SnO₂/polypyrrole hollow spheres with improved cycle stability as lithium-ion battery anodes

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ABSTRACT

SnO₂/polypyrrole (SnO₂/PPy) hollow spheres were fabricated by a liquid-phase deposition method using colloidal carbon spheres as templates followed by an in-situ chemical-polymerization route. The obtained SnO₂/PPy composite particles had a size of 610–730 nm. The thickness of inner shell (SnO₂) and outer shell (PPy) for composites was about 35 and 90 nm, respectively. As an anode for lithium ion batteries, the SnO₂/PPy composites electrode showed superior rate capability and excellent long-term cycling performance. After a long-term cycling of 600 cycles at different current densities, a capacity of 899 mAh g^{-1} was achieved at the current density of 100 mA g^{-1} for SnO₂/PPy composites. The excellent electrochemical performance was attributed to the synergistic effect between the PPy coating layer and the hollow SnO₂ spheres, which guaranteed vast lithium storage sites, good electronic conductivity, fast lithium ion diffusion, and sufficient void space to buffer the volume expansion.

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1. Introduction

Lithium batteries (LIBs), as a main power source or back-up power source for electric and hybrid vehicles have attracted much attention due to their superior properties such as high energy density, long cycle life, and no memory effect [1]. Many metal oxides have been intensively studied as potential high-performance anodes for LIBs due to their high theoretical capacities, and natural abundance [2–5]. Tin oxide (SnO₂) stands out as one of the attractive anode candidates considering its abundance, environmental benignity, and high theoretical capacity (780 mAh g^{-1}) [6,7]. However, the practical implementation of SnO₂ materials is still hindered by its poor cycle life, which is caused from enormous volume expansion and contraction during repeated discharge/charge process [8].

To overcome the problems related with SnO₂ anodes for LIBs, one strategy is to utilize hollow SnO₂ nanostructures, such as nanotube [9], nanobox [10], and hollow sphere [11], to decrease the absolute volume variation. Among them, SnO₂ hollow spheres have been investigated as a way to improve its electrochemical properties due to the advantages of providing more reaction sites, short Li$^+$ diffusion lengths and local empty space for partial accommodation of large volume change during cycling [12]. Up to now, the SnO₂ hollow spheres have been fabricated by numerous efficient methods, including either template (hard and soft templates) assisted synthesis or template-free routes. Between them, template assisted synthesis, especially using hard templates (carbon, polystyrene, SiO₂, etc), is an effective approach for the preparation of controllable SnO₂ hollow spheres [13–15].

Another important strategy is to prepare SnO₂ composite electrodes with other effective conducting materials, such as carbon [16–18], carbon nanofiber [19], graphene [20], and conductive polymers [21,22]. Among these materials, conducting polymers have gained significant attention given its good flexibility and electronic conductivity. For example, Sun et al. reported that Polypyrrole (PPy) coated ZnFe₂O₄ hollow spheres electrode showed excellent cycling stability for LIBs [23]. So, an appreciable improvement is thus expected upon the integration of SnO₂ hollow spheres with conducting polymers since the pulverization of SnO₂ will be greatly alleviated owing to the hollow interior, the presence of void spaces between the SnO₂ nanoparticles and a superior structural integrity from the

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polymer. More recently, core-shell structured hollow SnO$_2$/PPy has been reported to demonstrate limitedly improved cycling performance of LIB anode (448.4 mAh g^{-1} after 100 cycles) [24] using a hydrothermal method followed by an in-situ chemical-polymerization route. However, it is still a challenge to develop more effective synthesis process for the SnO$_2$/PPy hollow spheres with uniform size distribution and better electrochemical performance.

Herein, we report a facile synthetic strategy for SnO$_2$/PPy hollow spheres via liquid-phase deposition (LPD) method using colloidal carbon sphere templates followed by an in-situ chemical-polymerization route. The SnO$_2$/PPy composites electrode shows superior rate capability and excellent long-term cycling performance. The enhanced electrochemical performance can be ascribed to the synergistic effect of PPy matrix and SnO$_2$ hollow spheres structure. It is believed that the hollow SnO$_2$ structure created a pathway for rapid lithium diffusion along with alleviating the volume expansion during the cycling process. The PPy coating layer can improve the electronic conductivity and hold the whole structure integrity.

2. Experiment

2.1. Synthesis of sample

As shown in Fig. 1, SnO$_2$ hollow spheres were synthesized by LPD method using carbon spheres as templates [25]. Carbon spheres were fabricated via a hydrothermal approach. In a typical process, glucose (4 g) was dissolved in 30 mL of distilled water under stirring. Then the aqueous solution was sealed in a 50 mL Teflon-lined stainless steel autoclave and maintained at 180 °C for 20 h. The precipitates were centrifuged and rinsed with distilled water, and finally dried at 80 °C for 12 h. The SnO$_2$ hollow spheres were prepared using same method detailed in our previous paper [26]. Carbon spheres (300 mg) were dispersed in aqueous solution of SnF$_2$ (0.02 M) under stirring at 50 °C for 8 h. Then the products were centrifuged and rinsed with distilled water. In order to produce SnO$_2$ hollow spheres, washed precipitates were dried at 80 °C for 12 h and finally were calcined in air at 500 °C for 4 h.

The SnO$_2$/PPy hollow spheres were prepared through chemical-polymerization route [27]. Briefly, 60 mg SnO$_2$ hollow spheres were dispersed into 60 mL distilled water containing 5 mg sodium dodecylsulfate (SDS) under ultrasonication for 20 min and then stirring for 10 h at room temperature. Next, 0.035 mL pyrrolemonomer and 0.5 mL 1 M HCl solution (as a dopant) were successively added into the suspension. Afterward, (NH$_4$)$_2$S$_2$O$_8$ (APS) (0.114 g in 5 mL H$_2$O) was added as an oxidant into the system to start the polymerization. After stirring the mixture in an ice/water bath for ~3 h, the SnO$_2$/PPy hollow spheres were centrifuged and rinsed with distilled water. The final samples were dried at 80 °C for 12 h.

2.2. Characterizations

The samples were characterized by scanning electron microscope (SEM, JEOL 6335), transmission electron microscopy (TEM, JEOL JEM-2200FS), X-ray diffraction (XRD, SIEMENS-D5000),

Fourier transform infrared spectroscopy (FTIR, JASCO FT/IR 4100 spectrometer), and thermogravimetric analysis (TGA, SDT Q600). Nitrogen adsorption/desorption isotherms were obtained using a NOVA2000e surface area analyzer at 77 K.

2.3. Preparation of electrode and electrochemical measurements

Electrochemical properties of the samples were measured using CR2032 coin-type cells assembled in a dry argon filled glove box. The material was fabricated into working electrode consisting of 80 wt% active materials, 10 wt% Super P Li, and 10 wt% polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP) and casted on a copper foil, drying at 80 °C under vacuum for 24 h. A lithium foil was used as both counter electrode and reference electrode. A Celgard 2400 microporous polypropylene was used as a separator. The electrolyte was 1 M LiPF$_6$ dissolved in ethylene carbonate (EC): diethyl carbonate (DEC) in the volume ratio of 1:1. Cyclic voltammetry (CV) was performed using Bio-logic versatile multichannel potentiostat (VMP3). All electrochemical cells were galvanostatically cycled at room temperature using a NEWARE BTS-610 Battery Test System. All the voltages mentioned in this manuscript are vs. Li/Li$^+$.

3. Result and discussion

Fig. 2a shows SEM images of carbon spheres. The average diameter is ~460–520 nm. After LPD process and calcination, the SnO$_2$ hollow spheres are found with a diameter of ~430–550 nm (Fig. 2b). From Fig. 2c, it can be seen that the SnO$_2$/PPy hollow spheres have average diameters of ~610–730 nm. A more detailed view of the morphology and microstructure of hollow spheres have been obtained by means of TEM. Carbon spheres have a regular and entity structure (Fig. 3a). From Fig. 3b it can be seen that the hollow structure of the SnO$_2$ spheres is discerned apparently. Careful examination shows that the shell of SnO$_2$ hollow spheres has a thickness of ~35 nm. The corresponding selected scale electron diffraction (SAED) pattern is shown in the inset of Fig. 3b, all the dominant diffraction rings can be indexed to rutile SnO$_2$ phase. Fig. 3c depicts representative TEM image of SnO$_2$/PPy hollow spheres. It is evident that a PPy layer is covered on the SnO$_2$ shell uniformly with a thickness of ~90 nm. The above results show that the general shape of SnO$_2$ hollow sphere cannot be changed by introducing PPy, but results in increased surface roughness and particle size.

The crystalline structures of the samples were examined by XRD (Fig. 4a). All the diffraction peaks of SnO$_2$ and SnO$_2$/PPy products can be indexed to the tetragonal rutile structure of SnO$_2$ (JCPDS Card Files, No. 3-1114). It can be seen that PPy is amorphous [24,27], and shows a broad diffraction peak in the region of 2θ = 10–30° due to the pyrrole intermolecular spacing [28]. FTIR spectroscopy was used to characterize the presence of PPy in the SnO$_2$/PPy composites. Fig. 4b compares the FTIR spectra of pure PPy, SnO$_2$ hollow spheres and SnO$_2$/PPy composites. The characteristic bands for PPy and SnO$_2$/PPy are almost same, but the intensity of the
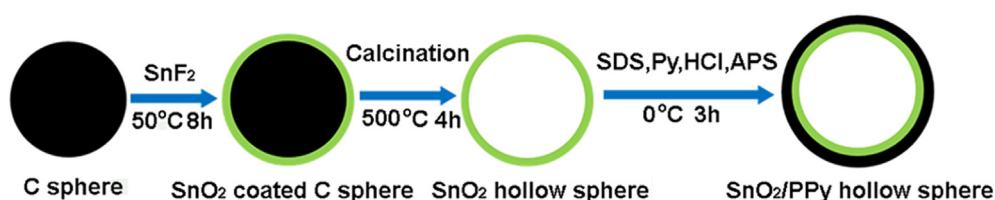

Fig. 1. Scheme of synthesis for the SnO$_2$/PPy hollow spheres.