A Polyaniline-coated Mechanochemically Synthesized Tin Oxide/Graphene Nanocomposite for High-power and High-energy Lithium-ion Batteries

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Abstract

Although intensive efforts have been made during the past decades, development of an anode material with high specific capacity and stable cycling performance for lithium-ion batteries (LIBs) using a cost-effective preparation method still remains challenging. Herein, we report a polyaniline (PANI)-coated mechanochemically synthesized SnO₂/graphene (SG) nanocomposite via *in situ* polymerization. PANI-coated nanocomposites are successfully prepared with different raw material mass ratios (aniline:SG, 0.15:1, 0.2:1, 0.25:1). The nanocomposite with initial aniline:SG mass ratio of 0.2:1 (20%PANI-SG) contains an optimal structure housing genuine PANI nanofibers as conductive bridges and a relatively high surface area of 158.5 m² g⁻¹; furthermore, it exhibits a stable cycling performance over 100 cycles at high current density (1000 mA g⁻¹) with a specific capacity of more than twice that of the starting SG electrode at the 100th cycle. Additionally, this material achieved an outstanding cycling rate with current densities changing stepwise from 100 to 3000 mA g⁻¹ and back, and exhibited a specific capacity of 467 mA h g⁻¹ even at 2000 mA g⁻¹. In terms of the electrochemical stability, rate capability and cost-effective preparation process, the PANI-SG nanocomposite is a viable anode material for next-generation high-power and high-energy LIBs.

Keywords: polyaniline, tin oxide, graphene, mechanochemical method, *in situ* polymerization, lithium-ion batteries

1. Introduction

Rechargeable lithium-ion batteries (LIBs) are the dominant power source for commercial personal electronic devices and are now being applied to other technologies including electric/hybrid electric vehicles and energy storage for renewable resources to address the rise in energy usage and environmental issues [1-7]. The very common commercial anode material graphite no longer meets the significantly increasing demands for high electrochemical performance [8-12]. Development of novel electrode materials with high reversible capacity, good rate capability and long-term stability is the key to the next-generation LIBs. The biggest challenge may be finding a material that meets all three desired characteristics: (1) electrochemical stability; (2) high specific capacity; and (3) cost-effective preparation method. For example, lithium titanate, a well-known “zero-strain” anode material for LIBs, could achieve excellent cycling stability and high-rate capability. However, its theoretical capacity is very low at only 175 mA h g^{-1} [13-16], thus limiting its commercial application.

Tin oxide (SnO_2), with a high theoretical capacity of 782 mA h g^{-1} , is a very promising anode material candidate for LIBs [17-19]. However, its large volume variation during the lithium insertion/extraction process [20-21] leads to degradation of the electrode, resulting in poor cycling stability. Many efforts have been carried out to improve the cycling stability of SnO_2 , such as synthesis of nanostructures to minimize the strain [22-25] and formation of composites with carbon, metals or oxides to accommodate the volume variation [26-30]. Notably, the synthesis of nanostructured SnO_2 on conductive and flexible graphene forms a composite and has been recognized as an effective approach to achieving a stable cycling performance.

To date, various methods, including the hydrothermal method [31-33], the microwave-assisted method [34], atomic layer deposition (ALD) [35] and the reflux method [36], have been developed to obtain SnO₂/graphene nanocomposites. However, these methods often involve complicated processes, uncommon conditions or additional chemicals, which limit the broad commercial application of these advanced SnO₂/graphene nanocomposites as anodes for LIBs. Recently, we successfully prepared an outstanding composite anode with ~4 nm SnO₂ nanocrystals on graphene via a facile mechanochemical synthesis using 3-30 μm metallic Sn and graphite oxide as the raw materials [37]. The process could easily be employed for large-scale applications, and the optimal composite as an electrode for LIBs exhibited a stable cycling performance with a specific capacity of 891 mA h g⁻¹ after 50 cycles at a current density of 100 mA g⁻¹. Although a high specific capacity and cost-effective preparation process were demonstrated for this nanocomposite, the cycling stability at a current density of 100 mA g⁻¹ is still not attractive to commercial application for LIBs. Conducting polymers have attracted increasing attention for improving the electrochemical performance of electrode materials for LIBs because they are conductive, low cost, lightweight and mechanically flexible materials. As a conductive semi-flexible rod polymer, polyaniline (PANI) is easily prepared from aniline monomers by oxidizing and doping [38-43]. Additionally, the PANI-coating layer could also accommodate the large volume variation of SnO₂ during the charge/discharge process. For example, He et al. [42] synthesized a SnO₂/PANI composite by coating PANI on spherical SnO₂ nanoparticles using the polymerization reaction. The composites exhibited a specific capacity of 609.3 mA h g⁻¹ after 80 cycles at a current density of 70 mA g⁻¹ in the voltage range of 0.01-3 V. Liang et al. [43] prepared a composite with SnO₂ loading on the surface of PANI-reduced-graphene-oxide using a hydrothermal synthesis method. As an anode of LIBs, the

hybrid structure showed a high specific capacity of $573.6 \text{ mA h g}^{-1}$ after 50 cycles at a current density of 156 mA g^{-1} between 0.01 and 3 V. However, the electrochemical performances of the above composites were tested at low current densities, and the graphene-based composite was synthesized by liquid hydrothermal synthesis limiting the commercial application of these composites.

Herein, mechanochemically synthesized $\text{SnO}_2/\text{graphene}$ (SG) nanocomposites are further studied for their application as a faster lithium storage material fabricated via an *in situ* polymerization. The SG and PANI-coated SG nanocomposites were investigated as electrodes for LIBs at a high current density of 1000 mA g^{-1} . Different initial aniline amounts were explored, and a PANI-coated SG nanocomposite with an initial mass ratio of 0.2:1 aniline to SG (named 20%PANI-SG) demonstrated an optimal structure with a PANI layer on the surface and PANI nanofiber conductive bridges connecting the SG particles. The 20%PANI-SG nanocomposite exhibited a stable cycling stability through 100 cycles at 1000 mA g^{-1} and an excellent charge-discharge rate capability, indicating that it is a significantly promising anode material capable of replacing the commercial graphite anode for LIBs in state-of-the-art applications.

2. Experiment section

2.1 Preparation of polyaniline-coated $\text{SnO}_2/\text{graphene}$ composite (PANI-SG)

A nano- $\text{SnO}_2/\text{graphene}$ composite (SG) was first prepared by a facile mechanochemical method, which was reported recently by our group [37]. Briefly, graphite oxide (GO) from a modified Hummers method and coarse metallic Sn with mass ratio of 1:1 were ground in Ar via ball-milling at a rotational speed of 400 rpm for net grinding times of 8 h 20 min to obtain the nanocomposite, and then it was further calcined at 300°C for 1 h under Ar atmosphere.

PANI-SG composites were synthesized by *in situ* polymerization of aniline on SG samples with different mass ratios of aniline:SG (0.15:1, 0.2:1 and 0.25:1) and were named 15%PANI-SG, 20%PANI-SG and 25%PANI-SG, respectively. As per the typical synthesis process, SG samples and aniline were added to a 1 M HCl solution and were stirred for 1 h. Then, an HCl solution with ammonium persulfate (mass ratio of ammonium persulfate to aniline, 1.5:1) as an oxidant was added to the above suspension, and it was kept at 0~5 °C for 6 h. After the polymerization reaction, the as-prepared samples were washed by deionized water and ethanol several times, assisted by centrifugation, and then were dried for 12 h under vacuum. Pure PANI was also synthesized in the same process without the addition of SG.

2.2 Characterization

X-ray diffraction (XRD) measurements were carried out to study the compositions and phase structures of the samples on a Bruker D8 Advance diffractometer with Cu K α radiation. Field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) was used for the observation of the morphology and microstructure of the samples. Transmission electron microscopy (TEM) and bright-field STEM images were acquired using an FEI Tecnai G2T20 electron microscope operating at 200 kV, and corresponding EDX mappings were obtained by an FEI Tecnai G2F30 S-TWIN field emission transmission electron microscope equipped with EDAX energy-dispersive X-ray spectroscopy operating at 300 kV. Fourier transform infrared (FT-IR) spectra and Raman spectra were recorded using a Nicolet 380 FT-IR Spectrometer (Thermo Scientific, USA) and a HR800 UV Raman microspectrometer (JOBIN YVON, France), respectively. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI5000 VersaProbe spectrometer equipped with an Al K α X-ray source. The nitrogen adsorption-desorption

isotherms were acquired using a BELSORP II instrument at the boiling point of liquid nitrogen. The Brunauer-Emmett-Teller (BET) method and the Barret-Joyner-Halenda (BJH) method were used to calculate the corresponding specific surface area and pore size distribution of the samples, respectively. Thermogravimetric analysis (TGA, NETZSCH STA 449 F3 apparatus) was performed in air with a heating rate of 10 °C min⁻¹.

2.3 Electrochemical measurement

The samples were prepared for use as working electrodes using a traditional slurry-coating technique. First, 80 wt% active material was mixed with 20 wt% LA-132 binder to form a slurry and was coated onto a copper foil, followed by drying under vacuum at 100 °C. The electrochemical measurement was performed at room temperature using CR2016-type coin cells, which were assembled in an argon-filled glovebox using metallic lithium foil as the counter electrode, microporous polypropylene film (Celgard 2400) as the separator and 1 M LiPF₆ solution in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, vol/vol) as the electrolyte. The cell performance was recorded on a LAND Battery Testing System (Wuhan, China) within a potential range of 0.01-3.0 V. Princeton Applied Research potentiostat/galvanostat model 273A was used to study cyclic voltammetry test between 3.0 and 0.01 V at the sweep rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurements of the cells were performed using a Princeton Applied Research PARSTAT 2273 advanced electrochemical system in the frequency range of 100 mHz–100 kHz with the AC modulation of 5 mV at 0.8 V (discharge state).

3. Results and discussion

The simple *in situ* polymerization process for formation of the PANI-SnO₂/graphene (PANI-SG) composite was carried out in an HCl solution using the mechanochemically synthesized SnO₂/graphene nanocomposite and aniline as raw materials. The preparation process of PANI-SG could easily be applied for large-scale commercial fabrication. Different mass ratios of aniline:SG (0.15:1, 0.2:1 and 0.25:1) were studied to explore the optimal PANI-SG composite as an advanced anode for LIBs. The compositions and phase structures of the samples were initially investigated by XRD with results shown in **Fig. 1**. The SG sample prior to *in situ* polymerization appeared to be a typical SnO₂ phase with the characteristic peaks at 2 θ of 26.6, 33.8, 37.8 and 51.8° (JCPDS, No.: 41-1445), respectively. Two broad peaks at 2 θ of approximately 20 and 25° were observed for the pure PANI sample without the addition of SG. After the *in situ* polymerization, the characteristic peaks of the SnO₂ phase were well maintained, indicating the *in situ* polymerization process did not affect the phase structure of the SG sample. A broad peak appeared at 2 θ of approximately 20° in the PANI-SG composite especially for 20%PANI-SG and 25%PANI-SG samples suggested that the PANI was successfully synthesized from aniline monomers in the composites. The oxidation states of PANI were known to be very important for their electrical conductivity [43]. The as-prepared PANI was emeraldine, suggesting that the PANI was in the conductive oxidation state.

The morphologies of the PANI, SG and PANI-SG composites were analyzed by FE-SEM imaging. As shown in **Fig. 2a&b**, the pure PANI polymerized from aniline monomers without the addition of SG appeared to be cross-linked nanofibers with diameters of approximately 80 nm. Before *in situ* coating with PANI, the initial SG sample made by mechanochemical synthesis appeared to be micrometer-sized architected chips that were relatively independent, as shown in **Fig. 2c&d**. The morphologies of the PANI-SG composites obtained by *in situ* polymerization are

shown in **Fig. 2e-j**. The 15%PANI-SG composite after *in situ* polymerization (**Fig. 2e&f**) was much different from the pure cross-linked PANI nanofibers; it became edgeless and cross-linked compared to the initial SG sample, suggesting the *in situ* polymerized PANI was successfully coated on the surface of the SG samples. By increasing the amount of PANI, the composite particles became more cross-linked (**Fig. 2g& 2i**). As shown in **Fig. 2g**, very few PANI nanofibers were located on the surface of the 20%PANI-SG composite. However, the PANI nanofibers appeared embedded in the 20%PANI-SG composite as seen from a crack (**Fig. 2h**), indicating that the PANI also formed nanofibers as conductive bridges to connect SG particles beyond the coating layer. For the 25%PANI-SG composite, obvious cross-linked PANI nanofibers were observed on the surface of the sample, as shown in **Fig. 2i&j**, suggesting that the amount of polymerized PANI may be superfluous.

The chemical structures of the samples were investigated by Raman, FT-IR and XPS analysis. **Fig. 3a** shows the Raman spectra of PANI, SG and PANI-SG composites. The peaks centered at $\sim 1350\text{ cm}^{-1}$ and $\sim 1591\text{ cm}^{-1}$ in the Raman spectrum of the SG sample were attributed to D band (in-plane vibrations of disordered carbon) and G band (E_{2g} mode of graphite) of the existing graphene. Similar D and G bands were observed in the PANI-SG composites, indicating the structure of graphene was maintained after the polymerization process. In the pure PANI, characteristic peaks centered at ~ 1600 , ~ 1370 and $\sim 1173\text{ cm}^{-1}$ were assigned to the C-C stretching vibration of the benzenoid ring, the C-N^+ stretching vibration demonstrating the PANI was in the doped state, and the C-H bending vibration of the benzenoid or quinoid rings; the peaks at $\sim 1504\text{ cm}^{-1}$ and $\sim 1240\text{ cm}^{-1}$ were attributed to the C=N and C-N stretching in the emeraldine state, respectively [44-46], suggesting that the as-synthesized PANI was in the conductive state, which was consistent with the presence of the emeraldine color. In the Raman spectra of all PANI-SG

composites, the characteristic peaks of PANI were also observed, suggesting the successful formation of conductive PANI in the composites after the *in situ* polymerization. Moreover, there was no additional peak corresponding to other chemicals in the Raman spectra of the PANI-SG composites, suggesting that there were no secondary reactions between PANI and SG during the *in situ* polymerization. The strength of the characteristic peaks of the PANI, such as peaks at $\sim 1504\text{ cm}^{-1}$ and $\sim 1173\text{ cm}^{-1}$, increased from the 15%PANI-SG sample to the 25%PANI-SG sample, indicating an increase in the amount of as-synthesized PANI. FT-IR analysis was carried out in the range of $400\text{--}2000\text{ cm}^{-1}$ to further obtain information about structures in the composites and results are shown in **Fig. 3b**. The characteristic absorption peaks for pure PANI also appeared for the PANI-SG composite analyses. For example, the absorption peak at 1570 cm^{-1} corresponded to C=C stretching band in quinoid rings; the absorption peak at 1465 cm^{-1} was assigned to C-C stretching of benzenoid rings [47]; the absorption peaks at 1300 and 1238 cm^{-1} were ascribed to C=N and C-N stretching; the absorption peak at 1118 cm^{-1} indicated the existence of protonated imine; and the absorption peak of C-H bending vibration out of the plane of the para-disubstituted benzene rings was observed at 796 cm^{-1} [48]. Additionally, a weak peak, which represented the vibration band of the dopant anion, appeared at 1143 cm^{-1} [49]. The results further confirmed that the conductive PANI was successfully synthesized in the composites via the *in situ* polymerization process. The peaks at 606 cm^{-1} corresponded to Sn-O [50] and the other main peaks shown in the SG sample were also almost observed in the PANI-SG composites even though some peaks were influenced due to the presence of PANI, further confirming the initial structure of SG was maintained after the *in situ* polymerization.

To understand the surface chemical composition, the as-prepared 20%PANI-SG composite was studied by XPS analysis with results given in **Fig. 3c**. C, O, N and Sn were detected in the

composite through the survey spectrum within the range of 0-1000 eV. The high-resolution spectrum of C 1s in the 20%PANI-SG sample is shown in the inset of **Fig. 3c**, which could be deconvoluted into five peaks with binding energies centered at 284.6, 285.5, 286.1, 288.0 and 289.0 eV, corresponding to C-C/C-H, C-N/C=N, C-O, C=O and O-C=O groups, respectively [37, 51-53]. Another inset of **Fig. 3c** shows the high-resolution spectrum of N 1s in the 20%PANI-SG sample. A strong peak with binding energy centered at 399.4 eV was present, corresponding to a -NH- group (benzenoid amine). The minor peaks with binding energies centered at 398.8 and 401.3 eV were assigned to =NH- and $N^{+\cdot}$ (nitrogen cationic radical), respectively [52, 53]. The results indicated that the sample surface was successfully coated by PANI. TEM analysis was used to further study the morphology and microstructure of the PANI-SG composites. The typical HR-TEM image of 20%PANI-SG sample is shown in **Fig. 4a**. Ultrafine SnO_2 nanocrystals with diameters of approximately 4 nm and 3-5 layers graphene sheets were observed. This was the typical morphology of SG composite from mechanochemical synthesis [37], indicating that the effect of the *in situ* polymerization process on the microstructure of SG was negligible. A coating layer on the edge was observed as having a different microstructure from the character of SnO_2 nanocrystals and graphene sheets, and it could be attributed to the as-formed PANI. To further verify that the SG particles were coated by PANI, bright-field STEM image with corresponding EDX mappings are shown in **Fig. 4b**. C, N, O and Sn were uniformly distributed, demonstrating that a PANI-coated SnO_2 /graphene nanocomposite was successfully formed.

According to the above results, a possible formation process of a PANI-SG composite was proposed, as shown in **Fig. 5a**. The polymerization of aniline monomer was carried out around the surface of the initial SG chips to form a coating layer instead of cross-liked nanofibers. By increasing the amount of PANI, the surface of the SG chips was gradually covered. With a

relatively low amount of initial aniline monomer, the surface of the SG chips could not be entirely covered. When the surface was covered by PANI, the aniline monomers polymerized to form cross-linked nanofibers as conductive bridges to connect the surface of PANI (**Fig. 2f**). Further increasing the amount of initial aniline resulted in the formation of superfluous cross-linked PANI nanofibers on the surface, as shown in **Fig. 2g&h**. Thus, the 20%PANI-SG sample was estimated to be the optimal material for fast lithium insertion.

The nitrogen adsorption–desorption measurements were carried out to evaluate the microstructures of the SG, 15%PANI-SG, 20%PANI-SG and 25%PANI-SG samples with results shown in **Fig. 5b**. On the basis of the IUPAC classification, all isotherms with distinct hysteresis loops were type IV, indicating that there were rich mesopores in all samples. **Fig. 5c** shows the corresponding pore size distribution plots of different samples according to the desorption branches of the isotherms. A peak centered at small pore size of 3.7 nm for all samples was observed, and it might be an artifact. However, the clear observation of nitrogen desorbing at a relative pressure between 0.4-0.5 indicates that there were real mesopores with diameters smaller than 4 nm in these samples [54]. Table 1 summarizes the specific surface areas and pore volumes of different samples. After coating with PANI, the BET specific surface area of the sample decreased, and it further decreased as the amount of the PANI coating increased. However, the specific surface area for even the 25%PANI-SG sample was still as large as $112.3 \text{ m}^2 \text{ g}^{-1}$. The pore volume of the 15%PANI-SG particles ($0.2205 \text{ cm}^3 \text{ g}^{-1}$) was larger than the SG particles ($0.1919 \text{ cm}^3 \text{ g}^{-1}$), which might be caused by the unique structure of PANI, indicating the as-formed PANI is porous instead of dense. However, when increasing the amount of PANI in the composite, part of PANI might be reunited, resulting in the decrease in pore volumes for 20%PANI-SG, and further for the 25%PANI-SG particles. After *in situ* polymerization, the surface area and pore

structure in the composite was still very attractive for effective electrolyte/electrode contact and lithium ion transportation. Thermogravimetric analysis (TGA) was employed to determine the content of PANI in 15%PANI-SG, 20%PANI-SG and 25%PANI-SG samples (**Fig. 5d**). The weight loss below 100 °C in all curves could be attributed to the evaporation of adsorbed moisture. According to the graphene content in the SG sample (29.3%) and the weight loss of PANI-SG composites, the content of PANI in PANI-SG composites was calculated to be 13.4%, 17.0% and 20.6% for 15%PANI-SG, 20%PANI-SG and 25%PANI-SG, respectively. On the basis of initial mass ratios of aniline:SG powders, the theoretical content of PANI was 13.0%, 16.7% and 20% for 15%PANI-SG, 20%PANI-SG and 25%PANI-SG, respectively, which were consistent with TGA results.

The lithium storage properties of the as-prepared PANI-SG composites were evaluated in coin cells for their potential use as anode materials for LIBs. The first and second discharge-charge curves of the cells with SG, 15%PANI-SG, 20%PANI-SG and 25%PANI-SG electrodes at a high current density of 1000 mA g⁻¹ between 0.01 and 3.0 V are shown in **Fig. 6**. The curves of the PANI-SG composites appeared to be similar in comparison with that of the SG sample. The discharge capacities of these samples were delivered below 1.0 V, which was consistent with that of common SnO₂-based materials. At a high current density of 1000 mA g⁻¹, the SG electrode (**Fig. 6a**) delivered an initial specific discharge capacity of 1260 mA h g⁻¹ (calculated based on the total weight of SG) and subsequent second discharge capacity of 748 mA h g⁻¹. After coating, the 15%PANI-SG electrode (**Fig. 6b**) demonstrated a higher initial discharge capacity of 1465 mA h g⁻¹ (calculated based on the total weight of PANI-SG) and second capacity of 900 mA h g⁻¹ compared to that of the SG electrode. Actually, the PANI usually delivers a low capacity of ≤170 mA h g⁻¹ as an electrode material for LIBs [43]. The electrochemical performance of pure PANI

synthesized in the same process without addition of SG was also investigated; a low initial specific discharge capacity of 137 mA h g^{-1} with subsequent charge capacity of 16 mA h g^{-1} were exhibited (**Fig. S1**), indicating the low capacity contribution of PANI. Thus, the enhanced initial capacity especially at around 0.5 V in 15%PANI-SG at the relatively high current density of 1000 mA g^{-1} might be a result of the enhancement in conductivity to promote the reduction of SnO_2 and irreversible formation of SEI on the surface of PANI. Interestingly, the second discharge capacity of 900 mA h g^{-1} for 15%PANI-SG electrode was calculated based on the total weight of PANI-SG, thus, the capacity of SnO_2 should be even higher since the capacity contribution from PANI was very low. Additionally, from the charge curves as shown in **Fig. 6b**, there are distinct capacity contributions above 2.0 V. Thus, the much higher capacity after coating compared to the commonly recognized theoretical capacity of SnO_2 (782 mA h g^{-1}) might be due to that the presence of PANI helped as-formed Li_2O to react with the metallic Sn to yield SnO_2 , the similar results with reversible conversion reaction from Sn to SnO_2 was also reported for those SnO_2 -based nanocomposites with coating [55-56]. By further increasing the amount of PANI, the initial capacity decreased, especially for the 25%PANI-SG sample (**Fig. 6d**), due to the low capacity contribution of PANI. For the 20%PANI-SG electrode (**Fig. 6c**), a first discharge capacity of 1350 mA h g^{-1} with a subsequent charge capacity of 797 mA h g^{-1} was observed with a Coulombic efficiency of approximately 60% at a high current density of 1000 mA g^{-1} . The low Coulombic efficiency was mainly attributed to some irreversible processes, including the formation of SEI layer and some irreversible amorphous lithium oxide, and lithium storage in the surface defects of PANI. Nevertheless, the Coulombic efficiency in the second cycle of the 20%PANI-SG electrode increased to 94.6%. The CV curve of 20%PANI-SG electrode for the initial cycle in the potential range of 3.0–0.01 V at a sweep rate of 0.1 mV s^{-1} is shown in **Fig. S2**.

A broad cathodic peak between 0.6-1.0 V could be attributed to the formation of solid–electrolyte interface (SEI) layer and Li_2O . The cathodic peak at 0.1 V and its corresponding anodic peak at 0.55V exhibited the alloying and de-alloying processes of Li_xSn .

The cycling performance of the different PANI-SG electrodes at a high current density of 1000 mA g^{-1} was then investigated, with results shown in **Fig. 7a**, in which the cycling performance of the SG electrode is also given as a comparison. Without the PANI coating, the SG sample demonstrated poor cycling stability at a high current density of 1000 mA g^{-1} . The discharge capacity decreased rapidly from 748 mA h g^{-1} at the 2nd cycle to 564 mA h g^{-1} at the 20th cycle and 387 mA h g^{-1} at the 50th cycle. After 100 cycles, the capacity was only 266 mA h g^{-1} with a capacity retention of 35.6% based on the second discharge capacity. After coating with PANI, the capacity for the 15%PANI-SG composite that demonstrated higher initial capacity decreased gradually to 502 mA h g^{-1} at the 100th cycle, which is still much higher compared to that of the SG sample. By increasing the amount of PANI, the initial capacity for the 20%PANI-SG electrode decreased slightly compared to that of the 15%PANI-SG electrode. However, the 20%PANI-SG electrode exhibited the best cycling stability throughout the 100 cycles at such a high current density of 1000 mA g^{-1} , and the a specific capacity at the 100th cycle was more than twice that of the SG electrode. A Coulombic efficiency of approximately 100% was demonstrated especially after 40 cycles, suggesting reversible lithium insertion/extraction at a fast rate. By further increasing the amount of PANI, the measured capacities of the 25%PANI-SG electrode clearly decreased compared to the 15%PANI-SG and 20%PANI-SG electrodes. The performance decrease may be related to a tightly formed PANI coating layer covering the surface and hampering the lithium insertion/extraction in the interior SnO_2 /graphene composite, and excess as-formed PANI nanofibers contributed low capacity. However, a specific capacity of 354 mA h

g^{-1} at the 100th cycle was demonstrated, which is still higher compared to that of the SG electrode. Thus, the 20%PANI-SG sample with an initial aniline:SG mass ratio of 0.2:1 was demonstrated to be a superior electrode material with high specific capacity and stable cycling performance at 1000 mA g^{-1} . **Fig. 8** shows the electrochemical impedance spectra for 20%PANI-SG sample after cycling for different cycles. After 100 discharge-charge cycles at such high current density of 1000 mA g^{-1} , the diameter of semicircle in the high-to-medium frequency range for the 20%PANI-SG electrode changed very slightly compared to that of the SG electrode (**Fig. S3**), suggesting that the 20%PANI-SG electrode was more stable during the fast lithium insertion and extraction processes, which was indeed consistent with cycling performances of SG and 20%PANI-SG electrode.

The cycling performance of a 20%PANI-SG electrode at different rates was further explored with results shown in **Fig. 7b**. The initial capacity at a current density of 100 mA g^{-1} is higher than that at 1000 A g^{-1} . With cycles performed at 100 mA g^{-1} , the capacity decreased slowly and the 20%PANI-SG electrode delivered an average capacity of 904 mA h g^{-1} (2nd to 10th cycle). By further increasing the current density to 500, 1000, 2000 and 3000 mA g^{-1} , the capacity became relatively stable at each stage. The specific capacities were 681 (16th cycle), 568 (26th cycle), 467 (36th cycle) mA h g^{-1} at 500, 1000 and 2000 mA g^{-1} , respectively. Even at a high current density of 3000 mA h g^{-1} , a specific capacity of 381 mA h g^{-1} (46th cycle) was achieved, which was still higher compared to the theoretical capacity of the commercial graphite anode material (372 mA h g^{-1}). When the current density decreased stepwise from 3000 to 100 mA g^{-1} , the capacity could almost fully recover, suggesting a stable electrochemical performance of 20%PANI-SG electrode due to the unique structure and enhanced conductivity resulting from the network constructed by the interaction of PANI and graphene. First, PANI tightly surrounded the SnO_2 nanocrystals and

graphene during the *in situ* polymerization process. This not only prevented SnO₂ nanoparticles and graphene sheets from aggregating and restacking, respectively, but also further decreased mechanical strains on the ultrafine as-formed SnO₂ nanocrystals through interactions with the graphene layers during the lithium insertion/extraction processes and accommodated the volume variation of SnO₂ nanoparticles. Second, the coated PANI and as-formed PANI nanofiber bridges that connected the SG particles are conductive, resulting in the current collecting effect in addition to enhanced conductivity of the composite. Additionally, the conductive PANI coating did not appear to be dense but porous according to the nitrogen adsorption–desorption measurement, thus enhancing the transport of lithium ion into/out of the SG composite. At the same time, the large surface area and rich mesopores of the composites increase the electrolyte/electrode contact area. All of the above characteristic properties result in enhanced electrochemical performance of the 20%PANI-SG composite, especially for fast lithium insertion, assuring its application as a competitive anode material for LIBs.

4. Conclusion

PANI-coated SnO₂/graphene composites were successfully prepared by an *in situ* polymerization reaction using aniline and mechanochemically synthesized SnO₂/graphene as raw materials with different mass ratios (0.15:1, 0.2:1 and 0.25:1, aniline:SG). The *in situ* polymerization reaction did not affect the structure of the initial SnO₂/graphene composite. The coated PANI was uniformly distributed according to the EDX elemental distribution in the TEM, and it appeared to be porous instead of dense, as determined by the nitrogen adsorption-desorption measurement. The porous structure indicates that the *in situ* polymerized PANI not only enhances electrical conductivity but also is beneficial to lithium-ion insertion/extraction. The optimal mass ratio of aniline to SnO₂/graphene was found to be 0.2:1, which results in a unique structure with a

conductive PANI coating layer and PANI nanofiber bridges and further demonstrates excellent electrochemical performance as an anode material for LIBs with a stable capacity throughout 100 cycles at a high current density (1000 mA g^{-1}) as well as an outstanding rate capability. The as-synthesized PANI-SG composite demonstrates great potential for commercial applications as an anode material in LIBs. The preparation process combining mechanochemical synthesis and *in situ* polymerization also establishes a novel avenue to realizing the large-scale commercial application of advanced next-generation electrode materials.

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Table 1

Samples	Specific surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
SG	262.1	0.1919
15%PANI-SG	216.0	0.2205
20%PANI-SG	158.5	0.1716
25%PANI-SG	112.3	0.1306

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Graphical Abstract