



Controllable synthesis and highly efficient electrocatalytic oxidation performance of SnO₂/CNT core-shell structures

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ABSTRACT

In this work, the nanocomposites, carbon nanotubes (CNTs) coated with nanosized uninterrupted SnO₂, were prepared controllably by a facile solvothermal method. The obtained nanocomposites have a thin overlayer which is made of nanoparticles with a diameter of ~3 nm. The products were characterized by X-ray diffraction and transmission electron microscopy. The obtained SnO₂/CNTs have an excellent electrocatalytic oxidation performance for the X-3B, a kind of dye. The parameters affecting the electrocatalytic activity were investigated in details. The excellent catalytic property of the SnO₂/CNT electrodes can be explained as follows: (1) high specific surface area gives more active sites for X-3B oxidation; (2) the formation of thin, uniform, and uninterrupted coverage of SnO₂ nanoparticles on CNTs raises the potential of oxygen evolution and the current efficiency; and (3) the CNTs increase the conductivity of the electrodes, which results in the increase of the current efficiency.

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1. Introduction

Highly concentrated dye wastewater causes serious environmental problems due to its bioreistance, high color, and high chemical oxygen demand [1,2]. Recently, the potential use of electrochemical methods in wastewater has attracted much attention, because it is a clean advanced oxidation technology. Some researchers [3–5] presented extensive reviews on the developments of the electrochemical oxidation process and anode materials in wastewater treatment, verifying that it is still far from being a solution to the highly concentrated organic wastewater in industry. The broad application of electrochemical technology in wastewater treatment is limited by the electrode lifetime and energy consumption which mainly depends on electrode materials [6,7]. The research and development of positive electrode materials would benefit extensive applications.

Carbon nanotubes (CNTs) are an ideal electrode material due to its high surface area and superior electronic property [8–10]. However, the low potential for oxygen evolution and uncontrollable surface property of CNTs limit their applications in this field. Recently, it has been demonstrated that CNTs functionalized with ultrathin foreign species coatings can lead to a significant

enhancement of properties relevant to various application fields, such as solar cells, electrochemical storage of energy materials, and catalysts [11–13].

Tin oxide (SnO₂) is a very important semiconductor, which has been extensively applied in electronic fields, battery technology, and transparent electrodes [14,15]. However, the low electrical conductivity of SnO₂ limits its applications to some extent. The hybrid of CNTs and SnO₂ shows exceptional conductivity and high surface area, and has the potential to be widely used in the above-mentioned fields. Previously, SnO₂/CNTs has been synthesized by hydrolysis methods, and found that it is good for gas sensors [16–18]. For example, Wang et al. [19] have observed the formation of thin, uniform, and uninterrupted coverage of SnO₂ nanoparticles on multi-walled CNTs and found that they are active components in NO and NO₂ detection. However, few studies on the electrocatalytic oxidation performance by using SnO₂/CNT core-shell structures as electrodes are reported [16–19].

Previously, we have synthesized SnO₂/CNT composite electrodes by a liquid deposition method and found that the electrodes showed a high electrocatalytic performance [20]. Recently, we have synthesized Eu₂O₃/CNT and CeO₂/CNT core-shell structures by a solvothermal method [21,22]. Herein we report a simple solvothermal method to synthesize a SnO₂/CNT core-shell structure, which show a higher electrocatalytic performance than that of the previous liquid deposition method, due to the high

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surface area and the superior conductivity of CNTs as well as the excellent electrocatalytic performance of SnO₂. The parameters affecting the electrocatalytic activity and the oxidation mechanism are systematically investigated.

2. Experimental section

2.1. Synthesis of SnO₂/CNT core-shell structures

The multi-walled CNTs used in this work were prepared by the catalytic decomposition of methane [23], and were 40–60 nm in diameter and 1–10 μm in length. All the other chemicals were purchased from National Chemical Reagent Company (Shanghai, China) and used without further purification. Deionized water was used throughout.

In a typical experiment, a given amount of CNTs was first refluxed in a 30% nitric acid at 140 °C for 24 h. The purified CNTs were first dispersed in a 40 mL 0.05 M SnCl₂·2H₂O pyridine solution at a concentration of 1.25 mg/mL, and then transferred into a 50 mL PTFE autoclave. Subsequently, the autoclave was placed in an oven and maintained at 140 °C for 24 h. After the autoclave was cooled to an ambient temperature naturally, the precipitates were collected and washed repeatedly with absolute ethanol.

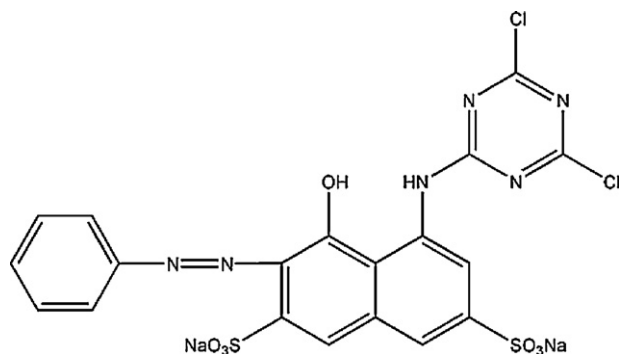
2.2. Preparation of SnO₂/CNT electrodes

The SnO₂/CNT electrodes were prepared as follows [20]: 10 wt.% PTFE was added into a given amount of SnO₂/CNTs, which was then dispersed in 10 mL absolute ethanol. After drying the mixtures at 60 °C for 24 h, the electrode plate (Ø 20 mm × 1 mm) was formed under the pressure of 25 MPa at the ambient temperature.

2.3. Catalytic activity evaluation

The reactive brilliant red X-3B (CAS Registry No. 12226-03-8) was selected as a model pollutant because it is hardly biodegradable by the conventional biological process, but also widely used in the textile, color solvent, ink, paint, varnish, paper, and plastic industries. The structure of the X-3B is shown in Scheme 1. The dye concentration was measured at 512 nm by a UV–vis spectrophotometer (722S, China).

The bulk electrolysis were performed in a one-compartment electrolytic cell with parallel plate electrodes applying a constant current density of 50 mA cm⁻² and with an initial voltage of 3 V, using a GPS-2303C potentiostat/galvanostat. The SnO₂/CNT electrode was used as anode and the stainless steel AISI 304 as cathode. The electrolyte was stored in a 100 ml glass reservoir (T = 25 °C), which contained 50 mg L⁻¹ X-3B and 0.2 mg L⁻¹ Na₂SO₄, and the initial pH was 2 [20].



Scheme 1. Structure of reactive brilliant red X-3B.

2.4. Materials characterization

The powder X-ray diffraction (XRD) measurements were performed with Rigaku D/MAX-RB X-ray diffractometer by using Cu Kα (40 kV, 40 mA) radiation and a secondary beam graphite monochromator. The morphologies were observed by field emission transmission electron microscopy (TEM, JEOL JEM-2010F), and powdered samples were dispersed in absolute ethanol by ultrasonication for 10 min in a KQ-250B ultrasonic bath. The Brunauer–Emmett–Teller (BET) specific surface area of the samples was characterized by nitrogen adsorption at 77 K with Micromeritics ASAP 2010. Electrochemical measurements were performed using the electrochemical workstation (CHI 660, Shanghai Chenhua, China) in a conventional three-compartment cell. The working volume of the cell was ca. 60 ml. A SnO₂/CNT electrode (Ø 20 mm × 1 mm) was employed as the working electrode; a Pt plate of the same size was used as the counter electrode, and a saturated calomel electrode (SCE) was employed as the reference electrode (all potentials were quoted against SCE). The solution contained 50 mg L⁻¹ X-3B, 0.2 mg L⁻¹ Na₂SO₄ and pH of 2 adjusted with H₂SO₄ solution.

3. Results and discussion

3.1. Characteristics of SnO₂/CNT composites

The as-prepared SnO₂/CNT composites were firstly examined by means of TEM. It is found that the solvothermal temperature and the weight percent of SnO₂ have a great effect on the morphologies of SnO₂/CNT composites. When the solvothermal temperature is 140 °C and the weight percent of SnO₂ is 40%, almost all the CNTs are fully coated with SnO₂, and few particles are dispersed in the solution, as shown in Fig. 1a. Fig. 1b clearly shows that the coating layer of CNTs is smooth and is ~3 nm in thickness. The HRTEM image (Fig. 2) confirms that the shell layer is composed of highly compact tiny SnO₂ particles. At the same solvothermal temperature (140 °C), when the weight percent of SnO₂ is increased to 70%, Fig. 1c shows that some particles are separated from the composites although all the CNTs are fully coated with SnO₂. If the solvothermal temperature is increased to 180 °C and the weight percent of SnO₂ is still 40%, not the coating layer but the adsorbed particles with a diameter of ~10 nm are observed in Fig. 1d. The TEM images show that the morphology of SnO₂/CNT composites can be controlled by adjusting the solvothermal temperature and the weight percent of SnO₂, which would result in the different catalytic activities as discussed below.

Fig. 3 shows the XRD patterns for the three samples. It is found that the solvothermal temperature has a great effect on the crystal structure of SnO₂ layer. It can be seen that at 120 °C and 140 °C, the feature peaks denote the orthorhombic SnO₂ (JCPDS No. 77-0452); while at 180 °C, SnO₂ nanoparticles present as cassiterite (SnO₂), which has a tetragonal rutile structure (JCPDS No. 29-1484) with two SnO₂ formula units per unit cell. This result is an evidence of a phase transition from orthorhombic to tetragonal in SnO₂ with increasing the treatment temperature, which is similar to the previous reports [24,25]. It is obvious that the high temperature and pressure in autoclaves favor the phase transition from orthorhombic to tetragonal for SnO₂. No obvious peaks corresponding to SnCl₂, Sn, or other tin oxides are observed in the powder pattern. It is noted that the peaks corresponding to the CNT (0 0 2) plane and the SnO₂ (1 1 3) plane for 120 °C and 140 °C or SnO₂ (1 1 0) plane for 180 °C markedly shift to the higher diffraction angles, suggesting the strong interactions between CNTs and SnO₂ nanoparticles [26] These interactions may result in a compressive stress, which changes the interplanar distance [27].

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