



Influence of surfactants on the microstructure and electrochemical performance of the tin oxide anode in lithium ion batteries



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ABSTRACT

Different SnO₂ micro–nano structures are prepared by precipitation using a surfactant-assisted process. The surfactants, such as cetyltriethylammonium bromide (CTAB) or sodium dodecyl benzene sulfonate (SDBS), can change the crystal growth direction and microstructure of SnO₂ primary and secondary particles. Larger SnO₂ nanosheets were synthesized without surfactant, and micro–fragments composed of small nanospheres or nanocubes were synthesized using CTAB and SDBS. The CTAB-assisted process resulted in smaller primary particles and larger specific surface area and larger pore volume, as a lithium-ion-battery anode that exhibits superior electrochemical performance compared to the other two anodes. Further investigation showed that the concentration of CTAB had a substantial influence on the growth of the crystal face, morphology and size of the SnO₂ secondary particles, which influenced the electrochemical performance of the anode. A simple mechanism for the influence of surfactants on SnO₂ morphology and size in the precipitation and annealing process is proposed.

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1. Introduction

Tin dioxide (SnO₂)-based materials, which are used as anodes in lithium ion batteries (LIBs), have been intensively studied for the last few decades due to their high theoretical lithium storage capacity of 1494 mAh g⁻¹ (that is much higher than that of the currently used graphite-based anode of 372 mAh g⁻¹), which corresponds to the maximum uptake of 8.4 mol of Li⁺ (SnO₂ + 4 Li⁺ + 4e⁻ ↔ Sn + 2Li₂O and Sn + 4.4Li⁺ + xe⁻ ↔ Li_{4.4}Sn) [1–5]. However, the practical use of SnO₂ based anodes is hampered by their poor capacity retention arising from the large volume change of up to approximately 300% for Li_xSn alloy during charge/discharge processes [4–6]. This would induce huge internal stress in the electrode material, which leads to disintegration and loss of electric contact, and eventually results in quick capacity fading upon extended cycling. Different strategies have been proposed to resolve the abovementioned problems of SnO₂-based anodes, and two of them are widely practiced. One is to introduce carbonaceous materials and other metal oxides into the SnO₂ electrodes [1]. The other effective way is to create uniquely nanostructured SnO₂, which includes nanotubes [7], nanorods [8], nanowires [9],

nanosheets [10], and 3D hollow or porous nanostructures [11–13]. It has been suggested that the nanostructures can exhibit excellent Li⁺ storage performance such as large and stable reversible capacity and good rate capability due to their small size and high specific surface area [1]. In particular, a hollow or porous structure electrode can provide sufficient void space to overcome the damage caused by the volume expansion of SnO₂ during the charge-discharge process, thus leading to improved lithium storage properties, and resulted excellent cycling performance. For example, Yin et al. synthesized mesoporous SnO₂ spheres that were 100–300 nm, and when the 3D mesoporous structure was used as an anode material, it delivered a capacity of 761 mAh g⁻¹ after 50 cycles at a current density of 200 mA g⁻¹. Even at 2 A g⁻¹, this anode retained a capacity of 480 mAh g⁻¹ after 50 cycles [14]. Zhang et al. reported a large and stable reversible lithium-ion storages from mesoporous SnO₂ nanosheets with ultralong lifespan over 1000 cycles. It exhibited outstanding durable cycling life (420 mAh g⁻¹ after 1000 cycles at a current density of 200 mA g⁻¹ at first stage and then 500 mA g⁻¹ at the end) [15]. These anode materials promote electrolyte and lithium ion transfer, minimize the severe volume change and greatly enhance the electrochemical performance, suggesting that structure modification could be a good solution to the poor cyclic retention of SnO₂-based anode materials. Various methods have been applied to synthesize SnO₂ nano-materials, such as thermal evaporation [16], hydrothermal method [17,18], solvothermal

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method [19], precipitation [20,21], microemulsion [22] and the sol-gel method [23]. Among these methods, the hydrothermal or solvothermal method assisted by surfactants have been extensively investigated. By adding surfactants, a number of geometrical morphologies of the SnO₂ nanocrystals have been prepared. For example: SnO₂ nanocubes [24,25], nanosheets [24,25], nanorods [25] and mixture of nano-flower and nano-prism [24], spherical and dumbbell-shaped SnO₂ nanoparticles [26], cauliflower and flower petals morphology [27], and nanocorals, nanofragments and nanogras [28] were synthesized in hydrothermal or solvothermal process assisted by different surfactants such as cetyltrimethylammonium bromide (CTAB) [24–27], sodium dodecyl sulfate (SDS) [24–27], polyvinylpyrrolidone (PVP) [25], tetrapropyl ammonium bromide (TPAB) [25], and polyethylene glycol (PEG) [26,28]. Here, most SnO₂ nano-materials were synthesized by surfactants-assisted hydrothermal or solvothermal process, and most of them were used as sensors [24,28], optical [26] and photocatalysis [27] materials. There are only a few reports that SnO₂ nano-materials were synthesized by precipitation method assisted by surfactants [29]. Jiang et al. [29] prepared a series of Co-doped SnO₂ nanoparticles surface-modified with different amount of CTAB by the co-precipitation of SnCl₄ and urea, and the mediation of surfactant molecules on the magnetic and optical properties was discussed. Zhao [30] prepared SnO₂ hollow spheres and rod bundles using SnSO₄ as raw material and sodium dodecyl benzenesulfonate (SDBS) and PVP as templates at room temperature through oxidation-crystallization of colloidal spheres, and investigated the catalytic performance toward CO oxidation. However, there has been a lack of systematic investigations of the surfactant-assisted precipitation method for synthesizing morphology and size controlled SnO₂, especially the electrochemical performance of this synthesized SnO₂ as anodes of LIBs.

Therefore, in this paper, morphology and size-controlled SnO₂ samples are prepared via a facile and surfactant-assisted precipitation method using oxalic acid as a precipitant followed by an annealing process. We choose a cation surfactant CTAB and an anion one SDBS to study the influence of the surfactants on the morphology and size of SnO₂ samples. And then, the SnO₂ samples are assembled as anodes in LIBs to determine the electrochemical performance. In addition, the influence of the CTAB concentration on the SnO₂ morphology and electrochemical performance was investigated. A simple mechanism for the influence of surfactants on SnO₂ morphology and size in the precipitation and annealing process is also proposed.

2. Experiment

2.1. Synthesis of SnO₂ nanostructures

All of the chemical reagents were of analytical grade and used without further purification. SnO₂ nanostructures were synthesized at room temperature as follows: first, 1.12 g of H₂C₂O₄·2H₂O was dissolved in 50 mL of distilled water under vigorously stirring, and 0.17 g of cationic surfactant (i.e., CTAB) (converts into

9.3×10^{-3} mol/L in the solution, which is larger than the first critical micelle concentration (CMC) of 9.0×10^{-4} mol/L) was added and ultrasonically dispersed for 15 min to form a homogeneous solution. Then, 2.12 g of SnCl₂·2H₂O was added into the above solution, and this mixture was aged for 10 min. Next, the precipitate was separated by centrifugation at 4500 r/min for 20 min and washed several times by water and ethanol. The precipitate was dried at 60 °C for 20 h in air. The dried precursors were placed in a muffle furnace, which was controlled with a heating rate of 2 °C min⁻¹ and annealed at 350 °C for 2 h followed by natural cooling to room temperature. Finally, the product (symbolized SnO₂-CTAB) was obtained. For comparison, we synthesized SnO₂ (symbolized SnO₂-SDBS) under the identical conditions as SnO₂-CTAB using 0.17 g of an anionic surfactant (i.e., SDBS) (converts into 9.8×10^{-3} mol/L, which is larger than the first CMC of 1.2×10^{-3} mol/L). In addition, different amounts of CTAB were used to modify the morphology of SnO₂. One is 0.367 g of CTAB, which is between the first and second CMC values, and the other one is 0.728 g of CTAB, which is larger than the second CMC value of 0.021 mol/L. The obtained samples were symbolized SnO₂-CTAB₁₋₂ and SnO₂-CTAB₂, respectively. For comparison, the same synthesis procedure was conducted without a surfactant to prepare a reference SnO₂ sample (symbolized SnO₂-R). For the sake of clarity, the detailed amount or concentration of CTAB and SDBS added in the synthesis process of each sample, and the CMC value of CTAB and SDBS are listed in Table 1. Here, it is worth pointing out that oxalate acid is used as precipitant of Sn²⁺ ions [31], but it can influence the CMC value of the surfactant in water. According to references [32–34], the CMC value of CTAB is decreased with increasing of the concentration of aliphatic dibasic acids (include oxalate acid). That means the micelles are easier to form in oxalate acid solution than in pure water. Unfortunately, the CMC values of CTAB and SDBS under the corresponding oxalate acid concentration used in this study are lack in literatures. So, the CMC values of CTAB and SDBS in water are used to comparatively study the influence of surfactant kinds and concentration on the morphology and structure of the SnO₂ particles with other conditions being consistent.

2.2. Characterization of the synthesized materials

Structural characterization of the prepared samples was performed using X-ray diffraction (XRD, Model Y2000, China) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 30 kV and 20 mA. The Brunauer-Emmett-Teller (BET) specific surface area was determined using nitrogen adsorption/desorption with an automatic specific surface area measuring equipment (ASAP 2020M, Micromeritics Instrument Corporation). The structure and morphology of the products were observed using a scanning electron microscope (SEM, Model ZEISS Ultra 55, Germany). The thermogravimetric analysis (TGA) was performed under an air flow of 100 mL min⁻¹ using PerkinElmer TGA instrument from room temperature to 800 °C with a heating rate of 10 °C min⁻¹. Infrared spectrum was performed on a Fourier transform infrared

Table 1
The amount and concentration of the surfactant added in the synthesis process of each SnO₂ sample and the CMC value of the surfactant.

Sample	CTAB amount (g); [C (mol/L)]	SDBS amount (g); [C (mol/L)]	First and second CMC of CTAB (mol/L)	First and second CMC of SDBS (mol/L)
SnO ₂ -CTAB	0.17; 9.3×10^{-3}	0	9.0×10^{-4} ; 0.021	
SnO ₂ -SDBS	0	0.17; 9.8×10^{-3}		1.2×10^{-3} ; 6.9×10^{-3}
SnO ₂ -CTAB ₁₋₂	0.367; 0.02	0		
SnO ₂ -CTAB ₂	0.728; 0.04	0		
SnO ₂ -R	0	0		

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