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

A R T I C L E   I N F O

Article history:
Received 28 August 2012
Received in revised form 9 April 2013
Accepted 13 May 2013
Available online 22 May 2013

Keywords:
ZrO2
MWCNTs
CTAB
Mesoporous-nanotube Composite

A B S T R A C T

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.

© 2013 Elsevier B.V. All rights reserved.

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%,
were provided by Prof. Fan’s research group (Physics Department, Tsinghua University, Beijing, China) [27]. Zirconium oxychloride (ZrOCl₂ · 8H₂O) 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 ZrO₂/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 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 ZrOCl₂ were slowly added to the mixture above with vigorous agitation. IV) The mixture was transferred into a stainless steel Teflon-lined autoclave of 50 mL in capacity and maintained for 15 h at 150 °C. V) The products were centrifuged and washed six times with ethanol to remove CTAB. The porous structure was complete. It was suggested that the ZrO₂/MWCNTs-2 composite was formed during the process of ZrO₂ nanocrystallite growth. This result is similar to a previous report [29].

For comparison, a sample denoted as ZrO₂/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 ZrO₂/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.

3. Results and discussion

3.1. Characterization of the ZrO₂/MWCNT composite

Fig. 1(a) shows the TEM image of ZrO₂/MWCNTs-1 obtained using the original MWCNTs as the starting material. The MWCNTs and the ZrO₂ nanoparticles are separated from each other. Fig. 1(b) shows the general morphology of the ZrO₂/MWCNTs. We can observe that the ZrO₂ 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 ZrO₂. 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 ZrO₂ effectively supported on CNTs. The selected area electron diffraction (SAED) analysis of ZrO₂/MWCNTs is shown in Fig. 1(c). The polycrystalline rings ascribed to the (111), (200), (220) and (311) were observed, which proved that the ZrO₂ 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 ZrO₂ attached to the MWCNTs was very crystalline. These results are consistent with results reported in the literature [28]. The mesoporous ZrO₂ 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 ZrO₂ nanoparticles separated from each other. 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 ZrO₂. 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].

3.2. N₂ adsorption–desorption curves

The N₂ adsorption–desorption isotherm curves of the composites ZrO₂/MWCNTs-2 and ZrO₂/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 ZrO₂/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/P₀. According to the IUPAC nomenclature, this curve is a characteristic of the different processes between adsorption.

![Fig. 1. TEM images of ZrO₂/MWCNTs-1 (a), ZrO₂/MWCNTs (b); SAED pattern of ZrO₂/MWCNTs (c); HRTEM of ZrO₂/MWCNTs (d).](image-url)
introduced into and desorption from the mesopores. The result confirmed the mesoporous structure of the ZrO2/MWCNTs.

Pore size distributions of the samples were investigated by using the BJH (Barrett-Joyner-Halenda) model shown in Fig. 3. The pore parameters of the samples were calculated by N2 adsorption-desorption isotherms. The pore size of ZrO2/MWCNTs-2 showed a broad distribution (Fig. 3, curve b), revealing bigger agglomerates which leads to a broader pore distribution. ZrO2/MWCNTs-2 was prepared in the absence of CTAB, which acts as a porogenic agent. In the preparation process, products with a mesoporous structure were assumed to be formed by the organization of inorganic precursors around CTAB under hydrothermal conditions. Thus, ZrO2/MWCNTs-2 was a macroporous or nonporous solid, and the pore size showed a broad distribution. The pore sizes of the ZrO2/MWCNTs were centered at 3.18 nm and 12.4 nm (Fig. 3, curve a). The pores centered at 3.18 nm are the MWCNTs inner cavities, close to the inner diameter of MWCNTs [30]. The pores centered at 12.4 nm mainly come from the aggregated ZrO2 nanocrystallines, which is consistent with the HRTEM analysis. Such porous materials with the bimodal pore size distribution are important and useful for catalysis because the small pores can contribute to a large area of the active surface for the strong interaction of adsorbed molecules with the active sites, whereas the large pores can provide channels for fast intraparticle molecular transfer [31]. Furthermore, the specific surface area of ZrO2/MWCNTs is 312 m2/g while that of the ZrO2/MWCNTs-2 is 110 m2/g. The pore volume of ZrO2/MWCNTs is 0.74 cm3/g while that of ZrO2/MWCNTs-2 is 0.39 cm3/g. The results indicate that a mesoporous structure was generated with the aid of CTAB.

According to the TEM analysis and the N2 adsorption–desorption analysis, it was concluded that the active groups (such as carboxyl and hydroxyl) of the MWCNTs surface and CTAB were necessary for the formation of ZrO2/MWCNTs. According to Wen’s work [32], the charge density matching between the inorganic species and the surfactants is very important for the formation of organic–inorganic mesophases. In this work, we used ZrOCl2·8H2O and CTAB as inorganic precursors and porogenic agents, respectively. On one hand, electronric groups such as carboxyl and hydroxyl present on MWCNTs could absorb positive CTA+ micelles on the surface of the MWCNTs via electrostatic interactions. On the other hand, due to hydrogen bonding interactions and electrostatic interactions, the micelles CTA+ were surrounded by OH− after sodium hydroxide was added. Afterward, the added Zr4+ ions reacted with OH− at the interface of the micelles and formed ZrO2 crystallites attached to the MWCNTs after the hydrothermal treatment and surfactant removal.
powders tended to stabilize cubic ZrO$_2$ at room temperature [36,37] because CNTs not only provide large nano-scale nuclear sites for ZrO$_2$ but also prevent ZrO$_2$ particles from aggregating and growing in the drying process, both of which are propitious for the stabilization of the cubic phase. Our result indicated that the structure of ZrO$_2$ was stabilized as a cubic phase with MWCNTs at room temperature.

4. Conclusions

In conclusion, we present a facile method to fabricate a ZrO$_2$/MWCNT mesoporous composite via an easy, efficient hydrothermal process with the aid of the cationic surfactant CTAB. A possible mechanism was proposed to explain the formation of the mesoporous–nanotube structure. Acid-treated MWCNTs were favorable for the stabilization of cubic ZrO$_2$; the active groups (carboxyl and hydroxyl) of the MWCNTs and CTAB played an important role in forming the mesoporous–nanotube composite. These results indicated that the cubic ZrO$_2$ nanocrystallites could be attached to the outside surface of the MWCNTs. This composite possessed novel properties, such as a high surface area (312 m$^2$ · g$^{-1}$) and a bimodal mesoporous structure (3.18 nm and 12.4 nm). Additionally, this mesoporous–nanotube structure not only can acquire a high surface area and a bimodal mesoporous and one-dimension structure but can also enhance the electrical conductivity with the combination of conductive CNTs. The composite can potentially be used as a catalyst, a sensor, an ideal reinforcement in other composites. The fabrication method is expected to extend the palette of available methods for the growth and assembly of different mesoporous materials-tube composites, which anticipates and encourages the extensive applications of these novel materials.

Acknowledgments

This work was financially supported by National Natural Science Foundation of China (authorized number: 20975056, 21275082 and 81102411), the Natural Science Foundation of Shandong (ZR2011BZ004 and ZR2011BQ005), JSPS and NSFC under the Japan–China Scientific Cooperation Program (21111140014), the State Key Laboratory of Analytical Chemistry for Life Science (SKLACLS1110) and the National Key Basic Research Development Program of China (973 special preliminary study plan, Grant no.: 2012CB722705).

Fig. 5. XRD patterns of MWCNTs (a) and ZrO$_2$/MWCNTs (b).