Hierarchical Assembly and Enhanced Lithium Storage Properties of 3D SnO$_2$/PC Hybrids

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Ultrasmall SnO$_2$ nanoparticles (~ 3 nm in diameter) confined in three dimensional hierarchical porous carbon (3D SnO$_2$/PC) were successfully prepared using a simple method in this work. The 3D SnO$_2$/PC has almost monodispersion of the SnO$_2$ nanoparticles with 73 wt% load. The 3D SnO$_2$/PC exhibits excellent performance with high rate capability and significant cycle stability. At 0.1 A/g in the 100th cycle, the reversible specific capacity is 1374 mAh/g. These outstanding characteristics are desirable and make 3D SnO$_2$/PC a promising anode material for LIBs.

Keywords: 3D porous carbon; Tin dioxide; Anode; Lithium ion battery

1. INTRODUCTION

Lithium-ion batteries (LIBs) have fascinated more and more interest recently. In the industrial sector, graphite is the first commercially available LIBs anode material. However, its low theoretical capacity (372 mAh/g) and poor rate capability are not conducive to the development of high-performance LIBs [1, 2]. Therefore, much effort is paid to develop new anode materials with a variety of nanostructures and configurations to meet the high performance requirements rechargeable LIBs [1, 2]. Among many anode materials, tin dioxide (SnO$_2$) is one of the most studied materials due to its high theoretical capacity (782 mAh/g), non-toxic and cheap features [3-5]. However, the intense volume expansion/shrinkage and low conductivity of SnO$_2$ lead to poor recyclability and rate capability [6, 7]. To avoid similar poor performance, scientific research personnel construct anode materials in different ways. One tactic is the fabrication of nano-structures to buffer the volume increase. Another way is the integration of SnO$_2$ with the carbon substrates [1]. Graphene-based SnO$_2$ composites have been investigated extensively [5, 8-16]. Nevertheless, the most graphene substrates were made from graphene oxide (GO) or reduced graphene oxide (rGO) precursor, which could lead to
the formation of a very thick solid electrolyte interphase during cycling. Meanwhile, the volume of SnO$_2$ nanoparticles on the graphene expands and shrinks dramatically [17, 18].

3D porous carbon (PC), due to its large specific surface area, abundant pores and excellent specific conductance, is good for the dispersion of SnO$_2$ nanoparticles, thereby their active sites can be fully utilized [19-24]. The porous structure can accelerate the electron transport and benefit to improve electrochemical performance. Used as electrode, 3D PC-SnO$_2$ presents excellent survival rate [19-21].

Herein, we exploit 3D SnO$_2$/PC with uniform structures as well as good SnO$_2$ dispersion. The prepared 3D SnO$_2$/PC exhibits super specific capacity (1499 mAh/g), excellent rate capability, and high reversibility (92% retention after 100 cycles), which owe to the combined action of 3D porous structure, electronic conductive network and SnO$_2$ nanoparticles, showing great potential prospects as LIBs electrode materials.

2. EXPERIMENTAL METHOD

2.1. Synthesis of 3D porous MgO whiskers

Typically, 100 mL 1 mol/L Na$_2$CO$_3$ solution and 100 ml 1 mol/L MgCl$_2$ solution were added into a four necked glass flask and kept for 0.5 h under mechanical stirring of 300 rpm at 80 °C. After cooling, the resulting white sediment was filtrated out and dried in an oven at 80 °C. Then the product was calcined at 650 °C to remove crystal water and CO$_2$ to finally form the 3D porous MgO whiskers.

2.2. Synthesis of 3D PC

In a typical experiment, first, 10 g 3D porous MgO whisker was added into a pitch solution (1 g pitch/30 mL toluene) with violent agitation. After drying, the as-obtained pitch/MgO mixture was heated at 700 °C for 60 min protected by Ar. After purified the 3D PC was obtained.

2.3. Synthesis of 3D SnO$_2$/PC composites

Typically, 45 mg SnCl$_2$·2H$_2$O, 16.5 mg 3D PC and 20 mL water were homogeneous mixing. After hydrothermal reaction (200 °C for 10 h), the 3D SnO$_2$/PC was obtained.

2.4. Characterization

The as-synthesized materials were characterized by SEM (Quanta 200F, FEI, Holand), TEM (F20), XRD (Bruker D8 Advance) and XPS (PHI Quantera Scanning X-ray Microprobe). The N$_2$ adsorption-desorption measurements with BET model on a JW-BK222 instrument.

2.5. Electrochemical tests

CR2025 coin-type cells were used for evaluation at room temperature. The test voltage range is from 0.01 V to 3.0 V. A slurry containing 70% carbon materials, 10% acetylene black and 20% polyvinylidene fluoride (7:1:1) was coated on copper foils to prepare the working electrodes. The
galvanostatic charge-discharge (GCD) cycles were tested at 25 °C from 0.1 to 1 A/g. The cyclic voltammetry (CV) measurement was tested at 0.1 mV/s performed on the electrochemical workstation (CHI660E). The test condition of AC impedance spectrum is from 100 kHz to 0.01 Hz.

3. RESULTS AND DISCUSSION

3.1 SEM and TEM analysis

The 3D SnO$_2$/PC composites were synthesized by friendly hydrothermal method. As shown in Fig. 1a, MgCO$_3$·3H$_2$O whiskers with ~13 μm in length and ~0.8 μm in diameter have a smooth surface before calcination. After calcination at 650 °C, abundant pores can be observed inside and outside the 3D MgO whiskers (Fig. 1b). The synthesis process for 3D PC is illustrated in scheme 1 using the calcined 3D MgO whiskers as templates.

![SEM images of MgCO$_3$·3H$_2$O whiskers (a) and 3D porous MgO whiskers after calcination at 650 °C (b).](image)

**Figure 1.** SEM images of MgCO$_3$·3H$_2$O whiskers (a) and 3D porous MgO whiskers after calcination at 650 °C (b).

![Scheme 1. Synthetic process of 3D PC and 3D SnO$_2$/PC](image)
Figure 2. TEM picture of 3D PC (a, b, c) and 3D SnO$_2$/PC (d, e, f), the inset of (b) shows the enlarged TEM picture of PC.

The different magnified TEM images of 3D PC after removing MgO whiskers by acidic washing are shown in Fig. 2 a, b & c, illustrating a unique 3D interconnected porous structure. Such abundant micropores and mesopores are in favour of the ion storage and transport. And as a support of metal oxide, the 3D PC would be able to easily form fine metal oxide nanostructures with uniform surface distribution [25].

The synthesis process of the 3D SnO$_2$/PC composite was illustrated in Scheme 1. From Fig. 2d the 3D PC is uniformly covered by the ultrasmall SnO$_2$ nanoparticles. The morphology of 3D SnO$_2$/PC is similar to that of 3D PC, suggesting that there is no change for the overall morphology after the introduction of SnO$_2$. The 3D PC facilitates the diffusion of the liquid electrolyte and increases the electronic conductivity, which is conducive to the realization of high speed energy [26-28]. For 3D SnO$_2$/PC nanocomposite, SnO$_2$ nanoparticles adhere to 3D PC and being separated spatially by the carbon skeleton avoiding accumulation at the same time, which helps to improve cycling performance [26, 29]. As is shown in Fig. 2e, SnO$_2$ nanoparticles (~ 3 nm in diameter) homogeneously distributed. The HR-TEM image (Fig. 2f) clearly displayed the monodispersed SnO$_2$ nanoparticles on 3D PC. The clear lattice fringe exhibits planar spacing of 0.24 nm and 0.34 nm respectively, which is well consistent with SnO$_2$ (200, 110) plane (PDF No.41-1445) [25]. The subsize and good dispersibility of SnO$_2$ particles can increase the specific surface area, buffering particle changes, helpful to improve performance.
3.2 X-ray diffraction, XPS spectroscopy, TG and Porosity analysis

**Figure 3.** (a) XRD pattern of SnO$_2$/PC and PC. (b) XPS spectra, (c) TG analysis (O$_2$ atmosphere) for SnO$_2$/PC. (d) N$_2$ adsorption-desorption isotherm at 77 K (inset the corresponding PSD).

The strong diffraction peaks in SnO$_2$/PC (Fig. 3a) indicate the tetragonal crystal of SnO$_2$ (PDF No. 41-1445) [1, 25, 26, 30]. There are no obvious carbon patterns in PC, because the carbon (002) diffraction peak overlaps the SnO$_2$(110) diffraction peak and PC strength is relatively weak compared to SnO$_2$. The average SnO$_2$ particle size is $\sim$ 3.2 nm (calculated by scherrer formula) consistent with TEM analysis. Fig. 3b shows the XPS spectra to investigate the composites of SnO$_2$/PC. C (50.4 atom%), O (31.3 atom%) and Sn (18.3 atom%) can be detected, confirming that SnO$_2$ is successful formation. Fig. 3c shows the TGA for SnO$_2$/PC measured in the O$_2$ atmosphere. From the TG curve, SnO$_2$/PC suffers a 24% weight loss from 280 to 800. The weight in loss is due to the combustion of PC to form CO$_2$. The TG curve manifests that the percentage composition of SnO$_2$ is $\sim$73%, higher than SnO$_2$-G composite (60%) [29].

**Table 1.** Physical characteristics of 3D PC and 3D SnO$_2$/PC composites

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET SSA (m$^2$/g)</th>
<th>Pore volume (m$^3$/g)</th>
<th>Pore size (nm)</th>
</tr>
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<tbody>
<tr>
<td>PC</td>
<td>452.01</td>
<td>0.70</td>
<td>7.40</td>
</tr>
<tr>
<td>SnO$_2$/PC</td>
<td>224.83</td>
<td>0.34</td>
<td>7.02</td>
</tr>
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</table>
It is clear in Fig. 3d that the N\textsubscript{2} adsorption-desorption isotherm (type III, H3 hysteresis loop at 0.55–0.98 (P/P0)) indicates abundant mesopores exists [31]. It also can be seen that there is an uptake at a lower relative pressure (P/P0< 0.05) indicating that there are more micropores in PC and SnO\textsubscript{2}/PC. Since the SnO\textsubscript{2} nanoparticles are confined in mesopores of PC, the BET specific surface area (SSA) and pore volume of the PC (452.01 m\textsuperscript{2}/g, 0.70 m\textsuperscript{3}/g) is higher than those of the SnO\textsubscript{2}/PC (224.83 m\textsuperscript{2}/g, 0.34 m\textsuperscript{3}/g) (Table 1). The pore size distributions are focus on 2-5 nm and 1.0-1.5 nm for mesopores and micropores respectively (Fig. 3d). Abundant micro/mesopores facilitate the permeability of electrolytes. They also provide channels for the transport of Li\textsuperscript{+}, and buffer the volume change in charging and discharging process [32].

3.3 Electrochemical performance analysis

For PC (Fig. 4a), the broad reduction peak (0.6 V) during the initial cathodic sweep is attributed to the formation of a solid electrolyte interface (SEI) for the irreversible Li\textsuperscript{+} consumption [33]. The CV behavior of SnO\textsubscript{2}/PC (Fig. 4b) is generally corresponding to those reported in literature [10, 11, 25, 34], indicating the same electrochemical reaction pathway.

![Figure 4. CV curves of PC (a) and SnO\textsubscript{2}/PC (b) composites at 0.1 mV/s](image)

During the first cathodic scan, three main cathodic peaks (0.85 V, 0.6 V and 0.1 V) were observed. The peak at 0.85 V represents the reduction reaction of SnO\textsubscript{2} with Li\textsuperscript{+} [1, 35]. The peak at 0.6 V manifests the formation of SEI consistent with that of PC without SnO\textsubscript{2}. The cathodic peak at 0.1 ~ 0.25 V is about Li\textsubscript{x}Sn alloys [1, 2, 36]. In the anodic oxidation process, there are two oxidation peaks (at 0.56V, 1.26 V) for SnO\textsubscript{2}/PC, meaning that the oxidation reaction was performed in two steps. The anodic peak at 0.56 V is the decomposing of LixSn. The peak at 1.26 V is ascribed to the reaction of SnO\textsubscript{2} and Li\textsuperscript{+}. The CV curves indicate that SnO\textsubscript{2}/PC and PC possesses excellent electrochemical stability.
Table 2 Comparison of SnO$_2$/graphene nanocomposites reported before and SnO$_2$/PC

<table>
<thead>
<tr>
<th>Current density mA/g</th>
<th>Initial capacity mAh/g</th>
<th>Cycle number</th>
<th>Remaining capacity mAh/g</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>810</td>
<td>30</td>
<td>570</td>
<td>[26]</td>
</tr>
<tr>
<td>55</td>
<td>765</td>
<td>100</td>
<td>520</td>
<td>[27]</td>
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<td>67</td>
<td>978</td>
<td>30</td>
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<tr>
<td>264</td>
<td>786</td>
<td>50</td>
<td>558</td>
<td>[29]</td>
</tr>
<tr>
<td>100</td>
<td>936</td>
<td>100</td>
<td>1156</td>
<td>[37]</td>
</tr>
<tr>
<td>50</td>
<td>862</td>
<td>50</td>
<td>665</td>
<td>[38]</td>
</tr>
<tr>
<td>100</td>
<td>1499</td>
<td>100</td>
<td>1374</td>
<td>This work</td>
</tr>
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</table>

Figure 5. The coulombic efficiencies of PC and SnO$_2$/PC for the 1$^{\text{st}}$ and 2$^{\text{nd}}$ cycle at 0.1 A/g (a). (b) Rate capabilities of PC and SnO$_2$/PC. (c) Cycling performance at 0.1 A/g and 1 A/g of PC and SnO$_2$/PC. (d) Nyquist plots of PC and SnO$_2$/PC. The inset shows the equivalent circuit model.

The first coulombic efficiency for 3D SnO$_2$/PC (56.1%) is higher than that for 3D PC (50.4%) (Fig. 5a). The synergistic effect of 3D PC and SnO$_2$ nanoparticles is in favour of less irreversible Li storage. From the curves of rate capabilities (Fig. 5b), the 3D SnO$_2$/PC exhibits higher delithiation capacity. The delithiation capacity for 3D SnO$_2$/PC reaches 1499 mAh/g at 0.1 A/g and 478 mAh/g at 1 A/g, higher than that of 3D PC (1254 mAh/g at 0.1 A/g and 308 mAh/g at 1 A/g). The Li storage performance for the SnO$_2$/PC is also higher than currently reported value for SnO$_2$/GNS composites (810 mAh/g at 50 mA/g, 765 mAh/g at 55 mA/g, 978 mAh/g at 67 mA/g, 936 mAh/g at 100 mA/g) [26-28, 37]. From Fig. 5c, the 3D SnO$_2$/PC exhibits excellent cycling stability and the reversible specific capacity of 1374 mAh/g and 478 mAh/g at 0.1 A/g and 1 A/g is maintained after cycling. The reversible specific capacity of 1122 mAh/g at 0.1 A/g and 278 mAh/g at 1 A/g is retained for the PC anode. The reversible specific capability of SnO$_2$/PC is also much higher than the value of
SnO$_2$/graphene hybrids reported previously (Table 2). The outstanding cycling performance might be owing to the good flexibility and structural stability. In addition, the 3D PC skeleton helps to accommodate the change of volume, and the separation and connection of SnO$_2$ species during discharge/charge cycles that prevents the pulverization of SnO$_2$ to a certain extent [26-29, 37, 38].

Fig. 5d shows the nyquist plots of PC and SnO$_2$/PC performed after the 300th cycle in order to further understand their electrochemical performance. The SnO$_2$/PC has much smaller semicircle diameter than that of the PC, manifesting that SnO$_2$/PC has lower charge-transfer resistance as well as contact resistance. This conclusion is consistent with previous reports [1, 15, 39]. Comparing with PC (139.0, 17.92 ohms), SnO$_2$/PC electrode has lower $R_t$ and $R_{ct}$ values (89.12, 9.87 ohms), which is enhanced by its 3D structure and ultrasmall SnO$_2$ nanoparticles.

4. CONCLUSIONS

In summary, 3D SnO$_2$/PC was successfully prepared using a simple method in this work. Benefiting from the advanced 3D hierarchical structure and ultrasmall SnO$_2$ nanoparticles, the nanohybrids have shown excellent electrochemical performances. At 0.1 A /g in the 100th cycle, the reversible specific capacity is 1374 mAh/g. These outstanding characteristics are desirable and make 3D SnO$_2$/PC a promising anode material for LIBs.

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