTG shows the best rate performance. Even at an ultra-high rate of 5 A g⁻¹, the capacity is still up to 230 mA h g⁻¹, which is much higher than those of TG (130 mA h g⁻¹) and PTTG (55 mA h g⁻¹). To understand the prominent electrochemical behavior inside the electrode materials, electrochemical impedance spectroscopy (EIS) measurements were performed. EIS spectra (Fig. 4d) show that the diameter of the semicircle of TTG in the high medium frequency region is much smaller than that of other samples, indicating lower contact and

Fig. 3 CV curves of (a) TG and (b) TTG at a scanning rate of 0.1 mV s⁻¹ in the first 2 cycles. Charging-discharging curves of (c) TG and (d) TTG at 0.1 A g⁻¹.

Fig. 4 (a) Variation of charge-discharge specific capacity versus cycle number of TG, TTG and PTTG at 0.1 A g⁻¹; (b) long-term cycling performance of TTG at a high current density of 1 A g⁻¹ (red and black circles), the Coulombic efficiency is plotted on the right axis (blue circles); (c) rate performance of TTG, TG and PTTG; (d) Nyquist plots of TTG, TG and PTTG electrodes obtained by applying a sine wave amplitude of 5.0 mV over the frequency range of 100 kHz–0.01 Hz; (e) Randles equivalent circuit for the TTG, TG and PTTG electrode-electrolyte interface. R_e is the electrolyte resistance and R_f is the resistance of the surface film formed on the electrodes. R_{ct} is the charge transfer resistance, Z_w is the Warburg impedance related to the diffusion of lithium ions into the bulk electrodes, and CPE represents the constant phase element.

charge-transfer impedances of TTG compared with TG and PTTG. The equivalent circuit model (Fig. 4e) of the studied system represents the internal resistance of the test battery according to the literature.⁴¹ The values of the film resistance (R_f) and the charge-transfer resistance (R_{ct}) for TTG were 34.0 and 149.4 Ω , respectively, which were significantly lower than those for TG (61.3 and 309.0 Ω) and PTTG (97.6 and 344.1 Ω).

Overall, the high capacity, good cycling stability, and excellent rate capability of TTG can be attributed to the following reasons. First, the conductive graphene sheets with 3D frameworks can serve as multidimensional pathways to facilitate the transport of electrons and the diffusion of electrolytes in the bulk electrode. Second, our fabrication approach allows the homogeneous distribution of TiO_2 and SnO_2 NPs in the 3D interconnected graphene scaffold. And the TiO_2 NPs standing by the side of SnO_2 NPs can effectively suppress the aggregation of inner-plane SnO_2 NPs during the charge-discharge cycle (Fig. S5, ESI†). Third, the mesopores generated by the condensed packing of TiO_2 and SnO_2 NPs can improve the surface area of the hybrid and thus provide more active sites for the storage of lithium.

Conclusion

In this work, we demonstrate an *in situ* synthesis and self-assembly approach to achieve high performance LIB anode materials by fabricating 3D hierarchical porous graphene hybrids with uniform staggered distribution of SnO_2 and TiO_2 nanoparticles on the surface. This synthetic strategy can be further extended to the production of 3D graphene-based hybrids with multiple components, which may have promising applications in catalysis, sensing, supercapacitors, and fuel cells.

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