



Fabrication and characterization of a zirconia/multi-walled carbon nanotube mesoporous composite

Zonghua Wang^{a,*}, Jianfei Xia^a, Yanzhi Xia^{a,**}, Caiyu Lu^a, Guoyu Shi^a, Feifei Zhang^a, Fuqiang Zhu^a, Yanhui Li^a, Linhua Xia^a, Jie Tang^b

^a Laboratory of Fiber Materials and Modern Textile, the Growing Base for State Key Laboratory, College of Chemical and Environment Engineering, Qingdao University, Shandong 266071, PR China

^b National Institute for Materials Science, Sengen 1-2-1, Tsukuba 305-0047, Japan

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ABSTRACT

A zirconia/multi-walled carbon nanotube (ZrO₂/MWCNT) mesoporous composite was fabricated via a simple method using a hydrothermal process with the aid of the cationic surfactant cetyltrimethylammonium bromide (CTAB). Transmission electron microscopy (TEM), N₂ adsorption–desorption, Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) techniques were used to characterize the as-made samples. The cubic ZrO₂ nanocrystallites were observed to overlay the surface of MWCNTs, which resulted in the formation of a novel mesoporous–nanotube composite. On the basis of a TEM analysis of the products from controlled experiment, the role of the acid-treated MWCNTs and CTAB was proposed to explain the formation of the mesoporous–nanotube structure. The as-made composite possessed novel properties, such as a high surface area (312 m² · g⁻¹) and a bimodal mesoporous structure (3.18 nm and 12.4 nm). It was concluded that this composite has important application value due to its one-dimensional hollow structure, excellent electric conductivity and large surface area.

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1. Introduction

Since the first report of silica-based mesoporous materials (M41S) in 1992 [1,2], mesoporous materials have attracted great interest in different areas of science because of their high surface area, narrow pore size distribution and large pore volume. Recently, many efforts have been focused on the synthesis of transition metal oxides with mesoporous structure due to their excellent catalytic, optical and electronic characteristics [3–5]. The well-developed mesoporous transition-metal oxides materials, which are synthesized through various surfactant-templated hydrothermal methods or modified sol–gel processes, have been extensively exploited in the past few years [6–11].

Carbon nanotubes (CNTs), as a new form of carbon nanomaterials with their unique electrical properties, high chemical stability and high surface-to-volume ratio, have been considered as a powerful reinforcement of transition-metal oxides to improve their electrical conductivity and mechanical and thermal properties [12–14]. Among the transition-metal oxides, there was particularly intensive focus on ZrO₂ because of its unique properties such as its high ion-exchange capacity and higher redox activity and selectivity [15–18], which made it an attractive

material for applications in separation, catalysis and sensors. ZrO₂ has three polymorphs: monoclinic (m-phase, below 1170 °C), tetragonal (t-phase, between 1170 and 2370 °C) and cubic (c-phase, above 2370 °C) [19]. The cubic ZrO₂ possesses much better mechanical properties and ionic conductivity, but it is difficult to obtain because reactions towards ZrO₂ typically lead to the formation of mixed phases [20].

There has been growing concern about functionalizing mesoporous materials with nanostructured carbon. Moriguchi and co-workers successfully synthesized CNT-containing mesoporous TiO₂ with a bicontinuous microemulsion-aided process [21]. Du and co-workers have successfully prepared a hierarchically ordered porous TiO₂-graphene composite via a confinement self-assembly method [22]. To the best of our knowledge, there have been few reports about ZrO₂-loaded CNTs, and most of the as-made composites are nonporous [23–26]. In this work, a new mesoporous–nanotube composite (ZrO₂/MWCNT) was fabricated with the aid of one type of cationic surfactant (cetyltrimethylammonium bromide, CTAB) via a hydrothermal process. The preparation and structural properties of the composite were investigated in detail.

2. Experimental

2.1. Reagents

Spaghetti-like multi-wall carbon nanotubes (MWCNTs) with an external diameter of 10 nm prepared by the CVD method, purity > 95%,

* Correspondence to: Z. Wang, Department of Chemistry, College of Chemistry, Chemical Engineering and Environment, Qingdao University, Qingdao 266071, China. Tel./fax: +86 532 85950873 (O), +86 13853219173 (mobile).

** Correspondence to: Y. Xia, Department of Chemistry, College of Chemistry, Chemical Engineering and Environment, Qingdao University, Qingdao 266071, China.

E-mail addresses: wang_zonghua@yahoo.com.cn (Z. Wang), qdxzyh@163.com (Y. Xia).

were provided by Prof. Fan's research group (Physics Department, Tsinghua University, Beijing, China) [27]. Zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) was purchased from Tianjin Bodi Chemical Holding Co., Ltd. CTAB was purchased from Shanghai Aibi Chemistry Preparation Co., Ltd. The other reagents used were all of analytical grade, and doubly distilled water was used.

2.2. Fabrication of the $\text{ZrO}_2/\text{MWCNT}$ composite

MWCNTs were treated with mixture of concentrated sulfuric acid and nitric acid (3:1, v/v) under ultrasonication for 10 h, followed by an extensive washing with doubly distilled water to $\text{pH} = 7$ and then drying at 60°C before use. Fifty milligrams of acid-treated MWCNTs and 20 mg of CTAB were dispersed into 30 mL of doubly distilled water. The preparation process was conducted as follows: I) The mixture was sonicated for 2 h to form a stable suspension. II) Then, 1 mL of 2 M NaOH was immediately added into the suspension under stirring. III) Next, 45 mg of ZrOCl_2 were slowly added to the mixture above with vigorous agitation. IV) The mixture was then transferred into a stainless steel Teflon-lined autoclave of 50 mL in capacity and maintained for 15 h at 150°C . V) The products obtained were centrifuged and washed six times with ethanol to remove CTAB. The final products were denoted as $\text{ZrO}_2/\text{MWCNTs}$.

For comparison, a sample denoted as $\text{ZrO}_2/\text{MWCNTs-1}$ was prepared following the I–V procedures using 50 mg of original MWCNTs and 20 mg of CTAB as the starting materials, and another sample denoted as $\text{ZrO}_2/\text{MWCNTs-2}$ was prepared following the I–V procedures using 50 mg of acid-treated MWCNTs as the starting material in the absence of CTAB.

2.3. Apparatus and measurements

TEM images were obtained on a JEOL JEM 1200FX II at an accelerating voltage of 100 kV. A high-resolution transmission electron microscopy (HRTEM) image was taken on a JEM2010F at an accelerating voltage of 120 kV. XRD patterns were obtained on a Philips X'Pert MPD diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). FT-IR spectra on pellets of the samples with KBr were recorded on a Nicolet5700 spectrometer (Nicolet, USA). N_2 adsorption–desorption analysis was performed at 77 K on a Micromeritics TriStar 3000 apparatus. The surface area was determined using the BET equation. The pore volume and the pore size distribution were calculated from the desorption branch of the N_2 adsorption isotherm using the Barrett–Joyner–Halenda (BJH) formula.

3. Results and discussion

3.1. Characterization of the $\text{ZrO}_2/\text{MWCNT}$ composite

Fig. 1(a) shows the TEM image of $\text{ZrO}_2/\text{MWCNTs-1}$ obtained using the original MWCNTs as the starting material. The MWCNTs and the ZrO_2 nanoparticles are separated from each other. Fig. 1(b) shows the general morphology of the $\text{ZrO}_2/\text{MWCNTs}$. We can observe that the ZrO_2 nanoparticles are attached to the acid-treated MWCNTs. It is assumed that the active groups (such as carboxyl and hydroxyl) on the surface of the acid-treated MWCNTs played an important role for the attachment of ZrO_2 . In addition, the acid-treated MWCNTs have a higher zeta potential value (-47.6 mV), which can prevent the treated CNTs from aggregating and thereby stabilize the suspension. These results are consistent with results reported in the literature [28]. Furthermore, the good dispersal stability can be maintained for 2 weeks at least, which is useful for making ZrO_2 effectively supported on CNTs. The selected area electron diffraction (SAED) analysis of $\text{ZrO}_2/\text{MWCNTs}$ is shown in Fig. 1(c). The polycrystalline rings ascribed to the (111), (200), (220) and (311) were observed, which proved that the ZrO_2 attached to the MWCNTs had a cubic phase polycrystalline structure. Fig. 1(d) shows the HRTEM image from the representative pores of the composite, from which we can observe a well-defined lattice fringe, revealing that the wall structure of ZrO_2 attached to the MWCNTs was very crystalline. The mesoporous ZrO_2 was assumed to be formed by the organization of inorganic precursors around CTAB under hydrothermal conditions, and the pores were formed after removing the CTAB. The porous structure was formed during the process of ZrO_2 nanocrystallite growth. This result is similar to a previous report [29].

3.2. N_2 adsorption–desorption curves

The N_2 adsorption–desorption isotherm curves of the composites $\text{ZrO}_2/\text{MWCNTs-2}$ and $\text{ZrO}_2/\text{MWCNTs}$ are shown in Fig. 2. Curve a shows a reversible type II isotherm, which is the normal form of an isotherm obtained with a non-porous or macroporous adsorbent according to the IUPAC nomenclature. The beginning of the almost linear middle section of the isotherm indicates the stage at which monolayer coverage is complete. It was suggested that the $\text{ZrO}_2/\text{MWCNTs-2}$ composite prepared without CTAB is macroporous or nonporous solid. Curve b exhibited the type IV isotherms with a distinct hysteresis loop at the relative pressure of P/P_0 . According to the IUPAC nomenclature, this curve is a characteristic of the different processes between adsorption

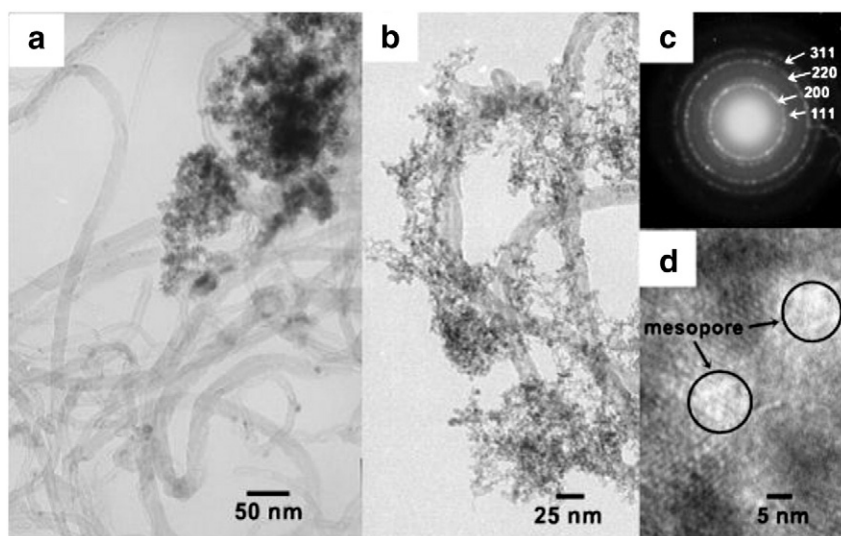


Fig. 1. TEM images of $\text{ZrO}_2/\text{MWCNTs-1}$ (a), $\text{ZrO}_2/\text{MWCNTs}$ (b); SAED pattern of $\text{ZrO}_2/\text{MWCNTs}$ (c); HRTEM of $\text{ZrO}_2/\text{MWCNTs}$ (d).

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