Two-dimensional SnO₂/graphene heterostructures for highly reversible electrochemical lithium storage

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ABSTRACT The ever-growing market demands for lithium ion batteries have stimulated numerous research efforts aiming at the exploration of novel electrode materials with higher capacity and long-term cycling stability. Two-dimensional (2D) nanomaterials and their heterostructures are an intense area of study and promise great potential in electrochemical lithium storage owing to their unique properties that result from structural planar confinement. Here we report a microwave chemistry strategy to integrate ultrathin SnO₂ nanosheets into graphene layer to construct surface-to-surface 2D heterostructured architectures, which can provide unique structural planar confinement for highly reversible electrochemical lithium storage. The as-synthesized 2D SnO₂/graphene heterostructures can exhibit high reversible capacity of 688.5 mA h g⁻¹ over 500 cycles with excellent long-term cycling stability and good rate capability when used as anode materials for lithium ion batteries. The present work definitely reveals the advantages of 2D heterostructures featured with a surface-to-surface stack between two different nanosheets in energy storage and conversion devices.

Keywords: two-dimensional heterostructures, graphene, tin oxide, microwave chemistry, electrochemical lithium storage

INTRODUCTION

Lithium ion batteries have realized remarkable achievement in portable electronics market, and promise great potential in upcoming large-scale applications including electric vehicles and integrated electric grids of renewable energy [1–5]. However, the practical large-scale applications are limited by low energy density and insufficient durability of current commercial lithium ion batteries [6–9]. The ever-growing market requirements have attracted intensive research on exploiting next generation lithium ion batteries based on advanced electrode materials [10–14]. Among the many proposed electrode ma-

terials, tin oxide (SnO₂) is considered as the most promising alternative anode material due to its high theoretical specific capacity of 782 mA h g⁻¹ [15–25]. Previous researches demonstrate that SnO₂ anodes follow a reversible Li-Sn alloying/dealloying mechanism in deep charge-discharge process [26,27]. Unfortunately, this process undergoes huge volume expansion (up to 250%) resulting in rapid capacity fading and poor cycling stability [28]. Nevertheless, most SnO₂ anodes are often subject to slow ion and electron transport due to the limited lattice space, causing relatively low power density [29]. The unfavorable electronic conductivity of Li₂O phase can further weaken their rate capability. Additionally, conventional SnO₂ anodes provide a finite number of sites for ion reaction, leading to reduced charge storage capability and low energy density.

To overcome the aforementioned issues, great effort has been devoted to exploiting advanced SnO₂-based anodes [30–35]. One effective solution is to fabricate surface-dominated ultrathin two dimensional (2D) SnO₂-based nanostructures [36,37]. Many very recently published researches have demonstrated the distinct advantages of 2D nanostructured electrodes in electrochemical lithium storage due to their unique structural and surface properties [38–41]. It is believable that such architecture with atomic thickness could expose the most electrochemical active sites on surface and provide favorable channels for charge transfer and mass transport. Despite of considerable achievements including high initial electrochemical reaction activity, enhanced lithium storage capacity, and good rate capability for 2D nanostructured anodes, the long-term cycling stability in most cases is still unsatisfactory because of the structural decay of individual 2D architectures. To improve the stability during extended cycling, one promising strategy is to fabricate 2D heterostructures by stacking two kinds

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of nanosheets into hetero-layered architectures [42–45]. The 2D heterostructures could enjoy a unique surface-to-surface heterointerface between layers with strong inter-layer interactions, which could provide an elastic buffer space to accommodate the huge volume change to improve long-term cycling stability.

Here we report a microwave chemistry strategy to fabricate a unique 2D SnO_2 /graphene heterostructures. With the assistance of hexadecyl trimethyl ammonium bromide (CTAB) surfactant and the microwave absorption property of graphene materials, ultrathin SnO_2 nanosheets can be confined on both sides of reduced graphene oxide with a surface-to-surface contact. With the unique structural and compositional advantages, the 2D SnO_2 /graphene heterostructures exhibit high reversible lithium storage capacity of 688.5 mAh g^{-1} over 500 cycles and excellent rate capability.

EXPERIMENTAL SECTION

Synthesis of 2D SnO_2 /graphene heterostructures

In a typical procedure, 2.1662 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 1.3995 g CTAB, and 1.3458 g hexamethylenetetramine (HMT) were dissolved into 240 mL ethanol/water solution. Then 0.2439 g reduced graphene oxide was dispersed into the above solution under ultrasonication for 30 min. The obtained mixture was shifted into a 250 mL round-bottom flask. The mixture was then used for the microwave-assisted synthesis. The solution was heated from room temperature to 90°C in only 2 min under ambient conditions in microwave reaction system. The microwave system was attached with a refluxing system in order to maintain the vapors in the reaction system. Thus the water could be retained and the temperature was stable around 90°C . After cooling down to room temperature, the black precipitate was collected by centrifugation, washed thoroughly with deionized water and ethanol, and then dried in vacuum at 100°C overnight. The final product was calcined at 500°C for 2 h in argon gas to remove the residual organic molecule.

Materials characterization

The crystallographic phase of the as-synthesized materials was characterized by X-ray powder diffractometer (XRD, Rigaku RU-200b, $\text{CuK}\alpha$ source, $\lambda=1.5418 \text{ \AA}$). The microstructures and morphology of the as-synthesized materials were identified by field emission scanning electron microscopy (FESEM, Hitachi SU8010), transmission electron microscopy (TEM, Hitachi H-800, 100 kV), and high-resolution TEM (HRTEM, JEOL

2100F, 200 kV) equipped with energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments, INCA). The specific surface areas and pore size distribution were evaluated by nitrogen adsorption-desorption isotherms on a NOVA4200e nitrogen adsorption apparatus (Quantachrome Instruments, USA) at 77 K under a relative pressure P/P_0 of 3.3×10^{-7} –0.995. Prior to the measurement, the samples were degassed at 574 K for 6 h under vacuum to remove adsorbed gas or moisture. The surface area was estimated by the multi-point Brunauer–Emmett–Teller (BET) theory. Pore size distribution was calculated from the adsorption data using Barrett–Joyner–Halenda (BJH) model. X-ray photoelectron spectra (XPS) were recorded on a ULVAC PHI Quantera microscope machine. The standard binding energies (284.6 eV) of C 1s peak was selected to calibrate experimental date. Raman spectra were taken using a Renishaw inViaTM confocal Raman microscope (Renishaw, England) with a 514 nm excitation laser under an intensity of 5 mW.

Electrochemical measurement

To investigate the electrochemical lithium storage properties of the as-synthesized 2D SnO_2 /graphene heterostructures, a two-electrode system was fabricated in the form of CR2025-type coin cells. The assembly processes were carried out in an Ar-filled glove-box. Briefly, the reference and counter electrodes were established by high-purity lithium foil. The as-synthesized products, Super P carbon black and polyvinyl difluoride (PVDF) were mixed uniformly at a weight ratio of 70:20:10 in *N*-methyl-2-pyrrolidone (NMP) solvent to form mixture slurry. After stirring for about 30 min, the relevant slurry was covered on a current collector (Cu foil) and dried at 80°C for about 12 h in a vacuum oven. The weight of active material loading on each collector was measured to be 1–2 mg, corresponding to a density of $\sim 1.2 \text{ mg cm}^{-2}$. 1 mol L^{-1} LiPF_6 dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC, 1:1, v/v) was used as the electrolyte solution, while a polymer membrane named Celgard 2400 was employed as the separator. LAND CT-2001A battery testing systems (Hannuo Electronics Co., Ltd. China) were used to check Galvanostatic charge-discharge cycles between 0.01 and 3.0 V vs. Li/Li^+ . Cyclic voltammetry (CV) was performed on an IM6e electrochemical workstation (Zahner, Germany) between 0.01 and 3 V (vs. Li/Li^+) at a scan rate of 0.1 mV s^{-1} .

RESULTS AND DISCUSSION

The 2D SnO_2 /graphene heterostructures were prepared

Figure 1 Schematic illustration of the fabrication of 2D SnO₂/graphene heterostructures.

through a microwave chemistry strategy as outlined in Fig. 1. Briefly, the graphene sheets were first dispersed in an ethanol/water solution of Sn²⁺, HMT, and CTAB by ultrasonic treatment. The resultant solution was refluxed at 90°C for 30 min in 250 mL round-bottomed flask under microwave irradiation. In refluxing procedure, hydrolysis of HMT results in the nucleation of Sn-OH precursors. The strong microwave absorption effect of

graphene could convert the electromagnetic energy into surface thermodynamic energy inhabited on graphene layer, and thus to provide a favorable environment for ion absorption and subsequent oriented attachment. With the assistance of CTAB surfactant, the Sn-OH precursors uniformly grow on the surface of graphene sheets with a surface-to-surface contact. After heat treatment, the 2D SnO₂/graphene heterostructures were obtained for lithium storage.

XRD (Fig. 2a) shows that SnO₂/graphene heterostructures deliver the similar diffraction characterizations as that of individual SnO₂ nanosheets. All identified diffraction peaks confirm a tetragonal rutile SnO₂ phase (JCPDF card No. 41-1445) without obvious crystalline impurities. The absence of diffraction peaks from the graphene matrix in the SnO₂/graphene heterostructures is ascribed to the relatively weak diffraction intensity of the graphene material (Fig. S1). The thermogravimetric analysis (TGA, Fig. 2b) suggests that SnO₂/graphene heterostructures undergo an outstanding weight loss in temperature programming at about 528.5°C under air atmosphere, and the weight fraction of contained graphene is detected to be about 10 wt%. Raman spectrum (Fig. 2c) evidently demonstrates the presence of graphene

Figure 2 Chemical composition and physical characterizations of 2D SnO₂/graphene heterostructures: (a) XRD patterns of 2D SnO₂/graphene heterostructures (HS) and SnO₂ nanosheets (NS). (b) Thermogravimetric curve. (c) Raman spectra. (d) N₂ adsorption-desorption isotherm. (e) Survey XPS spectrum. (f) High-resolution Sn 3d spectrum of 2D SnO₂/graphene heterostructures (I) and SnO₂ nanosheets (II).

matrix according to the well-defined characteristic peaks locating at 1,325, 1,580, and 2,655 cm^{-1} , normally designated to D, G and 2D band, respectively. The observed G/D intensity ratio is 0.67, which is lower than that value of 0.82 for the pristine graphene (Fig. S2), indicative of higher defect density in the SnO_2 /graphene heterostructures. Fig. 2d shows the nitrogen adsorption-desorption isotherm to investigate the surface feature of SnO_2 /graphene heterostructures. The observed hysteresis loop at relative pressures of 0.2–0.9 in isotherm could indicate a typical mesoporous structure. The average pore size is measured to be 2.4 nm with a total pore volume of 0.7617 $\text{cm}^3 \text{g}^{-1}$ according to BJH model. The SnO_2 /graphene heterostructures present a BET specific surface area of 104.6 $\text{m}^2 \text{g}^{-1}$, much lower than that (630.8 $\text{m}^2 \text{g}^{-1}$) of pristine graphene (Fig. S3). The reduced BET value is caused by the surface-to-surface stacking between SnO_2 nanosheets and graphene layer. The individual SnO_2 nanosheets exhibit BET specific surface area of 115.5 $\text{m}^2 \text{g}^{-1}$ with probable pore size of 2.2 nm (Fig. S4). The survey XPS spectrum (Fig. 2e) reveals three elements related to Sn, O and C existing in the samples. The Sn and O elements are ascribed to SnO_2 nanosheets, while the C is derived from graphene layer. In high-resolution spectra of Sn 3d region (Fig. 2f), two symmetrical strong peaks are observed at 487.0 and 495.5 eV, attributed to Sn 3d_{5/2} and Sn 3d_{3/2}, indicative of Sn^{4+} oxidation state for both the SnO_2 /graphene heterostructure (I) and the individual SnO_2 nanosheets (II). The high-resolution O 1s spectra (Fig. S5a) reveals that the oxygen bridge offer strong interlayer interactions between SnO_2 nanosheets and graphene layer [46]. The detected peak at 531.2 eV could be ascribed to the lattice oxygen of SnO_2 (Sn–O–Sn) and C=O groups. The high-resolution C 1s spectra (Fig. S5b) consists of three peaks locating at 284.5, 285.6, and 289.3 eV, which are assigned to C–C bonds in graphene lattice, epoxide C–O and carboxyl carbon O–C=O groups, respectively.

Fig. 3a shows that the pristine graphene exhibits a typical ultrathin 2D sheet-like structure with large-area and smooth surface. Through the same procedure as described in Fig. 1 except in the absence of graphene layer, the individual ultrathin SnO_2 nanosheets were also successfully synthesized. Fig. S6 shows that the as-synthesized SnO_2 nanosheets manifest a graphene-like morphology with well-defined skeleton and large planar area. The clearly flexible and transparent characteristic suggests an ultrathin thickness. When introducing graphene layer, the SnO_2 nanosheets can grow on two sides of graphene. Fig. 3b shows the low-magnification FESEM

Figure 3 Morphology and microstructure characterizations of 2D SnO_2 /graphene heterostructures: (a) typical field emission scanning electron microscopy (FESEM) image of pristine graphene for comparison. (b–e) FESEM images at different magnifications. (f) TEM image. (g) HRTEM image. (h) Selected area electron diffraction (SAED). (i, j) Scanning transmission electron microscopy (STEM) image and corresponding EDS mapping.

image of 2D SnO_2 /graphene heterostructures. It can be clearly found that both sides of the heterostructures are relatively rough, indicating that the ultrathin SnO_2 nanosheets are confined on both sides of graphene. Fig. 3c suggests that the surface of graphene is coated by a uniform layer of SnO_2 nanosheets. Fig. 3d and e display that the SnO_2 nanosheets combine with graphene with an efficient surface-to-surface binding rather than standing or one-side lying on the graphene surface. TEM was further employed to investigate the detailed structural features. As shown in Fig. 3f, the 2D SnO_2 /graphene heterostructures manifest an irregular texture, which is attributed to the intrinsic nonlayered crystal structure of SnO_2 phase. Fig. 3g shows the HRTEM image scanned on edge of heterostructures, where the marked lattice fringes are ascribed to the (110) plane of rutile SnO_2 , and the graphene layer can also be clearly observed. Fig. 3h shows the SAED pattern, which consists of a series of well-re-

Figure 4 Electrochemical lithium storage performances of 2D SnO₂/graphene heterostructures: (a) typical CV curves at a scan rate of 0.1 mV s⁻¹. (b) The first five galvanostatic charge–discharge profiles. (c) Rate capability at different current density. (d) Nyquist plots and the equivalent electrical circuit (inset). (e) Cycling performance at 200 mA g⁻¹.

solved concentric diffraction rings with occasional bright spots, indicative of the nano-crystalline nature. The three marked diffraction rings can be indexed to the (110), (101), and (211) plane. HAADF STEM image (Fig. 3i) and corresponding EDS spectral mapping (Fig. 3j) clearly show that three elements of O, C, and Sn are evenly distributed on the whole heterostructures.

The electrochemical reactivity of 2D SnO₂/graphene heterostructures was first investigated by cyclic voltammograms (CVs). The first five CV curves are shown in

Fig. 4a. In the first cathodic scan, two distinct peaks are present at 0.75 and 0.12 V; the former is attributed to initial irreversible reduction of SnO₂ to Sn together with the synchronous formation of Li₂O and solid electrolyte interphase (SEI) layer, and the latter to Li–Sn alloying process [21,47]. The well-defined oxidation peaks around 0.55 V in anodic scan for all CV cycles can be attributed to dealloying of the Li_xSn compounds. After the first cycle, the CV curves become stable and overlap, suggesting an excellent electrochemical reversibility.

The electrochemical properties of 2D SnO₂/graphene heterostructures were further evaluated by galvanostatic charge-discharge measurement at 200 mA g⁻¹ current density. Fig. 4b shows the first five discharge-charge voltage profiles. In accordance with the aforementioned CV results, the first discharge process profile presents two slope regions. The earlier long plateau at about 0.95 V is ascribed to the irreversible formation of solid electrolyte interface (SEI) film and Li₂O. As a result, 2D SnO₂/graphene heterostructures deliver ultrahigh initial lithium storage capacities. The first discharge and charge capacities are 2,232.4 and 1,180.1 mA h g⁻¹, respectively. The irreversible capacity loss during the first charge process may be ascribed to irreversible side reactions including SnO₂ reduction and SEI film formation [48]. Except the first discharge profile, the following ones are nearly similar and overlapped. The ultrahigh initial lithium storage capacities may be attributed to the ultrathin 2D architecture with enriched electrochemical active sites and favorable interfacial reaction.

Fig. 4c shows the rate capability of 2D SnO₂/graphene heterostructures at programmed varying current densities from 200 to 1,500 mA g⁻¹. The observed discharge and charge capacities decrease progressively with the increase of the loaded current density, but still maintain at high values. As the current density reaches 1,500 mA g⁻¹, 2D SnO₂/graphene heterostructures can still exhibit a stable charge capacity of 493.6 mA h g⁻¹. When current density is reduced back to 200 A g⁻¹, the charge capacity can resume to a high value of 720.1 mA h g⁻¹, indicative of good reversibility. The excellent rate capability could be ascribed to the favorable charge-transport features of the 2D heterostructures with graphene support and the short ions diffusion path in the thickness direction.

The electrochemical impedance spectra (EIS) were employed to investigate the reaction kinetic of 2D SnO₂/graphene heterostructures. Fig. 4d shows the EIS interpreted in terms of Nyquist plots for comparison. The depressed semicircles in high frequency are ascribed to the surface film and charge-transfer resistance ($R_{\text{sf+ct}}$) [49,50]. 2D SnO₂/graphene heterostructures can present a lower $R_{\text{sf+ct}}$ (33 Ω) than that (120 Ω) of individual SnO₂ nanosheets, and maintain stable values at about 30 Ω in the subsequent plots. Figs S7 and S8 show the fitting R_{ct} and Li-ion diffusion coefficient (D_{Li}) value of the 2D SnO₂/graphene heterostructures, SnO₂ nanosheets, and SnO₂ nanosheets and graphene mixture based on equivalent circuits after different cycles. It can be observed that the R_{ct} and D_{Li} of 2D SnO₂/graphene heterostructures show the least change after 60 cycles,

suggesting the superior structure stability and the favorable kinetic behavior. The significantly reduced and stable resistance could be attributed to the 2D heterostructures, where not only favorable ion diffusion is guaranteed, but excellent electron transfer allowed due to the flexible graphene matrix with good electronic conductivity.

To evaluate the long-term cycling stability, 2D SnO₂/graphene heterostructures were repeatedly charged and discharged at a current density of 200 mA g⁻¹ up to 500 cycles as shown in Fig. 4d. SnO₂/graphene heterostructures exhibit an initial Coulombic efficiency of 52.9%, equivalent to the theoretical value (52%). From the second cycle, the Coulombic efficiency climbs up to 87.9% and maintains over 98% in subsequent cycles. 2D SnO₂/graphene heterostructures exhibit excellent long-term cycling stability and deliver a high reversible capacity of 688.5 mA h g⁻¹ in the 500th cycle. By contrast, individual SnO₂ nanosheets show serious capacity decay after the 40th and the reversible capacity drops down to 234.9 mA h g⁻¹ in the 100th cycle (Fig. S9). For comparison, we also measured the electrochemical performance of a mixture of graphene and SnO₂ nanosheets. As shown in Fig. S10, the mixture without 2D heterostructures also exhibits serious capacity decay. These results indicate that 2D SnO₂/graphene heterostructures could provide structural planar confinement feature for long-term cycling stability. Note that the practical electrochemical performance of many nanostructured electrode materials is highly dependent on their microstructure and morphology. In the present research, we attribute the excellent electrochemical lithium storage performance of the 2D SnO₂/graphene heterostructures to their unique surface-to-surface 2D heterostructured architectures. For comparison, we also check some ever reported SnO₂-graphene configurations and the resultant electrochemical performance. For example, Wang and co-workers reported a SnO₂/graphene nanocomposite, where carbon coated SnO₂ nanoparticles with the size of 10–20 nm anchored on graphene layers [51]. When used as anode material, their SnO₂/graphene composite exhibited the reversible capacity of 703 mA h g⁻¹ after 80 cycles at a current density of 100 mA g⁻¹. Guo's group prepared the SnO_x/carbon nanohybrids with 1D nanostructure [52]. Their anode materials delivered a reversible capacity of 608 mA h g⁻¹ after 200 cycles. The difference in electrochemical performance between the SnO₂/graphene composites could be ascribed to the variety in their structure.

CONCLUSIONS

In summary, novel 2D SnO₂/graphene heterostructures

have been constructed by microwave chemistry protocol. The strong microwave absorption effect of graphene and the assistance of CTAB surfactant could allow for the uniform growth of SnO_2 nanosheets confined on graphene layer with a surface-to-surface contact. Most importantly, the 2D SnO_2 /graphene heterostructures exhibit highly reversible electrochemical lithium storage performances with excellent long-term cycling stability and good rate capability when used as anode materials for lithium ion batteries. Our present work definitely reveals the advantages of 2D heterostructures featured with a surface-to-surface stack between two different nanosheets in energy storage and conversion devices.

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二维SnO₂/石墨烯异质结构及其高可逆性电化学储锂性能

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摘要 对锂离子电池日益增长的市场需求已经引起巨大的研究热情来开发具有更高容量和超长循环性的新型电极材料. 由于具有独特的平面结构限域性能, 二维材料及其异质结构目前成为材料研究领域的热点, 并有望在电化学能量储存方面发挥巨大的潜力. 因此, 本文借助于微波化学策略把超薄SnO₂纳米片与石墨烯薄层耦合在一起构筑一种面对面型二维异质结构, 利用其独特的平面结构限域性能来获得高可逆性的电化学储锂性能. 实验结果表明, 所制备的二维SnO₂/石墨烯异质结构表现出良好的电化学性能, 连续500次循环之后其可逆容量仍能保持在688.5 mA h g⁻¹, 同时也具有很好的倍率性能. 本工作揭示了具有面对面型二维异质结构在能量储存与转化设备应用方面的明显优势, 为新型电极材料的制备提供了更多选择.