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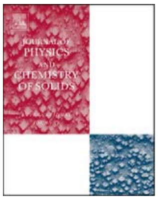

Electrochemical capacitance from carbon nanotubes decorated with titanium dioxide nanoparticles in acid electrolyte

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ABSTRACT

The electrochemical activity of an electrode of carbon nanotubes (CNTs) attached with TiO_2 nanoparticles was investigated. A chemical-wet impregnation was used to deposit different TiO_2 particle densities onto the CNT surface, which was chemically oxidized by nitric acid. Transmission electron microscopy showed that each TiO_2 nanoparticle has an average size of 30–50 nm. Nitrogen physisorption measurement indicated that the porosity of CNTs is partially hindered by some titania aggregations at high surface coverage. Cyclic voltammetry measurements in 1 M H_2SO_4 showed that (i) an obvious redox peak can be found after the introduction of TiO_2 and (ii) the specific peak current is proportional to the TiO_2 loading. This enhancement of electrochemical activity was attributed to the fact that TiO_2 particles act as a redox site for the improvement of energy storage. According to our calculation, the electrochemical capacitance of TiO_2 nanocatalysts in acid electrolyte was estimated to be 180 F/g. Charge–discharge cycling demonstrated that the TiO_2-CNT composite electrode maintains stable cycleability of over 200 cycles.

1. Introduction

Since their discovery, carbon nanotubes (CNTs) have received a great deal of attention due to a variety of technological applications such as gas separation, catalyst support, energy storage, environmental protection, and so on [1–4]. Among these applications, there has been increasing interest in CNTs serving as heterogeneous catalyst support. Recently, numerous researchers have paid attention to using CNTs as electrode materials [5–14]. They demonstrated that the carbon composites, composed of CNTs and electroactive materials (e.g., conducting polymer and metal oxide), exhibit the promising applicability to energy storage devices. However, the specific capacitance of CNTs is relatively low because of their relatively low surface areas [11]. Thus, this work intends to employ the other energy-storage contribution from metal oxide nanoparticles attached to CNTs that would offer more active sites for electrochemical redox reactions, thus giving rise to electrochemical capacitance.

Previous studies have developed several approaches to construct various types of CNT composites [15–19]. For instance, our previous work [20,21] has successfully deposited nickel nanoparticles on CNTs through chemical-wet impregnation. Experimental results demonstrated that (i) the Ni-attached CNT electrode exhibited great electrochemical H_2-storage capability in alkali electrolyte and (ii) the attached nickel nanoparticle showed the capacitance as high as 217 F/g. More recently, an interest in metal oxides, such as Al_2O_3, MgO, and TiO_2, has gradually emerged because the addition of oxides can improve the cycling stability of energy-storage devices [22]. This finding offers a clue that CNTs decorated with the nanosized metal oxides could enhance the performance of electrochemical electrodes. However, the roles played by the attachment of metal oxides to CNTs in the enhancement of capacitances have not yet been clearly elucidated.

This work aims to use a surface modification for fabricating well dispersion of TiO_2 nanoparticles onto CNTs, thus forming nanostructure composites. If the active species are uniformly deposited over CNT electrodes, the attachment of TiO_2 may provide redox activity to enhance the total specific capacitance. We prepared three TiO_2 surface densities on CNTs and investigated their electrochemical characterization in acid electrolyte. Electrochemical characteristics of the resulting electrodes, equipped with as-synthesized TiO_2-CNT composites, are examined by using cyclic voltammetry (CV) and charge–discharge cycling.

2. Experimental

2.1. Synthesis of TiO_2-CNT nanocomposites

The procedure for the preparation of TiO_2-attached multi-walled CNTs was described as follows: at first, the CNT samples

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were chemically oxidized with 0.1 N nitric acid at 90 °C for a period of 8 h. The acid treated-CNT samples were rinsed by D.I. water until the pH value of the slurry was higher than 5. This treatment could implant surface oxides in the defects of nanotubes, followed by binding metal ions and the oxygen groups in aqueous phase via ionic exchange or surface polarity. Each functional group may act as an active site, capable of specifically adsorbing with metal ions in aqueous solution. Then the CNTs were dried in a vacuum oven at 150 °C for 1 h. A Ti-containing polymeric sol was prepared by mixing titanium isopropoxide $Ti(OC_3H_7)_4$ (reagent grade, Aldrich) and ethanol/D.I. water (1:1 in v/v). Hydrochloric acid (0.1 N) was used to adjust the pH value of the Ti-containing sol ($pH = 2$). We prepared three molar concentrations of Ti-containing sols (0.4, 0.6, and 0.8 M). Then the transparent sols were magnetically stirred at room temperature for 8 h. Subsequently, about 1 g of CNTs were impregnated in the resulting Ti sols (30 mL), and then the wet-impregnation process was performed at ambient temperature for a period of 2 h, which enabled well dispersion of titania nanoparticles over the surface of CNT supports. After filtration, the as-prepared composites were heated from room temperature to the heat-treated temperature of 450 °C at a heating rate of 10 °C/min and maintained at this temperature for 0.5 h. The heat treatment was carried out under N_2 atmosphere in a tubular furnace.

2.2. *Characterization of TiO_2-CNT nanocomposites*

The TiO_2-CNT composites were characterized by transmission electron microscope (TEM) (Hitachi H-7500) and X-ray diffraction (XRD) with Cu-Kα radiation using an automated X-ray diffractometer (Shimazu Labx XRD-6000). Specific surface areas and pore volumes of the TiO_2-CNT composites were determined by gas adsorption. An automated adsorption apparatus (Micromeritics, ASAP 2000) was employed for these porosity measurements.

2.3. *Electrochemical measurements of TiO_2-CNT electrodes*

Prior to the formation of electrodes for electrochemical tests, TiO_2-CNT composites were added into a solution of polyvinylidenefluoride (PVdF) in N-methyl pyrrolidinone (NMP), and the mixture was mixed at ambient temperature to form carbon slurries. Electrodes were prepared by pressing the slurry on stainless steel foils with a doctor blade, followed by evaporating the solvent, NMP, with a blower dryer. The carbon layer, which consisted of 10 wt% PVdF as binder, was adjusted to have a thickness of 150 μm. This recipe is suitable for preparing a uniform CNT electrode with a coating thickness of ca. 90–100 μm.

Electrochemical measurements were carried out at ambient temperature using 1 M H_2SO_4 as the electrolyte solution. A Pt wire and Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The reference electrode used here was commercial Ag/AgCl electrode. The working electrodes were constructed by coating the TiO_2-CNT composites onto a stainless steel foil (as current collector). Epoxy resin was employed to seal the electrode, allowing an area ca. $2 \times 1\ cm^2$ to be exposed to the electrolyte solution. This sealed method can ensure prevention of unwanted reactions from the backing plate (current collector) in aqueous electrolyte. Cyclic voltammetric measurements of the TiO_2-CNT electrodes were made in the potential range of −0.2 to 0.8 V vs. Ag/AgCl at different scan rates: 1, 5, 10, 30, and 50 mV/s. Three-electrode cells were used to examine the charge–discharge cycling of the TiO_2-coated CNTs at different current densities. All electrochemical testes were performed at ambient temperature.

3. Results and discussion

3.1. *Characterization of TiO_2-CNT nanocomposites*

Fig. 1 shows typical TEM image for the CNTs attached to TiO_2 nanoparticles, prepared from chemical-wet impregnation and subsequent heat treatment. This observation reveals that after the deposition of titania, a large number of spherical particles are attached to the external surface of CNTs. The mean particle size falls in the region of 30–50 nm. Although TiO_2 particles are found to coat on the CNT surface, however, some TiO_2 aggregations may block both tips of nanotubes. To examine this speculation, the pore structures of CNT composites will be investigated using nitrogen physisorption.

To clarify the CNTs with different TiO_2 loadings, each CNT sample has been designated by using the nomenclature TCNT, followed by the order of TiO_2 loading to total weight, as shown in Table 1. The typical isotherms of N_2 adsorption–desorption onto oxidized and TiO_2-coated nanotubes are shown in Fig. 2. These isotherms exhibit obvious hysteresis behavior at high relative pressure, indicating that the CNTs are mainly mesoporous. The surface characteristics of TiO_2-CNT composites calculated according to the adsorption data are summarized in Table 1. In comparison to the oxidized CNT, TiO_2-CNT composites show an obvious decrease in specific surface areas and porosities. This decline in porosity can be attributed to two possible reasons: (i) some blockage of titania nanoparticles at both tips of CNTs occurs and (ii) the increase of the proportion of titania, thus reducing the available surface area and porosity for the adsorption of N_2. This table also reveals that all TiO_2-CNT composites are mainly mesoporous due to higher than 80% mesopore fraction.

Since the composites have mesoporous structure (i.e., $2\ nm < pore\ size < 50\ nm$), a Barret-Joyner-Halenda (BJH) method was used to analyze the pore size distribution, as shown in Fig. 3. In comparison, oxidized CNT exhibits a broad distribution, ranging between 20 and 70 nm. Judging from the TEM image, the nanotube diameter ranges between 30 and 50 nm, which is identical with the results from the BJH method. However, after the deposition of TiO_2, all distributions become two weak lumps, concentrated at 5 and 50 nm, respectively. The transformation of the distributions reflects that the deposition of TiO_2 nanoparticles

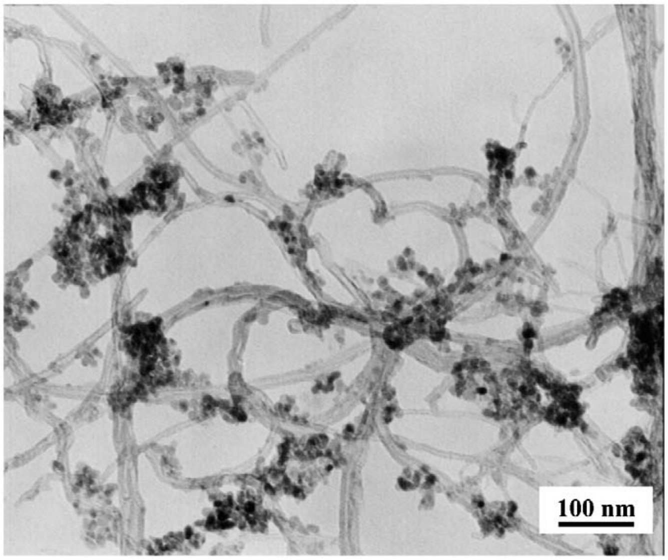

Fig. 1. TEM image for CNTs decorated with TiO_2 nanoparticles (TiO_2 loading: 17.4 wt%), prepared from chemical-wet impregnation and subsequent thermal treatment at 450 °C.