Rapid preparation of SnO$_2$/C nanospheres by using organotin as building blocks and their application in lithium-ion batteries†

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Constructing an electrode integrating ultralow SnO$_2$ size, stable carbon barriers and well-developed pore structure are effective to address the issues of crack and pulverization for SnO$_2$-based electrode during lithiation/delithiation process. But until now, it is still a challenge to exploit simple and robust method to fabricate ultrasmall SnO$_2$ particles embedded in a carbon matrix. Herein, we develop a rapid strategy to prepare SnO$_2$/C nanospheres using a simple Friedel–Crafts crosslinking of triphenyltin chloride for only 15 min and subsequent carbonization. The SnO$_2$/C nanospheres (~500 nm) have ultrasmall SnO$_2$ particles of 4 nm, which were dispersed in carbon continuous phase. Moreover, the pyrolysis of the polymer during carbonization creates considerable micropores inside the carbon phase and leads to a surface area of 463.3 m$^2$/g. When used as electrode materials in a lithium-ion battery, the ultrasmall SnO$_2$ particles can prevent the cracking of the electrode, the carbon continuous phase can act as a buffer to protect SnO$_2$ particles from aggregation, and micropores will supply expansive space for volume change. Thus, the SnO$_2$/C nanosphere exhibits superior electrochemical performance, e.g., the first discharge and charge capacities can reach 1453 and 719 mA h g$^{-1}$ respectively, and 120 cycles later, its capacity remains 629 mA h g$^{-1}$, indicating a capacity retention of 87.4% (C$^{100}/$C$^{120}$).

Integrating ultralow SnO$_2$ size, stable carbon barriers and well-developed pore structure in one electrode material is an effective way to overcome crack and pulverization of SnO$_2$-based electrode. First, it was reported that nanosized SnO$_2$ particles can mitigate the strain generated during discharge/charge process at a certain extent. Inspired by this phenomenon, a SnO$_2$/C nanocomposite with 4.3 nm-sized SnO$_2$ nanoparticles dispersed in carbon network was prepared by Wang’s group via decomposition of Sn(OH)$_4$ in polyacrylic acid hydrogel and subsequent carbonization. This SnO$_2$/C displayed an initial discharge capacity of 1460 mA h g$^{-1}$ and maintained a reversible capacity of 597.3 mA h g$^{-1}$ at a current density of 100 mA g$^{-1}$ after 200 cycles. Second, constructing stable carbon barrier has also been proved to be efficient way to improve electrochemical performance. For example, core-shell SnO$_2$/C composite developed by Yang’s group showed a stable capacity of 430 mA h g$^{-1}$ after 100 cycles. It is believed that the carbon shell protects SnO$_2$ particles from self agglomeration and cracking during lithiation/delithiation process. Besides, porous structure can serve as the transport access of lithium ions and provide expansive space to accommodate the volume change of SnO$_2$ particles, which is another frequently-used way to enhance the rate performance and cycle stability of SnO$_2$-based electrode. Ko and coworkers developed porous SnO$_2$/C nanocomposite by spray pyrolysis process, and the composite exhibited a reversible capacity of 509 mA h g$^{-1}$ after

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1000 discharge/charge cycles at a current density of 1.5 A g\(^{-1}\).\(^{14}\) These above-mentioned strategies have achieved great success in exploiting novel SnO\(_2\)-based anode materials with high capacity and stable cycling performance. However, these methods are based on inorganic Sn-containing salts with complicated preparation steps, and there are still few SnO\(_2\)-based anode materials that incorporate ultralow SnO\(_2\) particle size (<10 nm), carbon matrix and porous structure, simultaneously.

In this paper, we elaborate a novel, facile and rapid method of preparing SnO\(_2\)/C nanosphere with ultrasmall SnO\(_2\) particles simply by using a Friedel–Crafts crosslinking of triphenyltin chloride (Sn-Ph) in a short time of 15 min (Fig. 1). Crosslinking induced phase separation creates spherical crosslinked product with a diameter of ca. 600 nm, and Sn atoms are embedded in the nanospheres uniformly. During carbonization, the crosslinked polymer converts into carbon framework, meanwhile, Sn atoms aggregate in situ and result in the generation of 4 nm-sized SnO\(_2\) particles. In addition, pyrolyzation of polymer creates considerable micropores inside the carbon continuous phase and SnO\(_2\)/C nanospheres present a surface area of 463.3 m\(^2\) g\(^{-1}\). When the SnO\(_2\)/C nanospheres are applied in lithium-ion batteries, it exhibits four advantages: (i) an average diameter of ~500 nm can shorten the transport distance of lithium ions, (ii) ultralow size of SnO\(_2\) particles can prevent the crack of electrode, (iii) carbon matrix will act as buffer to protect SnO\(_2\) particles from aggregation and mitigate the absolute strain induced by large volume change during lithiation/delithiation process, (iv) porous structure provides pathways of lithium-ion transport and supplies nanospace for volume change of SnO\(_2\) particles to prevent cracking. Owing to these unique structure features, SnO\(_2\)/C nanospheres present high initial discharge and charge capacities of 1453 and 719 mA h g\(^{-1}\) respectively. 120 cycles later, the capacity remains 629 mA h g\(^{-1}\), demonstrating a high capacity retention rate of 87.4% (\(C_{120}\)/\(C_{1st}\)). Furthermore, the simple and rapid process of preparation, and low cost of raw materials make it easy to realize large-scale production while put the method into application.

**Experimental**

**Preparation of SnO\(_2\)/C nanospheres**

The SnO\(_2\)/C nanospheres were prepared using a method of organic crosslinking. At first, 2 g triphenyltin chloride and 4 g anhydrous AlCl\(_3\) were dissolved in 80 mL 1,2-dichloroethane at 60 °C for several minutes, and then 4 mL dimethoxymethane was transferred into the liquor. 15 minutes later, the product was filtered off and washed with deionized water and ethanol for four times. After drying in vacuum at 80 °C for 8 h, crosslinked triphenyltin chloride was collected. To obtain SnO\(_2\)/C nanospheres, crosslinked triphenyltin chloride was carbonized at 600 °C for 1 h with a heating rate of 2 °C min\(^{-1}\) under the atmosphere of nitrogen.

**Material measurements**

XRD patterns were gained from a powder X-ray diffraction system (XRD, D/MAX-Ultima IV, Rigaku Corporation, Japan). Thermal behavior of the composites was investigated by thermo-gravimetric analysis (TGA, Q50, TA Instruments Ltd, USA) in air from 100 to 800 °C. Micro-morphologies were observed by the scanning electron microscopy (SEM, SU8010, Hitachi, Japan) and transmission electron microscopy (TEM, JEM 2100F, Japan). Porosity test was performed on Nitrogen adsorption–desorption porosity measurement machine (ASAP 2460, Micromeritics, USA). Fourier Transform reflection-infrared spectra were measured using a Nicolet 6700 FTIR spectroscopy (Nicolet, USA).

**Electrochemical characterization**

The electrochemical performances of SnO\(_2\)/C nanospheres were tested by a coin-type cell (CR 2032). Working electrode was fabricated by pasting a mixture of SnO\(_2\)/C nanosphere (84 wt%), super P (10 wt%), sodium carboxymethyl cellulose (CMC) (3 wt%) and styrene-butadiene rubber emulsion (SBR) (3 wt%) on copper foil and then dried in vacuum at 80 °C for 24 h. Coin cells were assembled in an argon-filled glove box, taking polypropylene microporous film (Celgard 2400) as separator and lithium foil as the counter electrode.

Galvanostatic charge/discharge property was measured on LAND CT 2001A batteries measuring system (CT2001A, Wuhan LAND Corporation, China) with a voltage window from 0.01 to 3.0 V at room temperature. The cyclic voltammograms (CV) data of the material was tested on electrochemical workstation (CHI660E, Shanghai Chenhua, China) at a scan rate of 0.2 mV s\(^{-1}\) from 0.01 to 3 V.

**Results and discussion**

Generally, SnO\(_2\) nanoparticles were prepared by hydrolysis, condensation process of SnCl\(_4\) or SnCl\(_2\). But the hydrolysis process of SnCl\(_4\)/SnCl\(_2\) is hard to control because of the high reaction speed. In this paper, for the first time, we used an organic precursor, i.e., Sn-Ph, to prepare SnO\(_2\)/C nanospheres. Normally, Sn-Ph boils and decomposes during heat-treatment process, which makes it hard to synthesize SnO\(_2\)/C composites. To conquer this question, Friedel–Crafts reaction was adopted to immobile Sn-Ph and dimethoxymethane was chosen as the crosslinker (the obtained product was denoted as xSn-Ph)\(^{15}\) The Friedel–Crafts crosslinking mechanism is described in Fig. S1,\(^1\) in which methylene (–CH\(_2\)) was generated between phenyl rings of Sn-Ph owing to the replacement of hydrogen. FT-IR was measured to confirm the crosslinking (Fig. 2). The absorption peak of methylene (~2800 cm\(^{-1}\)) appeared and the absorption peak of C–H in phenyl (~3100 cm\(^{-1}\)) disappeared...
after crosslinking, demonstrating the successful crosslinking between Sn-Ph and dimethoxydimethane.

Owing to crosslinked-induced phase separation, xSn-Ph presents spherical morphology with an average diameter of 600 nm (Fig. 3a). It is not difficult to imagine that Sn atoms would be wrapped during crosslinking and dispersed in the polymer network. Judging from the TEM images, the Sn atoms are distributed in molecular scale with no aggregations (Fig. 3b and c). Accordingly, the XRD pattern of xSn-Ph shows no diffraction peaks, indication of no crystals (Fig. 4a). To obtain SnO2/C nanospheres, xSn-Ph was carbonized at 600 °C for 1 h with a heating rate of 2 °C min\(^{-1}\) under the atmosphere of N\(_2\) (denoted as SnO2/C-2-600-1). Because of rigid polymer network from highly crosslinked density, nanospherical shape was maintained integrally after carbonization (Fig. 3d). Meanwhile, owing to the pyrolyzation of polymer precursor, the diameter of SnO2/C-2-600-1 was reduced to ca. 500 nm slightly (Fig. 3d). Fig. 3e presents the TEM image of SnO2/C-2-600-1, it is unexpected that many ultrasmall SnO2 particles are embedded in amorphous carbon matrix uniformly, without any big aggregations (Fig. 3f). According to the high-resolution TEM image, the diameter of such SnO2 particles is ca. 4 nm, which is lower than most of current SnO2 nanomaterials.\(^{46}\) It is believed that rigid xSn-Ph network is significant for the formation of ultrasmall SnO2 particles, that is, highly crosslinked framework is strong enough to keep away from melt and soften, which acts like barrier to prevent SnO2 from agglomeration.

To confirm the crystal structure of SnO2/C-2-600-1, XRD pattern is given (Fig. 4a). The wide peaks at 26.6, 33.8 and 51.8° can be ascribed to the crystal planes (110), (101) and (211) of SnO2 (JCPDS file no. 41-1445), further confirming ultrasmall SnO2 particles embedded in carbon continues phase after carbonization. The SnO2 content was estimated by thermogravimetric analysis (TGA) under air, in which process the carbon component would burn off completely. As shown in Fig. 4b, the SnO2 percentage of SnO2/C-2-600-1 was tested to be 20%.

Pore structure of SnO2 nanospheres was measured by N\(_2\) adsorption method. The adsorption amount shows a rapid step at low relative pressure (Fig. 4c), demonstrating the generation of abundant of micropores owing to the pyrolysis of polymer network. Moreover, the coincidence of adsorption and desorption branches and no dramatic increase at \(P/P_0=1.0\) certified nearly no mesopores and macropores in SnO2/C-2-600-1. According to the DFT (density functional theory) pore size distribution (Fig. 4d), the micropore size is around 0.7 nm. Due to the well-developed pore structure, the SnO2/C-2-600-1 nanospheres present a specific surface area of 463.3 m\(^2\) g\(^{-1}\).

We further find that pyrolysis temperature, holding time and heating rate of carbonization play significant roles in determining the size and content of SnO2 in the composites. Primarily, to study the impact of temperature, xSn-Ph was carbonized at 700 (SnO2/C-2-700-1), 800 (SnO2/C-2-800-1) and 900 °C (SnO2/C-2-900-1) for 1 h with a heating rate of 2 °C min\(^{-1}\). It is found that the diffraction peaks of SnO2 crystal become sharper with increasing the pyrolysis temperature, indication of a size growth of SnO2 nanoparticles (Fig. 5a). Obviously, higher pyrolysis temperature accelerates the aggregation of Sn atoms and leads to the generation of larger nanoparticles. This size growth process also can be observed in TEM images, in which SnO2/C-2-800-1 and SnO2/C-2-900-1 have larger SnO2 nanoparticles than SnO2/C-2-700-1 (Fig. 6). To

**Fig. 2** FT-IR spectra of Sn-Ph and xSn-Ph.

**Fig. 3** (a) SEM, (b) TEM and (c) high-resolution TEM images of xSn-Ph. (d) SEM, (e) TEM and (f) high-resolution TEM images of SnO2/C-2-600-1.

**Fig. 4** (a) XRD patterns of xSn-Ph, SnO2/C-2-600-1 and commercial nano-SnO2. (b) TGA curve of SnO2/C-2-600-1. (c) N\(_2\) adsorption-desorption isotherm and (d) pore size distribution of SnO2/C-2-600-1. This journal is © The Royal Society of Chemistry 2017
further confirm the results, we statisticled the average diameter of SnO2 nanoparticles according to the TEM images (Fig. S5†). It can be found that SnO2/C-2-700-1 has a lowest SnO2 diameter of ca. 7 nm, and SnO2/C-2-800-1 has larger SnO2 nanoparticles with an average diameter of ca. 13 nm. Accordingly, when pyrolysis temperature is elevated to 900 °C, SnO2/C-2-900-1 has a highest SnO2 diameter of ca. 16 nm. Unexpectedly, diffraction peaks of Sn element appear at 30.6, 32.0 and 44.9° when the pyrolysis temperature is 900 °C (JCPDS file no. 04-673), illustrating the carbothermal reduction of SnO2. Content of SnO2/Sn was measured via TGA (Fig. 5b). The contents of SnO2 are around 20% when the pyrolysis temperature was varied from 600 to 800 °C. But it drops to 15.5% at 900 °C, which can be ascribed to the volatilization of Sn (melting point: 232 °C).

Furthermore, heating rate and holding time of carbonization have been studied as well. As the holding time was extended, XRD patterns of obtained samples were sharpening, i.e., the SnO2 size increased (Fig. S6a†). Similarly, the acceleration of the heating rate results in a distinct increase of SnO2 size and faster reduction of SnO2 crystal, which can be ascribed to that the aggregation of Sn atoms was intensified with the increasing of heating rate (Fig. S6b†).

The SnO2/C nanospheres have unique nanostructure integrating ultrasmall SnO2 particles, continuous carbon buffer and microporous structure, which motivate us to further investigate its electrochemical performance. Fig. 7 displays the cyclic voltammogram of SnO2/C-2-600-1 electrode at a scan rate of 0.2 mV s⁻¹ from 0.01 to 3 V. The peak from 0.1 to 0.6 V of the first cathodic sweep indicates the formation of solid electrolyte interphase (SEI), irreversible reduction of SnO2 to Sn and formation LixSn alloy, associating with loss of capacity during first cycle. In the anodic sweep, the peak at 0.6 V can be ascribed to the dealloying reaction of LixSn alloy to Sn, which is consistent with the curves of commercial nano-SnO2 (Fig. S7†). All peaks except the first cycle are reproducible and stable, implying superior cycling stability of the SnO2/C nanospheres electrode.

Fig. 8a shows the 1st, 2nd and 60th voltage profiles of SnO2/C-2-600-1 between 0.01 to 3 V at a current density of 200 mA g⁻¹. In discharge curves, the slopes at 0.6 V and between 0.5 and 0 V can be associated with the reduction of SnO2 to metallic Sn and formation of LixSn alloy. In charge curves, the platform from 0.3 to 0.8 can be associated with the delithiation of LixSn, which are consistent with the CV results. The first discharge and charge show specific capacities of 1453 and 719 mA h g⁻¹ respectively.
SnO$_2$/graphene nanocomposite (Table S1 at 87.4% (high discharge and charge capacities of 1239 and 809 mA h g$^{-1}$ respectively. Thirty-six cycles of testing at different current densities later, the capacity returns to 705 mA h g$^{-1}$ at 200 mA g$^{-1}$, explaining the tolerance of SnO$_2$/C-2-600-1 at high current charge and discharge. Fig. 8c displays the cycle performance of SnO$_2$/C-2-600-1 at the current density of 200 mA g$^{-1}$ between 0.01 and 3.0 V. For comparison, nacked nano-SnO$_2$ and pure carbon were chosen as control samples (Fig. S8†). It can be observed that commercial nano-SnO$_2$ shows high discharge and charge capacities of 1239 and 809 mA h g$^{-1}$ respectively, but its capacity decreases seriously to 47 mA h g$^{-1}$ after 120 cycles. Carbon exhibits a stable capacity of 213 mA h g$^{-1}$ near to the theoretical capacity of graphite (372 mA h g$^{-1}$). On contrast, SnO$_2$/C-2-600-1 presents a high and stable capacity of 629 mA h g$^{-1}$ for 120 cycles later, which is 3 and 13 times of the capacity of carbon and commercial nano-SnO$_2$, respectively. Accordingly, capacity retention of SnO$_2$/C-2-600-1 is as high as 87.4% ($C_{120th}/C_{2nd}$), which is much higher than that of SnO$_2$ (5%). As shown in Fig. 8d, SnO$_2$/C-2-600-1 composite presents a capacity of 360 mA h g$^{-1}$ even after 1000 cycles at the current density of 1 A g$^{-1}$, implying an outstanding long-term cycling capability. This result is also superior to many SnO$_2$/C composites reported previously,$^{6,9,10,12}$ and comparable to SnO$_2$/CNT$^{99}$ and SnO$_2$/graphene nanocomposite (Table S1†). Moreover, SnO$_2$/C composites pyrolyzed at 700 (SnO$_2$/C-2-700-1) and 800 °C (SnO$_2$/C-2-800-1) with a heating rate of 2 °C min$^{-1}$ are studied for electrochemical testing (Fig. S9†), in order to confirm the structural advantages of ultrasmall SnO$_2$ particles. It can be observed that the capacities of SnO$_2$/C-2-700-1 and SnO$_2$/C-2-800-1 decline at first 30 cycles followed by stable plateaus. After cycling for 120 times, SnO$_2$/C-2-700-1 remains a stable capacity of 448.1 mA h g$^{-1}$, which is inferior to that of SnO$_2$/C-2-600-1. In addition, SnO$_2$/C-2-800-1 with largest SnO$_2$ nanoparticle has lower stable capacity of 379.4 mA h g$^{-1}$. Due to the rising of holding temperature, Sn atoms form bigger SnO$_2$ particles, leading rapid capacity fading during the cycling process.

The superior performance of SnO$_2$/C nanosphere should be attributed to three aspects: (i) ultrasmall SnO$_2$ nanoparticle dispersed in porous carbon could reduce aggregation and strain caused by volume change during discharge/charge process, (ii) porous carbon structure would provide nanospace to mitigate the volume change of SnO$_2$ nanoparticles to prevent cracking and pulverization, (iii) micropores could enable the accessible surface area to electrolyte and favor the diffusion of lithium ions.

**Conclusion**

In conclusion, SnO$_2$/C nanospheres with ultrasmall SnO$_2$ particles have been prepared by facile and rapid Friedel–Crafts crosslinking. Benefiting from the ultralow size of SnO$_2$ nanoparticles (~4 nm) and porous carbon buffer, the as-prepared sample presents a superior electrochemical performance, including high first discharge and charge capacity of 1453 and 719 mA h g$^{-1}$ respectively, and high capacity remaining of 629 mA h g$^{-1}$ after 120 cycles at the current density of 200 mA g$^{-1}$. What’s more, rapid synthesis and low cost make this method easier to be put into application and realize large scale production.

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