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Carbon-wrapped core–shell nanospheres of tin-graphitized carbon for superior lithium-ion battery

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ABSTRACT

A simple strategy of controllable pyrolysis of metal-organic framework has been developed for the synthesis of carbon wrapped core–shell nanospheres of tin-graphitized carbon hybrid. This hybrid electrode exhibits superior electrochemical properties, achieving remarkable capacities of 550 and 430 mA h g^{-1} over 200 cycles at 0.5 and 1.0 A g^{-1}, respectively. The carbon matrix can buffer large volume variations of tin during lithium/delithium process and can avoid the electrode pulverization, resulting in outstanding cycling stability. The graphitized carbon shell and tin nanocrystals core could enhance the electrode conductivity and provide large electrode/electrolyte contact areas, leading to a high reversible capacity.

1. Introduction

Owing to the increased demand for green, environment-friend and sustainable energy resource, the design of novel electrode materials for high-performance lithium-ion battery has attracted great attentions [1–5]. Tin materials are regards as promising anode candidates due to their low charge-discharge potentials and high theoretical capacities [6–13]. However the tin battery shows inferior electrochemical properties because of sluggish kinetics and severe volume changes during the lithium and de-lithium process [14–19]. To solve such problems, we designed the hybrid structure of core–shell tin@graphitized carbon (GC) nanospheres wrapped in carbon matrix. First, the carbon matrix can accommodate the severe volume variations of tin core during the lithium/de-lithium process and avoid the pulverization of electrode, ensuring good cycling stability. Second, the GC shell could restrain the volume variations of tin and enhance the electrode conductivity, resulting in a high reversible capacity. Third, the nanosized tin cores can provide large electrode/electrolyte contact areas and short diffusion paths for electron and ions, which favors the good rate capability. Moreover, these small nanocrystals can also alleviate structural degradation and improve the cycling stability. As far as known, no such hybrid structure of graphitized carbon matrix wrapped core–shell nanoparticles has been reported yet.

Herein, we applied a simple strategy of controllable pyrolysis of metal-organic complex for the synthesis of carbon embedded core–shell tin-GC nanospheres hybrid. The result indicate that this hybrid exhibits excellent electrochemical performance, including high energy capacity, stable cycling properties and excellent rate performance.

2. Experimental

2.1. Preparation of the tin@GC core–shell nanoparticles-GCM hybrid

All reaction reagents are analytic grade and used without further purification. 0.4 g tin tetrachloride ($SnCl_4$, Aldrich) and 1.0 g sodium oleate (Na-oleate, TCI) were dissolved and mixed in an aqueous water. The above mixture was aged at 360 K until the self-organized precipitate, colored milky, was observed. Then the precipitate was centrifuged and dried at 383 K overnight. Finally, the solids were heated to 873 K at a heating rate of 10 K min^{-1} under a N_2 atmosphere for 3 h. After being cooled down naturally, the product was collected for further use. The mass of Sn in the hybrid is measured 63% in a weight.

2.2. Sample characterization

X-ray diffraction (XRD) measurements were carried out by using the Shimadzu XRD-600 X-ray diffractometer with a Cu Kα line of 0.1541 nm. Field emission scanning electron microscopy (JSM-7600F) and transmission electron microscopy (JEOL JEM2100) were used to characterize the morphologies and

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structures of the samples. Raman spectra were collected by using a micro Raman spectrometer with a 532 nm wavelength incident laser.

2.3. Electrochemical measurements

Firstly, the active material (80 wt%), sodium carboxymethyl cellulose (10 wt%) and super-P carbon black (10 wt%) were mixed in a de-ionized water solution to form a slurry. Secondly, the slurry was spread onto a Cu foil and dried at 343 K overnight under vacuum (*a*n active material mass is 7.5 mg/cm^{-2} in an electrode). Electrochemical performance was evaluated using CR2016 coin cells assembled with lithium foil as both the counter and reference electrodes and a microporous polypropylene membrane (Celgard 2500) as the separator in an argon filled glove box. The electrolyte was 1.0 m $LiPF_6$ dissolved in a mixture of ethylene carbonate and dimethyl carbonate (1:1 in volume ratio). The galvanostatic charge and discharge experiments were performed with a battery testing system (LAND-CT2001A) in the voltage range of 0.01–3.0 V at room temperature.

3. Results and discussion

The strategy of controllable pyrolysis of metal-organic complex was applied to design a hybrid structure of carbon wrapped core–shell nanospheres of tin-graphitized carbon. The synthetic illustration is shown in Fig. 1. Firstly, the self-organized complex of tin-oleate was obtained after mixing $SnCl_4$ and Na-oleate in a de-ionized water and aging at 360 K. Then the as-synthesized complex was pyrolysed at 873 K for 3 h under a N_2 atmosphere. The nanosized tin oxides, encapsulated in carbon matrix from primary pyrolysis of complex, were carbothermally reduced into the tin nanocrystals core, which further catalyzed the transformation of surrounding amorphous carbon into highly graphitized carbon shell. Then the carbon wrapped core–shell nanospheres of tin-graphitized carbon structure was obtained.

The strategy of controllable pyrolysis of metal-organic complex was applied to design a hybrid structure of carbon wrapped core–shell nanospheres of tin-graphitized carbon.

The scanning electron microscope (SEM) image in Fig. 2a–c shows the high quality of the uniform core–shell nanospheres embedded in ultrathin carbon matrix. It can been seen that the electron beam can penetrate through the carbon shell and ultrathin carbon matrix, proving the hybrid structure of core–shell nanospheres embedded in ultrathin carbon matrix. The core–shell nanospheres are nanosized, less than 200 nm in diameter. The transmission electron microscope (TEM) images in Fig. 2 d–f further reveal that the tin cores are encapsulated by the graphitized carbon shells, which enable the uniform thickness of ~10 nm. Furthermore, the selected area electron diffraction (SAED) pattern in the inset of Fig. 2d shows a series of obvious diffraction rings, indexed to the (200) and (112) planes of Sn nanocrystals [20]. And the presence of diffraction rings in SAED pattern indicates the polycrystalline nature of Sn.

The X-ray diffraction (XRD) pattern is depicted in Fig. 3a. The well resolved diffraction peaks located at 30.7°, 32.1° and 45.1° can be indexed to (200), (101) and (211) planes diffractions of Sn (JCPDS no. 04-0673), revealing that the SnO_2 species have been carbothermally reduced to Sn nanocrystals. The Raman spectrum are shown in Fig. 3b. Two peaks centered at 1358 and 1588 cm^{-1} can be ascribed to the vibration of sp^2 carbon atoms in a 2D hexagonal lattice (G band) and to the defects and disorder in the graphitic layers (D band) [9,21,22]. The low intensity ratio of I_D/I_G reveals the presence of graphitized carbon. As good agreement with HRTEM observation, this Raman result further confirmed that the reduced Sn nanocrystals successfully catalyzed the surrounding carbon into graphitized carbon shell.

The cycling performances of the hybrid electrode are shown in Fig. 4a and b. It can be seen that this hybrid electrode exhibits outstanding performances, in terms of both capacity and stability. At a high current density of 0.5 A g^{-1}, the electrode displayed a stable capacity of 600 m A h g^{-1} after the first 30 cycles, and the high reversible capacity of 550 m A h g^{-1} is retained after 200 cycles, which corresponds to a high capacity retention of 92%. The Coulombic efficiency maintained at 99% during the cycling process. Even twice the applied current density to 1.0 A g^{-1}, the high reversible capacity of 430 m A h g^{-1} is obtained after 200 cycles, representing a high capacity retention of 80%. Noted that the large volume variation of nearly 250% are present in Sn-based electrode between the lithium-delithium process during the cycling, this hybrid electrode shows the outstanding cycling stability due to the special feature of the hybrid structure. Other hybrid structures of Sn/C were also reported, such as Sn/mesoporous carbon [9], core–shell structure of Sn/carbon [22,23], Sn/graphitized carbon nanosheets [2,20]. And our as-synthesized Sn/C hybrid structure

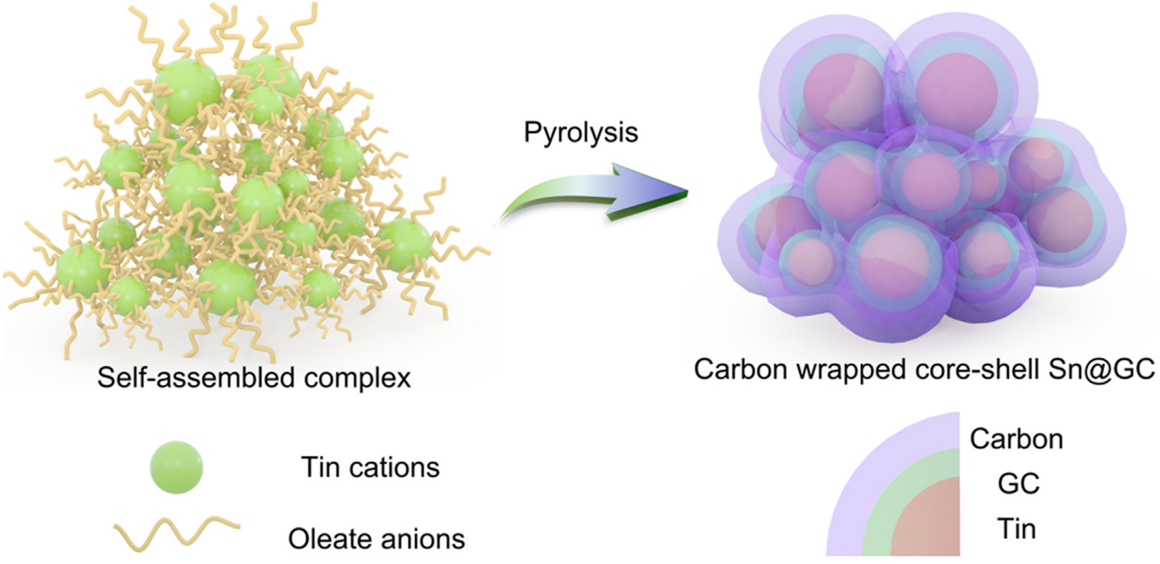

Fig. 1. Schematic representation of the hybrid synthesis of carbon wrapped core–shell nanospheres of tin-graphitized carbon.