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SnO_2/C composites fabricated by Bio-templating method from cotton and their electrochemical performances

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Biomorphic SnO_2/C composites were synthesized by a facile bio-templating method using natural cotton as structure template and bio-carbon source. The content of carbon in the composites could be easily adjusted by varying sintering temperature. Electrochemical tests demonstrated that the content of carbon in the obtained composites had great effects on their electrochemical performances, such as the biomorphic SnO_2/C composites prepared at 300 °C exhibited a reversible capacity of 530 mAh g^{-1} up to 100 cycles at a current density of 100 mA g^{-1}. The results suggest that the obtained biomorphic SnO_2/C composites prepared by the facile approach may be used as anode materials in practical lithium-ion batteries.

Introduction

Lithium-ion batteries (LIBs), currently as ubiquitous power sources for consumer electronics, are now considered for electric or hybrid vehicles.[1] To improve the energy density and cycling life capacity of battery system, a great deal of efforts have been made to take a further step in superior performance electrode materials.[2] As one of the most promising anode materials, SnO_2 has attracted extensive attention as a potential substitute for carbon anode (theoretical capacity 372 mAh g^{-1}) because of its higher theoretical capacity (782 mAh g^{-1}).[3] However, the practical application of SnO_2 is hindered by huge volume change of 300% during Li^+ insertion/extraction process, which leads to very rapid capacity decay and pulverization of electrodes.[4] To solve the problem and further enhance the structural stability, one effective strategy is to design different nanostructures, such as nanorods, nanowires, nanotubes and so on.[5-7] Another commonly used approach is to fabricate hybrid nanocomposites, such as metal oxide-graphene and nanocable-like architectures, to improve the cycling performances in energy storage applications because the micro-/nano-carbon based supports could improve the structural integrity.[8-13] Although the performances of electrodes have been improved a lot based on above ways, the preparation procedure was usually complicated and costly, and it is still difficult to synthesize anode materials with good electrochemical properties on large scale for practical applications.

Recently, biomorphic mineralization has been noteworthy as a new nanofabrication technique for functional materials.[14] The advantage of the biomorphic mineralization process is not only low-cost and environmentally benign, but also control of the structure, size, morphology and crystallographic orientation of inorganic materials.[15] For example, cotton fibre with more uniform morphology than other plant fibres has been used as template to prepare SnO_2 microtubules.[16]

Herein, a facile bio-synthesis strategy was proposed to prepare biomorphic SnO_2/C composites on large-scale by using cotton as template and biocarbon source. Electrochemical tests demonstrated that the content of carbon in the composites had great effects on their electrochemical performances.

Experimental section

Synthesis of biomorphic SnO_2/C composites

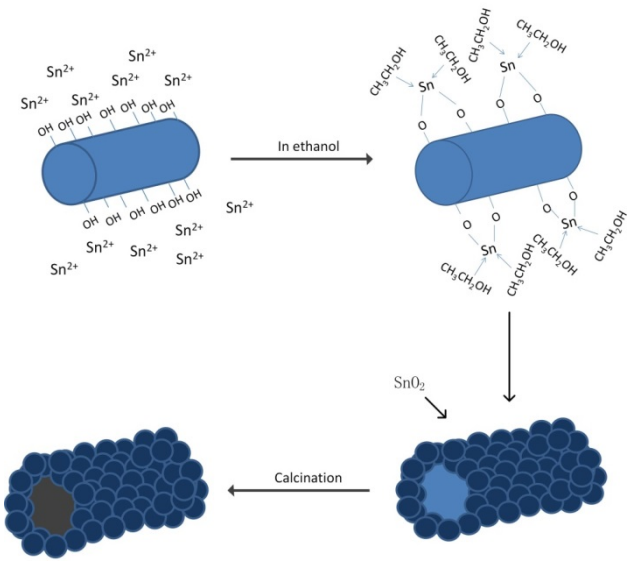
In a typical synthesis of biomorphic SnO_2/C composites, 0.05mol of tin dichloride dehydrate ($SnCl_2 \cdot 2H_2O$) was dispersed in 120 mL of ethanol. The solution was transferred into the conical flask and stirred for 4 hours at 60 °C. Then the dried and loose cotton fibres were immersed into above solution for 24 hours at room temperature. And then the cotton fibres were taken out and dried for 12 hours at 60 °C. Finally, SnO_2/C composites with cotton-like morphology were obtained by sintering the treated cotton fibres in air at 300, 400 and 500 °C for 1 hour, respectively.

Characterization

Morphology of the obtained products was characterized by FESEM (JSM-7401F) and TEM (JEOL, JEM-2100). Powder X-ray diffraction (XRD) was recorded on a Shimadzu XRD-6000 with Cu-Ka radiation, and the voltage and current of X-ray tube is of 40 kV and 30 mA, respectively. Thermogravimetric (TG) analysis was carried out on a Perkin-Elmer 7 instrument to determine the weight content of SnO_2/C composites.

Electrochemical testing

Electrode was made of active material (SnO_2/C composites), conductivity agent (acetylene black) and polymer binder (polyvinylidene difluoride, PVDF) in the weight ratio of 8:1:1. Electrolyte is 1 mol L^{-1} solution of $LiClO_4$ in a mixture of ethylene carbonate (EC)/diethylene carbonate (DEC) (1:1 vol%). Cells were assembled in an argon-filled glove box with SnO_2/C



Scheme 1. Schematic illustration of the preparation process for Biomorphic SnO_2/C composites

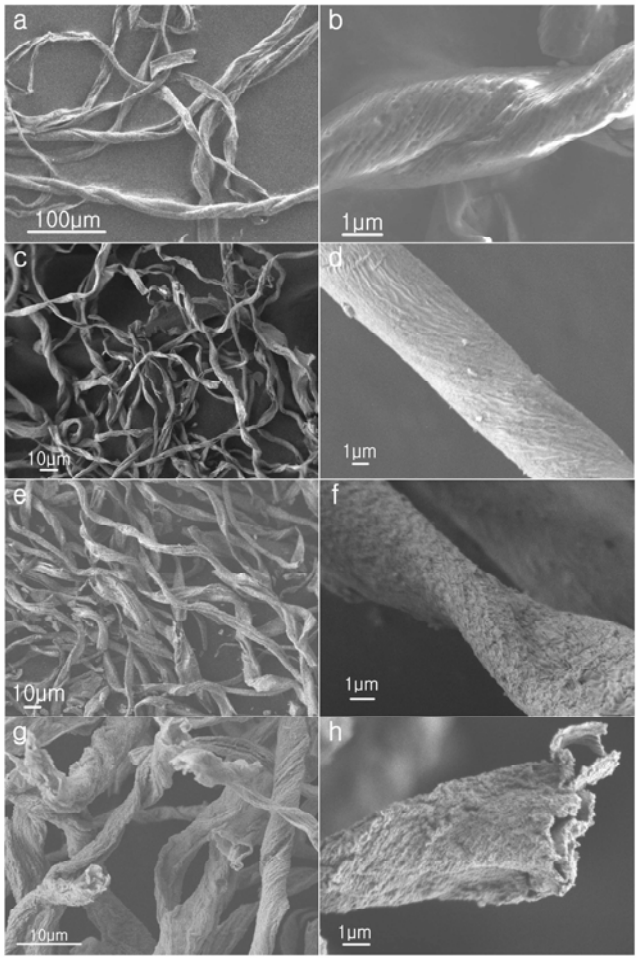


Fig. 1 FESEM images of cotton template (a, b) and SnO_2/C composites prepared at different calcination temperature: 300 °C (c, d), 400 °C (e, f), 500 °C (g, h).

composites electrode as working electrode and Li metal as counter electrode. Charge-discharge cycles of cells were measured between 0.01 and 3 V vs. Li^+/Li using a battery test instrument (LAND CT2001A model, Wuhan Jinnuo Electronics, China) at room temperature. Cyclic voltammetry (CV) was conducted on the workstation at a scanning rate of 0.1 mV/s in a potential range of 5 mV-3.0 V (vs. Li/Li^+).

Results and Discussion

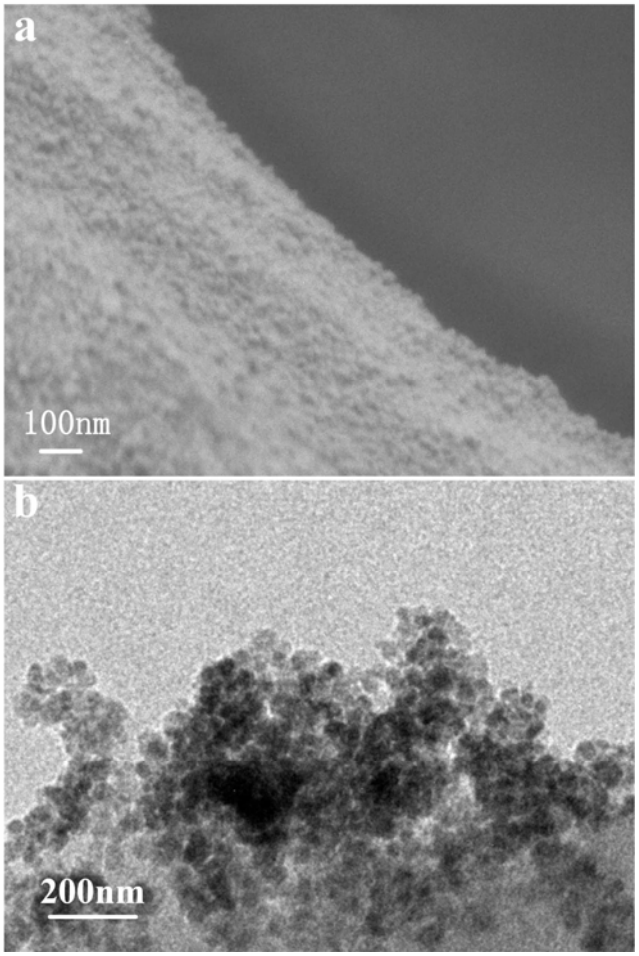


Fig. 2 SnO_2/C composite prepared at 300 °C: (a) FESEM image, (b) TEM image.

As illustratated in Scheme 1, natural cotton fibres possess abundant surface hydroxyl groups, so Sn^{2+} ions would be adsorbed onto the surface by electrostatic interaction, and then SnO_2 nanoparticles would form on it by the *in-situ* way. Than, SnO_2/C composites with cotton-like morphology were obtained by sintering the treated cotton fibres in air at 300, 400 and 500 °C for 1 hour, respectively. FESEM images of cotton template and the products prepared at different calcination temperature are shown in Fig. 1. The low-magnification SEM images (Fig. 1c, e, g) unambiguously show that all the obtained biomorphic SnO_2/C composites are in long and zonal structure, which is similar to that of cotton template (Fig. 1a). Obviously, all these SnO_2/C composites can duplicate the morphology of cotton template and present biomorphic structure. No notable differences can be observed for the SnO_2/C materials obtained at 300 °C and 400 °C (Fig. 1c, e), while the SnO_2/C composites obtained at 500 °C (Fig. 1g) are microtubule with porous structure. With the increase of calcination temperature, the surface of carbon microfibers turns

coarser (Fig. 1d, f, h).

In order to further investigate the microstructure of the obtained biomorphic SnO_2/C composites prepared at 300 °C, more detailed characterization was carried out. FESEM image (Fig. 2a) shows that the surface of the as-synthesized SnO_2/C composites is made of nano-sized small particles, and TEM image (Fig. 2b) further reveals that these SnO_2 NPs are about 20 nm in size. The tiny SnO_2 NPs are distributed into the pores or cover the surface of the biocarbon generated from cotton, so it can block the physical aggregation of SnO_2 NPs and enhance the structural stability, which is beneficial to improve the lithium-ion battery performance.

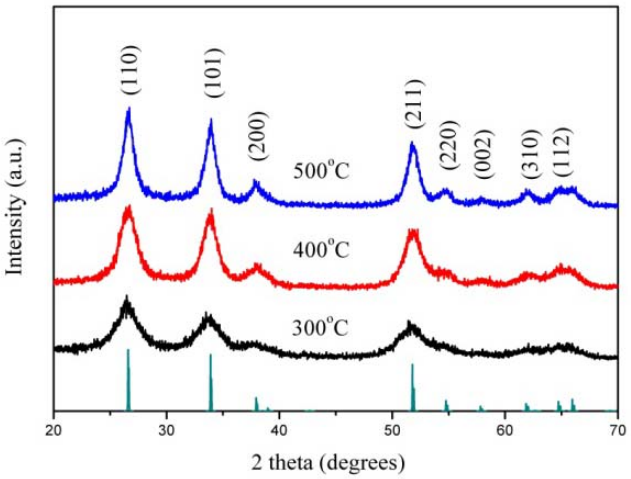


Fig. 3 XRD patterns of the SnO_2/C composites prepared at different calcination temperature.

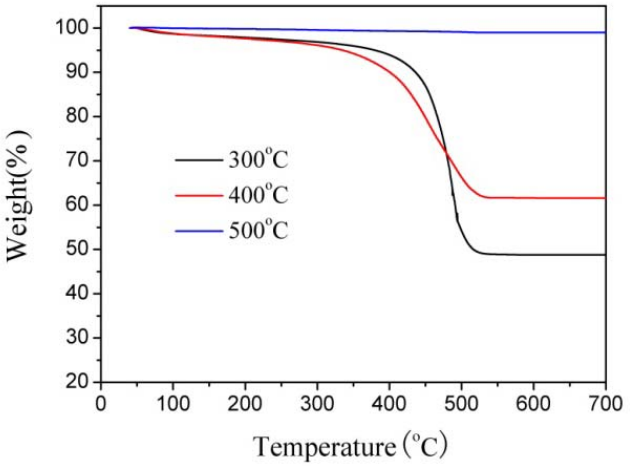


Fig. 4 TGA curves of SnO_2/C composites prepared at different calcination temperature.

XRD patterns (Fig.3) indicate that the as-prepared biomorphic SnO_2/C composites are a tetragonal rutile SnO_2 structure (JCPDS CARD No. 41-1445). No signals from possible impurities, such as SnO or Sn, are observed, implying high phase purity of the obtained products. The absence of carbon peaks suggest that carbon is mainly in amorphous phase. Fig. 4 shows the TGA curves of the biomorphic SnO_2/C composites prepared at different calcination temperature, and the samples were heated from 30 to 700 °C in air at a rate of 10 °C min^{-1}. The first weight loss occurs in the temperature range of 30-150 °C corresponding to the removal of water and the residual organic molecular absorbed on samples, while the second weight loss in the temperature range of 200-500 °C is ascribed to the oxidation of carbon template, and the carbon is burn off over 600 °C for all samples. Therefore, according to the change in weight before and after the oxidation of carbon, the content of carbon in samples can be calculated as 47.3%, 34.5% and 1.1% for the samples prepared at 300, 400 and 500 °C, respectively.

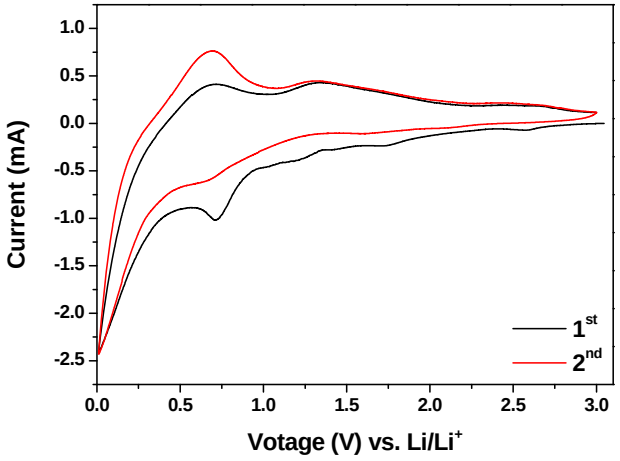


Fig. 5 CV curves of the SnO_2/C composites prepared at 300 °C.

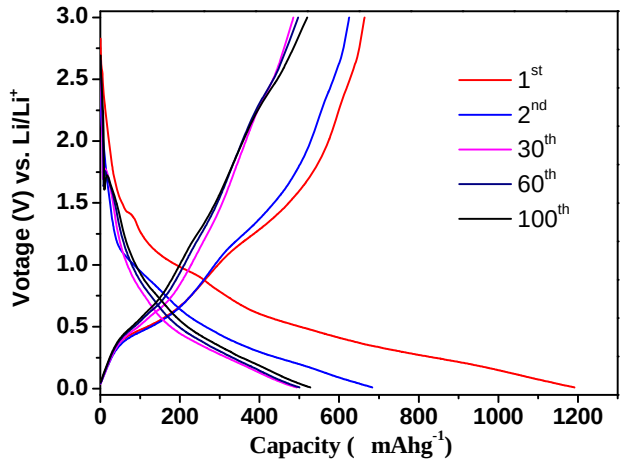


Fig. 6 Charge-discharge curves of the SnO_2/C composites prepared at 300 °C.

The properties of the biomorphic SnO_2/C composites as an anode material for LIBs were further studied. Fig. 5 shows the CV curves of the SnO_2/C composites prepared at 300 °C for the first two cycles. The CV behaviour is generally consistent with previous reports,[17] indicating the similar electrochemical reaction pathway. The two apparent reduction peaks around 1.62 and 0.69 V in the first cathodic sweep can be ascribed to the formation of solid electrolyte interface (SEI) layer and the reduction of SnO_2 to Sn and Li_2O, respectively.[18,19] The other dominant peaks between 0.6 and 0 V are related to the formation of Li_xSn alloys.[20,21]

Fig. 6 depicts the discharge/charge voltage profiles of the 1st, 2nd, 30th, 60th and 100th cycle for the biomorphic SnO_2/C

composites prepared at 300 °C cycled between 0.01 and 3.0 V at a constant current density of 100 mA g^{-1}. The initial discharge and charge capacities are around 1190 and 680 mAh g^{-1}, respectively. The large capacity loss in the first cycle is common for SnO_2-based anode, which is mainly attributed to the initial irreversible formation of Li_2O and inevitable formation of a solid electrolyte interface (SEI) layer as well as additional reaction from conducting agent.[22,23]

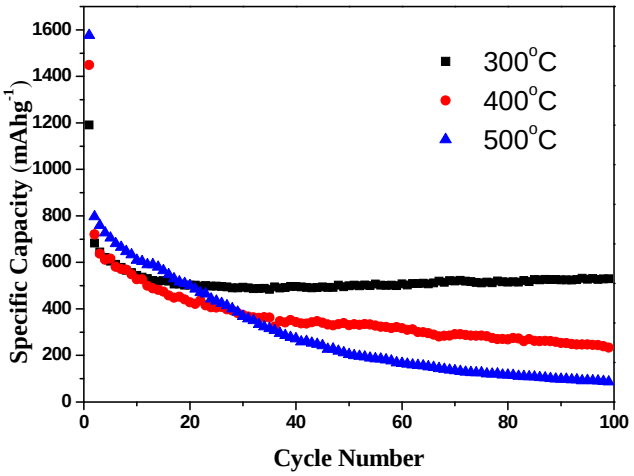


Fig. 7 The cycling performance of the biomorphic SnO_2/C composites prepared at different calcination temperature.

Fig. 7 shows the cycling performances of the biomorphic SnO_2/C composites prepared at 300, 400 and 500 °C, respectively. At the current density of 100 mh g^{-1}, the initial discharge capacities are about 1190 mAh g^{-1} (300 °C), 1450 mAh g^{-1} (400 °C) and 1570 mAh g^{-1} (500 °C), indicating that the initial discharge capacity increases with the decreasing content of carbon in samples. However, the discharge capacities of the samples prepared at high temperatures decline quickly. For example, the reversible capacity is only 230 mAh g^{-1} and 87 mAh g^{-1} after 100 cycles for the products prepared at 400 °C and 500 °C, respectively, while it can keep around 530 mAh g^{-1} for the biomorphic SnO_2/C composites prepared at 300 °C. One can note that the theoretical capacity of the biomorphic SnO_2/C composites prepared at 300 °C is 589 mAh g^{-1} (calculated by 782*53%+372*47%=589), it means that the capacity (around 530 mAh g^{-1}) of biomorphic SnO_2/C composites prepared at 300 °C corresponds to ~90% of the theoretical value.

The improved electrochemical performance the biomorphic SnO_2/C composites prepared at 300 °C could be attributed to the unique biomorphic structures. Firstly, tinny SnO_2 nanoparticles can mitigate the volume change effect and shorten the diffusion length for lithium ions. Secondly, SnO_2 nanoparticles are distributed into the pores or cover the surface of the biocarbon generated from cotton, so it can block the physical aggregation of SnO_2 NPs and enhance the structural stability. Furthermore, the biocarbon can act as a buffer layer during the charge-discharge cycling process to improve the performance of the biomorphic SnO_2/C composites.

Conclusion

In summary, a facile bio-synthesis method was designed to fabricate biomorphic SnO_2/C composites by using simple cotton as both template and biocarbon source on large-scale. Further studies indicated that the content of carbon in the composites could be easily tuned by varying the sintering temperature and have important effects on the electrochemical properties as anode materials for lithium-ion batteries, such as the biomorphic SnO_2/C composites prepared at 300 °C exhibited better reversible capacity of 530 mAh g^{-1} after 100 cycles. This strategy is simple, low-cost and green, which could be extended to other biomorphic metal oxides/C composites for lithium-ion batteries.

Acknowledge

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Notes and references

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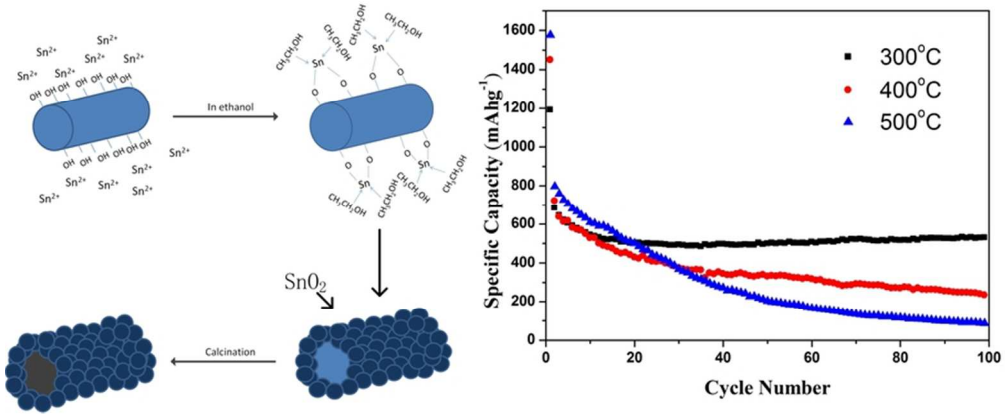

Biomorphic SnO_2/C composites were synthesized by a facile bio-templating method using natural cotton as structure template and bio-carbon source. The biomorphic SnO_2/C composites calcinated at 300 °C exhibited a reversible capacity of 530 mAh g^{-1} up to 100 cycles at a current density of 100 mA g^{-1}.

76x31mm (300 x 300 DPI)