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A freestanding composite film electrode stacked from hierarchical electrospun SnO$_2$ nanorods and graphene sheets for reversible lithium storage

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A freestanding hierarchical SnO$_2$ nanorod/graphene composite film electrode was designed and fabricated by a general route including electrospinning and film casting processes. With dual adaptable strategies (hierarchical nanorod structure and graphene “overcoats”), the composite film electrode exhibited enhanced cycling stability.

Since Sony Corporation developed and released the first commercial lithium-ion battery (LIB) in 1991, rechargeable LIBs have become one of the most popular power sources for portable personal electronics due to their high energy density, environmental compatibility and the fact that they display no memory effect.$^{1-3}$ However, the rapid development of personal electronic devices has led to a rapid growth in the demand for higher capacity LIBs. Tin oxide (SnO$_2$) is a promising candidate as an anode for LIBs due to its extremely high theoretical capacity (782 mA h g$^{-1}$), which is more than twice that of commercial graphite anodes (372 mA h g$^{-1}$).$^{4,5}$ The drawback to conventional bulk SnO$_2$-based materials is their characteristically large variation in volume (>200%) during the lithium insertion/extraction process,$^{6,7}$ which easily leads to pulverization and delamination of the electrode from the current collector; thus, a quick decay of the electrochemical performance is often observed. To solve these problems, two leading approaches have been applied. One method is the preparation of various SnO$_2$ nanostructures, such as nanoparticles,$^8$ nanotubes,$^9$ nanoboxes,$^{10}$ nanowires,$^{11,12}$ nanorod arrays$^{13}$ and hollow spheres$^{14,15}$. Another effective method is the synthesis of SnO$_2$-based composites, such as SnO$_2$/Cu,$^{16}$ SnO$_2$/carbon,$^{17,19}$ SnO$_2$/graphene$^{20,21}$ and SnO$_2$/carbon nanotubes$^{22,23}$.$^{24}$ SnO$_2$ nanostructures are able to release mechanical strain, and the introduction of the void space from the special structures and carbon are helpful in accommodating the volume variation during the lithium insertion/extraction process.

Recently, there has been a growing interest in the development of flexible, lightweight and high-power thin-film electrodes for LIBs.$^{24-26}$ During the conventional electrode preparation process, a conductive agent and binder are necessary.$^{10,21,27,28}$ The binder, which is insulating and electrochemically inactive, will decrease the effect of the current collection and reduce the contact area between the active material and the liquid electrolyte. By applying thin films as binder-free anodes for LIBs, the conventional process of electrode preparation, which involves slurry mixing and coating, is replaced, and the additional conductive agent and binder are avoided. This results in a reduction in the electrode resistance and an improvement of the volumetric/gravimetric energy densities.

Electrospinning is recognized as a simple and versatile method for fabricating nanofibers from various raw materials.$^{26,29-31}$ Meanwhile, a nonwoven thin film can be easily obtained by the deposition of nanofibers using the electrospinning technique. In contrast to other methods for producing thin films, there is no requirement of complex equipment or special substrates for electrospinning. Moreover, electrospinning is a continuous process with a high production rate, and the produced film is freestanding. SnO$_2$-based fibers have been successfully fabricated using electrospinning combined with a calcination process.$^6,32,35$ However, most of these fibers were converted into electrodes using the conventional electrode preparation because SnO$_2$ itself is inflexible and the film after calcination in air has poor mechanical strength. Introduction of carbon into the electrospun film could enhance the mechanical properties and make the film flexible.$^{26,35}$ However, a high temperature was necessary for carbonization of the polymer; SnO$_2$ is easily reduced to Sn in the presence of carbon and reducing gas (e.g., CO), which is produced from the polymer decomposition at a high temperature. The melting point of Sn is only 232 °C,$^{36}$ which leads to rapid growth of Sn/SnO$_2$ nanoparticles. Thus, complicated fabrication steps, such as coaxial electrospinning$^{32}$ or the use of high carbon contents (>70 wt%)$^{35}$, were needed to prevent agglomeration of the SnO$_2$ nanoparticles. Thus, it is difficult to fabricate flexible freestanding electrospun films with a high content of SnO$_2$ through a facile electrospinning method. Recently, graphene oxide (GO) was found to be easily assembled into films due to the attached oxygen-containing functional groups.$^{37,38}$ After a deoxygenating process, a freestanding conductive graphene film could be obtained. However, the ordinary pure graphene film exhibited poor electrochemical performance due to the loss of its large surface area caused by the tight stacking of the graphene sheets.$^3$ Thus, the preparation of composite...
films may be a promising strategy. The interconnecting graphene matrix may show superior electrical conductivity, and the high flexibility of the graphene sheets could be able to accommodate the large volume variation of the active material during the lithium insertion/extraction process.

In this work, a freestanding hierarchical SnO$_2$ nanorod/graphene composite film was prepared as a binder-free anode for LIBs. The hierarchical SnO$_2$ nanorods, which are composed of SnO$_2$ nanoparticles 11–20 nm in diameter, were fabricated by facile electrospinning and sedimentation separation processes. The hierarchical nanorod structure is an adaptable design for accommodating the large volume variation during the charge/discharge cycles. The compact conductive graphene sheets in the formed composite film act as the other adaptable strategy. With these dual adaptable strategies, the hierarchical SnO$_2$ nanorod/graphene composite film electrode exhibited a high reversible capacity and enhanced cycling stability.

Fig. 1 shows the preparation process of hierarchical SnO$_2$ nanorods/graphene film. SnO$_2$ nanofibers were first fabricated using an electrospinning method with a subsequent calcination process (500 °C in air). Then a facile sedimentation separation process was used for obtaining well-dispersed SnO$_2$ nanorods from the SnO$_2$ nanofibers. And a subsequent film casting process together with GO solution was conducted for the formation of composite film. Finally, a calcining treatment in Ar was carried out to obtain the SnO$_2$ nanorods/graphene film. The morphology and microstructure of the electrospun SnO$_2$ nanofibers after calcination were investigated by field-emission scanning electron microscopy (FE-SEM). Typical FE-SEM images are shown in Fig. S1 (see ESI†). The diameters of the nanofibers were mostly 210±90 nm (Fig. S1a). There was also a small amount of ultrafine nanofibers with diameters of ~70 nm, which may have formed due to the fluctuations during the electrospinning process. A magnified image (Fig. S1b) reveals that the surface of these SnO$_2$ nanofibers was rough. Each nanofiber was in a hierarchical structure composed of ultrafine SnO$_2$ nanoparticles.

For the film preparation, the direct dispersion of the as-obtained SnO$_2$ nanofibers in the GO solution was first attempted using a probe ultrasonic homogenizer. The solution was then transferred to the polytetrafluoroethylene (PTFE) cell and placed in the drying oven at 60 °C. However, before all of the solvent (water) could evaporate, parts of the white nanofibers sunk to the bottom. After drying, one side of the obtained film was white in color, suggesting that large
calcination process in air, the organic material was oxidized to gas, while the (IV) source was converted to solid crystallized SnO$_2$. The produced gases diffused rapidly at the high temperature, which prevented the agglomeration of the SnO$_2$ particles. Due to the relatively low calcination temperature (500 °C), the hierarchical structure stacked with SnO$_2$ nanoparticles was retained, thus fulfilling the first adaptable strategy. Fig. 2d shows the SAED pattern of the SnO$_2$ nanorods, which is composed of a series of concentric rings corresponding to the (110), (101) and (211) lattice planes, suggesting the polycrystalline character of the nanorods and the tetragonal SnO$_2$ phase structure.

Fig. 3. (a) XRD pattern, (b, c) FE-SEM images (b) surface and (c) cross-section) and (d) TEM image of the SnO$_2$ nanorod/graphene film.

By using the well-dispersed SnO$_2$ nanorods together with the GO solution for film casting, a homogeneous SnO$_2$ nanorod/graphene composite film was easily fabricated. The phase structure and purity of the SnO$_2$ nanorod/graphene composite film were investigated by XRD. As shown in Fig. 3a, the composite after the calcination in Ar at 500 °C for 3 h also exhibited a tetragonal SnO$_2$ phase structure (JCPDS, No.: 41-1445), free from Sn or SnO impurity phases. The broadened peak of graphene was merged with the (110) peak of SnO$_2$. The intensity and width of the peaks were similar in comparison with the pattern of the pure SnO$_2$ nanorods, suggesting that the additional calcination did not significantly affect the SnO$_2$ crystalline size. Fig. 3b presents the surface morphology of the SnO$_2$ nanorod/graphene composite film.

The hierarchical structure of the SnO$_2$ nanorods was well maintained. There were some SnO$_2$ nanorods deposited on the surface of the graphene sheets, and the graphene sheets covered the SnO$_2$ nanorods. It should be mentioned that the surface morphology of both sides of the composite film was similar, indicating a high homogeneity of the composite film. Fig. 3c shows the cross-sectional morphological image of the SnO$_2$ nanorod/graphene composite film. It is clear that the nanorods (some of them are hollow) were well sandwiched between the graphene sheets. During the film casting process, the SnO$_2$ nanorods and GO sheets were randomly deposited and assembled into a composite film with the evaporation of water. After calcination, the conductive graphene sheets in the composite film acted as “overcoats” of the SnO$_2$ nanorods to provide the second adaptable strategy. Graphene structure was confirmed by the TEM observation (Fig. 3d) and the XPS analysis (Fig. S3, see ESI†). The Raman spectrum (Fig. S4, see ESI†) shows two broad peaks at approximately 1352 and 1598 cm$^{-1}$, corresponding to the D (defect-related) and G (doubly degenerate zone center $E_g$ mode) bands of the carbon material. The strong D band suggests the presence of a large numbers of defects for the graphene in the composite film. The carbon content in the composite was 44.6 wt.%, estimated from the thermogravimetric analysis (TGA) in air (Fig. S5, see ESI†).

Fig. 4. (a) The discharge/charge curves of SnO$_2$ nanorod/graphene film at 100 mA g$^{-1}$ between 0.005 and 2.0 V, the inset is a digital photo; (b) the cycling performance (discharge capacity) of the various electrodes at 100 mA g$^{-1}$ between 0.005 and 2.0 V: i) SnO$_2$ nanorod/graphene film, ii) graphene film and iii) SnO$_2$ nanorod electrode prepared using a slurry coating technique with Super P; (c) electrochemical impedance spectra of the cells with SnO$_2$ nanorod/graphene film and graphene-free SnO$_2$ nanorod+Super P electrode.

The electrochemical performance of the hierarchical SnO$_2$ nanorod/graphene composite film (inset of Fig. 4a) was evaluated as the anode in a half cell without any additional conductive agent or binder. Fig. 4a shows representative discharge/charge curves of the SnO$_2$ nanorod/graphene composite film electrode. The first discharge capacity of the composite film was 1264 mA h g$^{-1}$ (calculated based on the mass of SnO$_2$ nanorods and graphene), and the subsequent charge capacity was 484 mA h g$^{-1}$. The Coulombic efficiency for the first cycle was only 38%. The low coulombic efficiency was due to the irreversible formation of lithium oxide (Li$_2$O undergoes a conversion reaction with SnO$_2$) and the solid-electrolyte interface (SEI) layer.$^{2,5}$ However, the Coulombic efficiency increased to 94% at the second cycle and almost kept higher than 95% at subsequent cycles (Fig. S6). And the cycling performance after the first cycle was relatively stable through 50 cycles (Fig. 4a&b). A pure graphene film electrode was also prepared in a similar fashion and investigated as free-standing electrode, delivering discharge capacities of 792, 341, 281 and 247 mA h g$^{-1}$ at the first, second, fifth and 50th cycles, respectively. These values were substantially lower than those of the hierarchical SnO$_2$ nanorod/graphene composite film. For comparison, the SnO$_2$ nanorods were also prepared to be a graphene-free electrode using a conventional slurry coating procedure. As shown in
In summary, we have successfully prepared a freestanding hierarchical SnO$_2$ nanorod/graphene composite film using an electrospinning and film casting route. The well-dispersed SnO$_2$ nanorods could be easily obtained from electrospun SnO$_2$ nanofibers by a facile sedimentation separation process. By applying the composite film with dual adaptable strategies (hierarchical SnO$_2$ nanorod structure and graphene overcoats) as a binder-free anode for LIBs, it exhibited an enhanced cycling performance with a capacity of 467 mA h g$^{-1}$ even after 50 charge-discharge cycles. We believe that the facile sedimentation separation process could also be used to separate various nano-materials and that the general synthesis route presented here could also be used to fabricate other composite anodes or cathodes for reversible lithium storage.

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**Notes and references**