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Preparation and Structure Analysis of Tin-oxide Coated Carbon Nanotube Composites

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Nano tin oxide is a typical n-type semiconductor material with special photoelectric and gas sensing properties. Hence, to study the nano tin oxide cladding carbon nanotubes, it will make for changing the semiconductor, optical, electrical, sensitive and thermal properties of carbon nanotubes, thereby facilitating the application of carbon nanotubes in the fields of ceramic, optoelectronic and gas sensing materials. This paper takes SnCl4, 5H2O and NaOH as raw materials to fully dope the tin oxide and the carbon nanotubes by one-step hydrothermal method, whereby the tin oxide cladding carbon nanotube composites SnO2/CNTs is available. More than that, various characterization technologies are introduced here to analyze and discuss the structure of the composite in detail, in conjunction with its electrochemical property.

1. Introduction

As the electrochemical performance of tin-based materials may be improved by the tin-carbon based composite nanomaterial, this topic has become a hotspot in the field of lithium ion battery cathode materials in recent years. The study results reveal that the inorganic surface finish of carbon nanotubes helps improve the dispersibility of carbon nanotubes and enhance its compatibility with metal matrix, reduce the difference in specific gravity between them, and thus boost the enhancement effect (Yan et al., 2010; Lu et al., 2014; Tang et al., 2015). For example, tinplating on the surface of the carbon nanotubes can increase its wettability with the copper matrix, hence to elinminate the interface problems between both, thereby improving the mechanical properties of the carbon nanotube composite. Nano tin oxide has a broad application prospect in the fields of gas sensors, humidity sensors, thin film resistors, optoelectronic devices, wave-absorbing materials, electrode materials and solar cells (Sun et al., 2015).

In this context, the study of nano tin oxide cladding carbon nanotubes will be helpful to change the semiconductor, optical, electrical, sensitive and thermal properties of carbon nanotubes, thereby facilitating the application of carbon nanotubes in many fields such as ceramic, optoelectronic and gas sensing materials. (Ha et al., 2010; Kim et al., 2015). This paper takes SnCl4, 5H2O and NaOH as raw materials to dope tin oxide and carbon nanotubes by one-step hydrothermal method. In this way, the tin oxide cladding carbon nanotube composites SnO2/CNTs are available. A depth analysis resorts to various characterization technologies for composite structure, and electrochemical behaviors of the composite. This paper takes SnCl4, 5H2O and NaOH as raw materials to fully dope the tin oxide and the carbon nanotubes by one-step hydrothermal method, whereby the tin oxide cladding carbon nanotube composites SnO2/CNTs is available. More than that, various characterization technologies are introduced here to analyze and discuss the structure of the composite in detail, in conjunction with its electrochemical property.

2. Experiment

Tin oxide features high lithium storage capacity (781m/Ahg-1), easy control of morphology, simple preparation process and low cost. It has found wider application in the electrode materials of lithium ion batteries as studied extensively now. The tin oxide nanoparticles deposite on the surface of the carbon nanotubes so that the aggregation phenomenon will be avioded. In doing so, the specific surface area gets higher while the

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apparent conductivity is improved, thus contributing to various properties of the tin oxide nanoparticles (Rigoni et al., 2014).

2.1 Experimental materials, instruments and characterizations

The principal raw materials, reagents, instruments and characterization methods used in this study are listed in Table 1.

Table 1: Experimental main raw materials, reagents, instruments and characterization methods

	Name	Manufacturer
Main raw materials and reagents	CNTs	Shenzhen nangang Co., Ltd.
	SnCl2.5H2O	Tianjin Komiou Chemical Reagent Co., Ltd.
	Stannous sulfate	Tianjin Komiou Chemical Reagent Co., Ltd.
	Sodium hydroxide	Shanghai Chemical Reagent Factory
	Hydrazine	Alfa Aesar (China) Chemical Co., Ltd.
Instruments	Coating machine AFA-III	Hefei Kejing Material Technology Co., Ltd.
	Cutting machine WLK-30	Hefei Kejing Material Technology Co., Ltd.
Mehtods	Transmission electron microscope (TEM)	The fine structure of the composite was analyzed using a FEI TECNAL/G20 transmission electron microscope.
	Thermogravimetric analysis (TGA)	Using the STA-409PC thermogravimetric analyzer from Germany NETZSCH, the thermogravimetric tests were carried out on different samples from room temperature at a heating rate of 20 °C/min to 800-900 °C.

2.2 Preparation of tin oxide cladded carbon tube composite

The preparation process of the tin oxide cladding carbon tube composite in this study is shown in Figure 1.

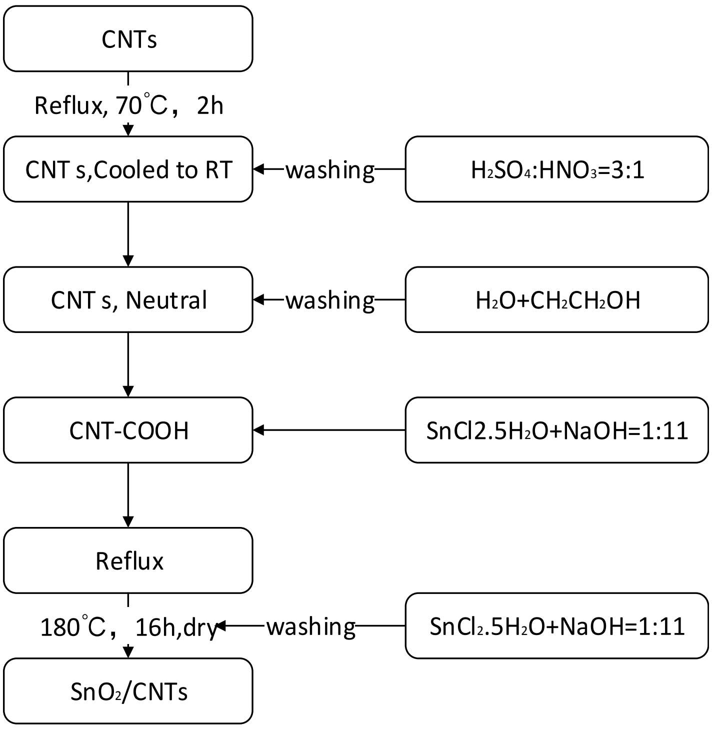
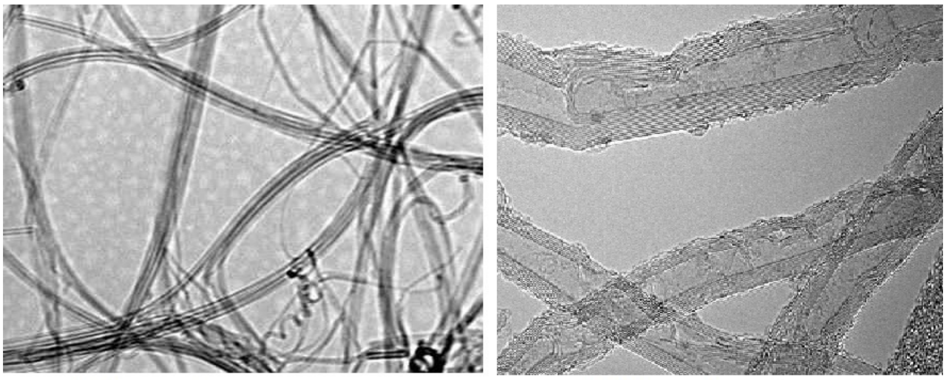


Figure 1: Preparation process of tin oxide coated carbon nanotube composite material

3. Structural characterization of tin oxide coated carbon tube composites

3.1 Transmission electron microscope (TEM)

The TEM images of carbon nanotubes and tin oxide cladding carbon nanotube composites are analyzed and compared. The results are shown in Figure 2.



(a)TEM image of carbon nanotubes (b)TEM image of composite material

Figure 2: TEM image of carbon nanotube (3a) and tin oxide coated carbon tube composite (3b)

As shown in Fig. 2, the diffraction peak of tin oxide is broadened, which shows that the grain size of tin oxide is tiny. As shown in Fig. 2, the tin oxide nanoparticles are uniformly and continuously cladded on the surface of the carbon nanotubes to form a SnO2/CNTs shell/core structure. High resolution TEM (HRTEM) images show that the carbon nanotube is covered with a layer of SnO2 (Lorestani et al., 2015). It is about 6 mm thick, and the grain size of SnO2 in the cladding layer falls within 3 nm ~ 6 nm. With the reagents, under the reaction conditions given in this study, the growth process of tin oxide cladding carbon tube composites is shown as follows:

$$Sn^{4+} + OH^{-} \rightarrow Sn(OH)_4 \tag{1}$$

$$Sn(OH)_4 + OH^{-} \rightarrow [Sn(OH)_6]^{2-} \tag{2}$$

$$[Sn(OH)_6]^{2-} \rightarrow SnO_2 + 2H_2O + 2OH^{-} \tag{3}$$

That is, under the alkaline conditions, Sn^{4+} first reacts with the $OH^{-}$to form Sn $(OH)_4$ (Formula 1), and then reacts with the excess OH^{-}according to the formula 2 to form [Sn $(OH)_6]^{2-}$. Afterthat, it transfers into the tin oxide nanoparticle (Formula 3) (Zhao et al., 2014).

3.2 Thermogravimetric analysis (TGA)

The TGA results of the tin oxide cladding carbon tube composites are shown in Figure 3.

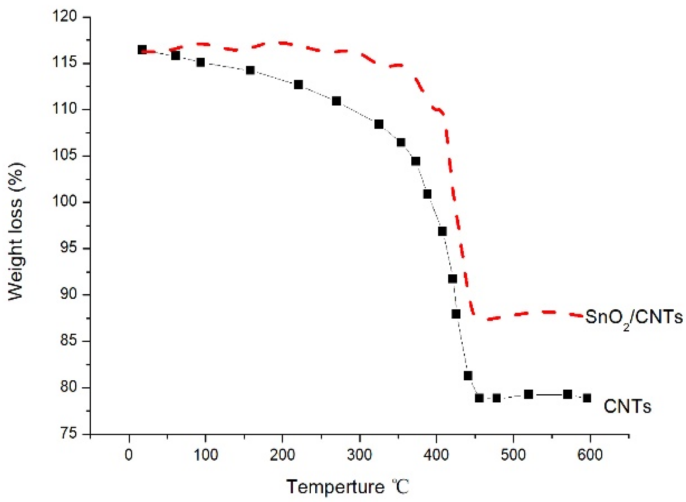


Figure 3: Thermogravimetric analysis of carbon nanotubes and composites

4. Electrochemical properties of tin oxide coated carbon tube composites

In order to explore the reaction mechanism of Li+ deintercalation during the charge-discharge process of composite materials, the charge and discharge behaviors and cyclic voltammetry are tested here.

4.1 Test of charge and discharge property

As shown in Figure 4, it is a graph of the charge and discharge behaviors of SnO2/CNTs. As shown in the figure, the discharge curve in the first week has a niche plateau at the voltage range of 0.5-1.5 V, which does not exist in the subsequent cycle. It is known that the plateau corresponds to the formation of SEI film and irreversible reaction of Li2O between SnO2 and Li during the first indischarge. Besides, it is also the main source of irreversible capacity in the first cycle. The charge curve has a plateau that appears frequently in the cycle at a voltage range of 0.4-0.6 V, corresponding to the reversible reaction that Sn and Li form the alloy. The prepared coaxial SnO2 nanocrystalline cladding CNTs inhibit the agglomeration of SnO2 nanoparticles, increase the specific surface area of the electrode material, while boosting the contact area between the electrolyte and the electrode material (Golobostanfard et al., 2015; Hwang et al., 2016). It further inhibits the phenomenon of material fragmentation and detachment, and ultimately improves the lithium capacity and cycle stability of the electrode material.

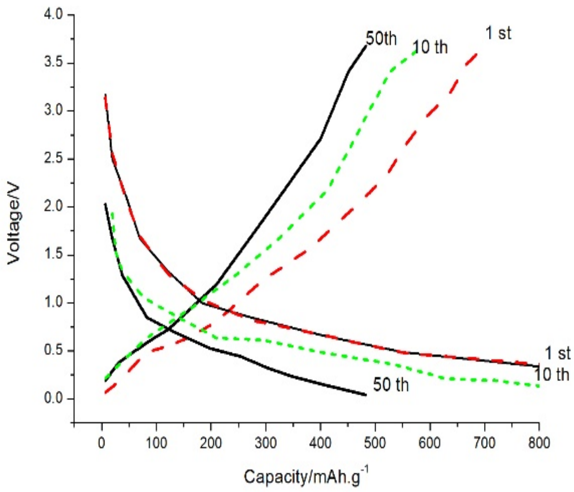


Figure 4: Lithium battery performance curve of SnO2/CNTs

4.2 Test of cyclic voltammetry

Cyclic voltammetry can be tested to acquire some information about electrochemical reaction, voltage plateau and reversibility of the electrode materials during the lithium ion charge and discharge, thus playing an indicative function on the lithium storage property and mechanism. The SnO2 based electrode generally carries out the reaction by the following steps (Lin et al., 2014):

$$SnO_2 + 4Li^+ + 4e^- \rightarrow Sn + 2Li_2O \quad (4)$$

$$Sn + xLi^+ + xe^- \leftrightarrow Li_xSn (0 \le x \le 4.4) \quad (5)$$

$$xLi^+ + C + xe^- \leftrightarrow Li_xC \quad (6)$$

As shown in Figure 5, cyclic voltammograms of pure carbon tube, tin oxide cladding carbon tube composite are give. What we can see is that during the cathode scan for the first time, a more obvious reduction peak appears at 0.82V; while in the process of anode scan, two anodic peaks appeare at 1.3V, which corresponds to the alloying and de-alloying processes between tin and lithium ions, as described in Equ. 4. 5 and 6.

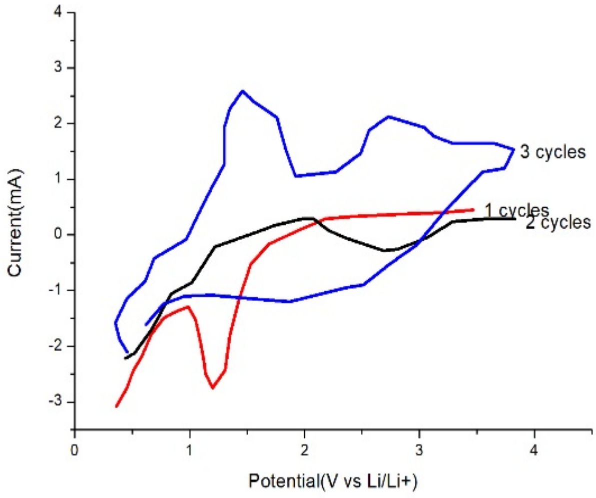


Figure 5: Cyclic voltammetry curve of SnO2/CNTs

4.3 Specific capacity of composite materials

As shown in Figure 6, the curves of the specific capacities of pure carbon nanotubes and tin oxide cladding carbon tube composites as a function of cycles are plotted. Obviously, the specific capacity of SnO2/CNT is higher than that of CNT, and the SnO2/CNT cycle property performs very good, so that the electrochemical properties of composites made of SnO2 and carbon nanotubes are significantly improved. We attribute this to good dispersion effect and good conductivity of tin oxide on the carbon nanotube matrix. The irreversible capacity loss in the first cycle of the two samples is much higher, this may be due to the electrolyte decomposition on the high specific surface and the formation of the SEI layer; while for the SnO2/CNT sample, it may be attributed not only to the electrolyte decomposition and the formation of the SEI layer on the surface of CNT, but also to the formation of the SEI layer on the surface of the metal.

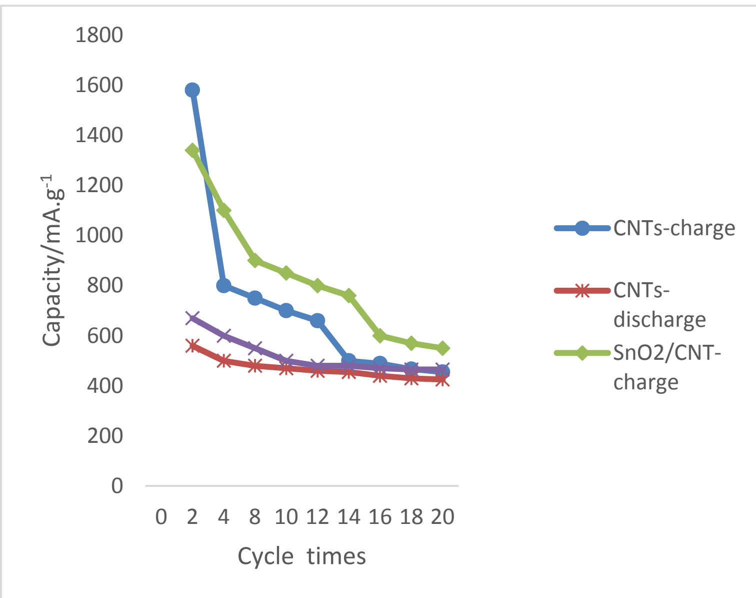


Figure 6: Specific heat capacity changes of CNTs and SnO2/CNTs during charge and discharge

5. Conclusion

The carbon nanotubes or tin metals are used as a negative electrode material for lithium ion batteries since they have their own strengths and defects. The carbon nanotube has a lower specific capacity, but a good cycle property. On the contrary, the metallic tin has very high lithium intercalation capacity, but its cycle property is very poor. The tin oxide cladding carbon nanotube composite will show a good electrochemical behavior. The results from the experiment in this study reveal that the good electrochemical property of tin oxide cladding carbon nanotube composites attributes to the good conductivity of carbon nanotube matrix, good dispersion effect of tin oxide and the unique geometry properties of the composite.

Acknowledgments

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