Facile Synthesis of Mesoporous SnO$_2$ Submicrospheres by Microemulsion Approach as High-Capacity Anodes Material for Lithium-Ion Batteries

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Based on a strategy for precipitation of a product with lower solubility product constant ($K_{sp}$) by introducing a phase with higher $K_{sp}$, we firstly report a facile microemulsion route through introducing ZnSO$_4$ for synthesizing mesoporous SnO$_2$ submicrospheres at ambient temperature followed by annealing treatment at 873 K for 2 h. As-prepared SnO$_2$ submicrospheres exhibit uniform morphology, high specific surface area. SnO$_2$ nanoparticles achieved here feature high crystallinity, small particle sizes (ca. 4.4 nm) and narrow size distributions, contributing to SnO$_2$ submicrostructures with large reversible capacity (846 mAh·g$^{-1}$ after 50 cycles at a current density of 100 mA·g$^{-1}$) and significantly improved cycling performance. We expect our methodology could act as a reference for preparing a variety of nanoscale materials with novel structure and function in nanotechnology.

Keywords: Lithium-ion batteries; Submicrospheres; SnO$_2$; Anode materials

1. INTRODUCTION

Recently, many efforts have been made to implant a Sn-based anode into a Li-secondary battery since it was first reported by Idota and co-workers in 1997 [1-4]. With high theoretical reversible lithium storage capacity (782 mAh·g$^{-1}$), more than twice that of the currently commercialized graphite (372 mAh·g$^{-1}$), and low potential of lithium ion intercalation, tin oxide (SnO$_2$) is regard as one of the most promising candidates for anode materials [5-7]. However, similar to other alloy-type anode materials, the main factor limiting the application of SnO$_2$ is the poor cyclic performance due to pulverization and subsequent electrical disconnection of the electrode caused by the extremely large volume change (up to about 300%) during the insertion and extraction processes of Li$^+$ [8-10]. To enhance the cyclability of the electrode, hybridizing SnO$_2$ with carbon is effective, but
this approach sacrifices the capacity itself due to the introduction of carbon and is usually complicated in fabrication [11-14]. It is well established that nanomaterials, especially in hollow or porous nanostructures, hold the key to fundamental advances in shortening path, accommodating large volume change, affording high capacities and rechargeability, owing to the high specific surface area and quantum size effects [15-16].

Consequently, the current strategies mainly address the synthesis of SnO$_2$ nanostructures with different geometrical morphologies, including nanoparticles [17-20], nanorods/belts/wires [2, 21-25], nanodisks [26], nanotubes [27-28], nanoboxes [3, 29], hollow spheres/octahedral [9, 30-32] and hierarchical/mesoporous structures [33-38], by various synthetic approaches such as sol-gel [17-18], solution-phase growth [6, 19-23, 32-36], vapor-phase evaporation [7, 24-26], template-based method [3, 27-28, 31], and molten salt synthesis [21], and so forth.

Since the term “microemulsion” was introduced by Schulman, Stoeckenius and Prince for the first time in the late 1950s [39], microemulsion process (reverse micelle synthesis) has been developed to a powerful route to controlling particle size and size distribution and has been widely used for synthesizing various nanoscale crystallines, such as metallic, metal oxide, semiconductor nanoparticles, and even more complex ceramic nanomaterials [40-43]. A microemulsion is considered as a thermodynamically stable isotropic dispersion of two immiscible liquids since the microdomain of either or both liquids has been stabilized by an interfacial film of surface-active molecules [39-41]. Among all chemical processes, the microemulsion method has proved to be particularly versatile and reproducible superior to many others in terms of delivering homogenous and monodisperse nanoparticles. Therefore, the size, morphology and chemical homogeneity of the resulting nanoparticles can be effectively controlled by proper choice of the composition of the microemulsion system [41-46].

Herein, we report a facile strategy for preparing mesoporous SnO$_2$ submicrospheres via crystalline nanoparticle aggregates by a simple microemulsion route. By introducing ZnSO$_4$, SnO$_2$ precursors will precipitate from microemulsion solutions at room temperature, which is further converted to well-dispersed crystalline nanoparticles (ca. 4.4 nm) after annealing treatment at 873 K for 2 h, leading to high lithium ion storage capacity.

2. EXPERIMENTAL

2.1 Materials synthesis

Analytical grade SnCl$_4$·5H$_2$O, ZnSO$_4$·5H$_2$O, n-pentanol, cyclohexane and cetyltrimethylammonium bromide (CTAB) were used as received without further purification. Deionized water was used in the experiments. The reaction was carried out in a 50 mL glass coneshaped bottle at ambient temperature (298 K). In a typical procedure to synthesize SnO$_2$ nanomaterials, two microemulsion solutions were prepared by adding 2.5 mL of 5 mmol SnCl$_4$·5H$_2$O and 2.5 mL of 10 mmol ZnSO$_4$·5H$_2$O aqueous solutions to n-pentanol/CTAB/cyclohexane systems (n-pentanol/CTAB = 18 (mol ratio), H$_2$O/CTAB = 185 (mol ratio), [CTAB] = 0.09 M), respectively,
which were magnetically stirred for 10 min until they became homogeneous and transparent. After that, the two solutions were mixed rapidly, continued to stir for 30 min, and then were set aside at room temperature for 48 h. A white precipitate was harvested after centrifugation, washed with deionized water and absolute ethanol several times, and then dried in an oven at 333 K for 6 h. The precipitates were then transferred to a tube furnace and annealed in air at various temperatures of 673, 773 and 873 K for 2 h to form final products.

2.2 Materials characterization

The synthesized products were characterized by powder X-ray diffraction (XRD, Rigaku-D/Max 2500PC/Japan, using Cu Kα radiation, λ=1.5406 Å), field emission scanning electron microscopy (FESEM, FEIXL-30/USA), transmission electron microscopy (TEM, FEI-TECNAI G2 F20/USA, operating at an accelerating voltage of 200 kV) equipped with energy dispersive X-ray spectroscopy (EDS, EDAX-Genesis/USA). Brunauer-Emmett-Teller (BET) surface area and pore volume were estimated using ASAP 2420 (USA).

2.3 Electrochemical measurements

The annealed products at 873 K for 2 h were mixed with acetylene black (AB) and a binder (poly (vinylidene fluoride), PVDF), in weight ratios of 80:10:10 and 40:40:20, respectively, in a solvent (N-methyl-2-pyrrolidone, NMP). The slurry was uniformly pasted on Cu foil. Such prepared electrode sheets were dried at 393 K for 12 h in a vacuum oven and pressed under a pressure of approximately 4 MPa. The CR2025-type half-coin cells were assembled in an argon-filled glove box with H₂O and O₂ contents below 1 ppm. Metallic lithium foil was used as the counter and reference electrode. The electrolyte consists of a solution of 1M LiPF₆ in ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) (with a EC:EMC:DMC volume ratio of 1:1:1). Charge–discharge performances were evaluated by a LAND CT2001A battery instrument at a constant current density within a cutoff window of 0.05-3.0 V at room temperature. Cyclic voltammetry (CV) measurements were carried out on a CHI650D electrochemical workstation over the potential range 0.05-3.0 V vs. Li/Li⁺ at a scanning rate of 0.1 mVs⁻¹.

3. RESULTS AND DISCUSSION

Figure 1a-d show XRD for as-synthesized precursors and annealed products at various temperatures (673, 773 and 873 K), respectively. Without annealing treatment, diffraction peaks detected are relatively weak, broad and overlapped (Figure 1a), revealing the presence of imperfect lattice sites and amorphous phases. With the annealing temperature rising from 673 to 773 K, peak intensities increase gradually while the full width at half maximum (FWHM) decrease gently (Figure 1b and c), implying improved crystallinity and expanded particle sizes. As the temperature further
grows to 873 K, the peaks become comparatively sharper (Figure 1d), revealing nanoparticles achieved having better crystallinity. All peaks can be well indexed as tetragonal rutile-like SnO$_2$ (cassiterite, Joint Committee on Powder Diffraction Standards (JCPDS) card No. 41-1445, space group: $P4_2/nmn$ (136)). No other peaks are detected. Average lattice constants of SnO$_2$ nanoparticles are estimated to be $a=b=4.739$ and $c=3.198$ calculated from (110), (101) and (211) diffraction peaks (Figure 1d).

**Figure 1.** XRD patterns of (a) SnO$_2$ precursors and after annealing treatment for 2 h at (b) 673, (c) 773 and (d) 873 K, respectively.

**Figure 2.** Morphological and EDS analyses of SnO$_2$ submicrospheres: (a) FESEM images; (b) TEM images; (c) HRTEM image (SAED pattern is shown in the lower left corner); and (d) EDS analysis.
Figure 2a displays typical FESEM image of annealed products at 873 K for 2h. One can see that products prepared here exhibit coarse surface and spherical morphology with average size of ~350 nm. To explore inherent structures, SnO\textsubscript{2} submicrospheres are further characterized by the TEM. Figure 2b clearly show disordered wormhole-like mesoporous pores. The high-resolution TEM image displays SnO\textsubscript{2} nanoparticles with ~3.0-5.0 nm size distributions, and lattice fringes of the ones with (110) and (101) planes are frequently observed in Fig. 2c. The selected-area electron diffraction (SAED) pattern (inset in Fig. 2c) indicates that the submicrospheres are polycrystalline, and diffraction rings can be indexed to the (110), (101), (200), (211) and (301) planes, coinciding with the tetragonal SnO\textsubscript{2}. From typical EDS results (Fig. 2d), the compositions of SnO\textsubscript{2} submicrospheres are dominated by O and Sn signals and Cu peaks (derived from the copper foil substrate) accompanying a small Si peak (derived from the EDS probe). No Zn peak is detected under EDS analysis, even though a high concentration of Zn\textsuperscript{2+} (with a designed Zn\textsuperscript{2+}:Sn\textsuperscript{4+} molar ratio of 2:1) is introduced into the microemulsion system.

According to XRD and EDS results, we speculate that SnO\textsubscript{2} formation reactions in microemulsion systems might be as follows:

\begin{equation}
Sn^{4+} + 4OH^- \rightarrow Sn(OH)_4^{\downarrow}
\end{equation}

\begin{equation}
Sn(OH)_4^{\downarrow} \rightarrow SnO_2 + 2H_2O
\end{equation}

Note that the OH\textsuperscript{−} in reaction (1) is produced by the self-ionization reaction of H\textsubscript{2}O. Since the solubility product constant (K\textsubscript{sp}) for Sn(OH)\textsubscript{4} (1×10\textsuperscript{-56}) is much lower than that for Zn(OH)\textsubscript{2} (3×10\textsuperscript{-17}) [47], it is not surprising that the precipitation reaction for the former is the dominant reaction when the two microemulsion solutions are mixed together. Moreover, the mixed solutions after precipitation reactions was tested to be acidic (pH=1.0), further confirming that reaction (1) did occur. The acid mixed solution hinders the precipitation reaction of Zn(OH)\textsubscript{2} owing to the release of H\textsuperscript{+} by the self-ionization reaction of H\textsubscript{2}O. Moreover, the particularly low OH\textsuperscript{−} concentration in an acidic microemulsion system significantly retards the precipitation and growth of Sn(OH)\textsubscript{4} and further makes the growth of SnO\textsubscript{2} nanoparticles with small sizes favorable (~3.0-5.0 nm). More importantly, the synthesis process is performed at ambient temperature, which also restricts the growth of precipitates. To the best of our knowledge, this is the lowest temperature reported by far for the synthesis of fine nanoparticles of SnO\textsubscript{2}.

From TEM images (Fig. 2b and 2c), we can conclude that SnO\textsubscript{2} submicrospheres (~350 nm) consists actually of crystalline SnO\textsubscript{2} nanoparticle aggregates. It is believed that the impetus for the aggregation of nanoparticles is to eliminate surface energy, which is largely different from classical crystal growth mechanisms of “Ostwald-ripening” [30-31] and “oriented attachment” [48]. It is acknowledged that the crystal growth is generally at the expense of surface area, which impairs the desirable physical and chemical properties of nanoparticles. In this study, however, the aggregates of crystalline SnO\textsubscript{2} nanoparticles with wormhole-like mesoporous structure still retain the nature of large specific surface area.

N\textsubscript{2} adsorption/desorption isotherms were employed for the products (Fig. 3). One can see that
the samples display a typical IV isotherm curve with a clear adsorption/desorption hysteresis loop, indicating the existence of abundant mesoporous structures in the architectures [49]. The Brunauer-Emmett-Teller (BET) specific surface area are 99.5 m$^2$g$^{-1}$ for SnO$_2$ submicrospheres. To further analyze the pore structure, pore size distribution curves have been investigated by using Barrett-Joyner-Halenda (BJH) method. The pore size distribution measurement indicates that the SnO$_2$ submicrospheres exhibit a very narrow pore-size distribution with an average pore diameter at ca. 3.6 nm (inset of Fig. 3). The pore size obtained from BJH is consistent with the result from TEM image (Fig. 2c).

**Figure 3.** Nitrogen adsorption and desorption isotherms of SnO$_2$ submicrospheres with corresponding pore-size distribution (inset) calculated by BJH method from desorption branch.

Motivated by the inherent structure of SnO$_2$ submicrospheres, we have performed lithium storage tests as an anode material with different weight ratios of carbon 10% (sample-1) and 40% (sample-2). Figure 3a and b show initial discharge/charge voltage profiles and cycling performance at a current density of 100 mA·g$^{-1}$ within a cutoff window of 0.05-3.0 V, respectively. The initial discharge and charge capacities are 1733 and 960 mAh·g$^{-1}$, and 2801 and 1566 mAh·g$^{-1}$ for sample-1 and sample-2, respectively. The large capacity loss in the first cycle for both samples is mainly attributed to the initial irreversible formation of Li$_2$O, and other irreversible processes such as trapping of some lithium in the lattice, inevitable formation of solid electrolyte interface (SEI layer) and electrolyte decomposition, which are common for most anode materials [28, 30]. Moreover, it is clearly that the first discharge and charge capacities of the sample-2 are significantly higher than those of sample-1. More importantly, the sample-2 exhibits a much better cycling performance than sample-1 (Fig. 4b). For the sample-1, the reversible capacity rapidly decreased with the increasing cycle numbers. The capacity was only 203 mAh·g$^{-1}$ after 30 cycles, which is below capacity of pure carbon (302 mAh·g$^{-1}$). In contrast, the reversible capacity of the sample-2 retains 846 mAh·g$^{-1}$ after 50 cycles. This improvement of cyclability indicated that the conductive carbon content affect the SnO$_2$ submicrospheres performance as anode material for lithium ion batteries. Similar phenomenon has been observed in previous literature [50].
Figure 4. Electrochemical performance of SnO$_2$ submicrospheres: (a) discharge/charge profiles; (b) cycling performance; and (c) cycling properties with various current densities.

In addition, the sample-2 exhibits better rate capability at various current densities of 100, 200 and 500 mA·g$^{-1}$ (Fig. 4c). The discharge capacity at the 100 mA·g$^{-1}$ is 1347 mAh·g$^{-1}$ over 6 cycles, and the capacity at the 200 mA·g$^{-1}$ is 929 mAh·g$^{-1}$ over 12 cycles. Even at a high current density of 500 mA·g$^{-1}$, it retains high capacity of 774 mAh·g$^{-1}$ over 18 cycles. After the current density bounces to 200 mA·g$^{-1}$, the electrode delivers a capacity of about 805 mAh·g$^{-1}$ over 24 cycles.

4. CONCLUSION

In summary, mesoporous SnO$_2$ submicrospheres via crystalline nanoparticle aggregates with uniform morphology can be facilely synthesized by microemulsion method at ambient temperature followed by annealing treatment at 873 K for 2 h. The SnO$_2$ nanoparticles achieved here feature high crystallinity, small particle sizes and narrow size distributions. As an anode material in lithium-ion batteries, SnO$_2$ submicrospheres exhibit a particularly large reversible capacity (846 mAh·g$^{-1}$ after 50 cycles) and significantly enhanced cycling performance. A synthesis strategy for precipitation of a product with lower K$_{sp}$ by introducing a phase with higher K$_{sp}$ can also be developed for the preparation of other nanoscale products during microemulsion synthesis.
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References

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