FIXATION OF CARBON NANOTUBE WITHIN MESOPOROUS TITANIA PARTICLES

SUNG SOO KIM, JIN HOE KIM, JEONG AH YOON, MINGSHI JIN, JUNG-NAM PARK, JEONG KUK SHON, YOON YUN LEE, JIN-HYO BOO and JI MAN KIM*

Department of Chemistry, BK21 School of Chemical Materials Science and Department of Energy Science and SKKU Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon, 440-746, Korea

*Corresponding author. jimankim@skku.edu

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Carbon nanotube (CNT) and mesoporous TiO$_2$ composite (CNT/meso-TiO$_2$) was synthesized by a nanocasting method using CNT-implanted mesoporous silica material as the template. The CNT was successfully incorporated within a mesoporous TiO$_2$ particle, and the CNT/meso-TiO$_2$ composite obtained exhibits a high surface area and well-established mesoporosity. Moreover, the composite material exhibits much lower electric resistance than those of mesoporous TiO$_2$ only and physical mixture of CNT and mesoporous TiO$_2$, which probably due to the large interface area and strong junction between the implanted CNT and TiO$_2$ framework in the composite.

Keywords: Mesoporous TiO$_2$; carbon nanotube; nanocomposite; nanocasting; electric resistance.

Titanium dioxide (TiO$_2$) is one of the most important transition metal oxides due to its chemically and physically useful properties.\cite{1,2} TiO$_2$ materials have been applied to several areas such as gas sensing, photocatalysis and dye-sensitized solar cells.\cite{1-5} In general, large specific surface area and electron mobility of TiO$_2$ crystalline are crucial to achieve high activities for the applications. Thus, a lot of methods have been developed for increasing the surface area and facilitating electron travel on the TiO$_2$ materials.\cite{6-9} One of the most attractive methods to obtain TiO$_2$ material with high surface area is the synthesis of mesoporous materials which can be produced as diverse forms such as thin film, powder and monolith.\cite{10-12} In order to increase the electron conductivity, an effective strategy is the formation of composites between TiO$_2$ and electrically conducting materials such as carbons. There have been lots of efforts to combine TiO$_2$ with activated carbon or carbon nanotube (CNT) in the form of physical mixture or composite for more highly reactive photo-catalysts.\cite{13,14} However, it is necessary to increase the interface area of each component and to control the TiO$_2$ crystal size on CNT carefully so that we can create effective composite materials.

Kamat et al. reported that the photovoltaic properties of single-walled CNT and TiO$_2$ composite materials were enhanced by increasing the CNT and TiO$_2$ interface.\cite{15} Eder et al. also showed a different strategy to increase interface and control of crystal size of TiO$_2$ on CNT by adding additive such as benzyl alcohol during the synthesis of CNT.\cite{16} Many synthesis methods have also been introduced by sol–gel, chemical vapor deposition and physical vapor deposition methods.\cite{17-19} These former works, however, mainly illustrate various kinds of synthesis strategies to increase the performances, instead of incorporation of CNT within TiO$_2$ particle. Moreover, the composite materials may exhibit limitations for the applications due to low surface area of the TiO$_2$ particle.

Recently, we reported the synthesis of mesoporous silica by implanting the CNT (CNT/meso-SiO$_2$) inside the particles using the sol–gel method.\cite{20} It is well-established to obtain mesoporous transition metal oxides using the mesoporous silica materials as the template via a nanocasting method.\cite{11,21} In the present work, the CNT/meso-SiO$_2$ were successfully utilized as the template for the synthesis of CNT-incorporated mesoporous TiO$_2$ material (CNT/meso-TiO$_2$). Because the mesostructure of replicated TiO$_2$ material is an inverse phase of the mesoporous silica template, it is reasonable that the mesoporous TiO$_2$
material obtained should contain the CNT within the particles. The present CNT/meso-TiO₂ composite exhibits high surface area, well-defined mesoporosity and low sheet resistance.

The present CNT/meso-TiO₂ composite material was synthesized and modified following the methods detailed in the reference. The CNT/meso-SiO₂ composite material was synthesized and modified following the methods detailed in the reference. Titanium tetraethoxide (Ti(OEt)₄, Aldrich) was used as a TiO₂ precursor. In a typical nanoreplication, 0.6 g of Ti(OEt)₄ and 30 mL of water are mixed, giving a white precipitate. The precipitate was collected by centrifuge and subsequent decantation of the supernatant, and dissolved with 0.8 g of HCl (35 wt.%) at room temperature. This clear TiO₂ precursor sol was impregnated into 1.1 g of the templates by a simple incipient wetness method, and the composites were dried at 373 K for 15 min. This impregnation-drying process was repeated 10 times in order to maximize the amount of TiO₂ precursor within the mesopores of the templates. Subsequently, the samples were dried at 373 K for 24 h. The materials were heated to 623 K for 3h under ambient conditions. Finally, the silica templates were removed by using 1 M NaOH aqueous solution, resulting in the removal of more than 99% of the SiO₂, which was confirmed by an elemental analysis by energy dispersive X-ray spectroscopy (EDS).

X-ray diffraction patterns were obtained with a Cu Kα X-ray source using Rigaku X-ray diffractometer (Model SWXD 18kW and D/MAX-2200 Ultima for 10–80° and 0.5–5°, respectively). N₂ adsorption–desorption isotherms were collected on a Belsorp-Mini instrument (Bel-Japan) at liquid N₂ temperature after degassing the sample at 423 K for 10 h, and pore size distributions were calculated by BJH (Barrett, Joyner and Halenda) method. Field emission scanning electron micrographs (FE-SEM) were obtained with a JSM-700F instrument (JEOL), operating at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) images were collected using a JEM-2100F instrument (JEOL), operating at 200 kV. Sheet resistances of the materials were measured under the pressure of 300 kg/cm² by a four-point-probe instrument (Changmin Tech., pellet diameter = 1 cm).

The characteristics of the CNT/meso-SiO₂ template are shown in Fig. 1. Mesostucture of the template is determined to be 2-D hexagonal, which is similar to those of mesoporous MSU-H and SBA-15, as shown in XRD pattern. Figure 2 shows the XRD patterns and N₂ adsorption–desorption isotherms of the CNT/meso-TiO₂ composite material. The XRD pattern in Fig. 2 indicates that the CNT/meso-TiO₂ material also exhibits a 2-D hexagonal symmetry with three peaks which could be indexed as due to the (100), (110), and (200) planes, indicating successful nanocasting process because the structure of the CNT/meso-TiO₂ composite comes from the CNT/meso-SiO₂ template. High angle XRD in Fig. 2 shows that an intense peak around 25° for anatase structure, and a peak around 26° for rutile structure. The content of the anatase in the whole composite material is about 82 wt.% which is calculated by comparing the intensity of the peaks.

The average size of the crystalline TiO₂ is estimated to be about 13 nm by the Scherrer equation, which corresponds to the pore sizes of the silica templates (Table 1). The N₂ sorption isotherms of the composite material are typical type IV isotherms with hysteresis loops. The presence of a narrow distribution of mesopores is determined from the N₂ adsorption–desorption curves between the relative pressures (p/p₀), 0.4–0.7. The specific surface area of the composite material by the BET equation is 246 m²/g and the total pore volume is 0.34 cm³/g. The result of the pore size distribution calculated by the BJH equation indicates that the composite material has around 3.0 nm, which coincides with the wall thickness of
Table 1. The characteristic properties of CNT/mesoporous silica and CNT/mesoporous TiO₂ composite materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>S_BET (m²/g)</th>
<th>V_b (cm³/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT/meso-SiO₂</td>
<td>585</td>
<td>1.15</td>
<td>13</td>
</tr>
<tr>
<td>CNT/meso-TiO₂</td>
<td>246</td>
<td>0.34</td>
<td>3.0</td>
</tr>
</tbody>
</table>

*BET surface areas calculated in the range of relative pressure (p/p₀) = 0.05–0.20.

*Total pore volumes measured at (p/p₀) = 0.99.

*Mesopore sizes obtained from the N₂ adsorption branches using the BJH method.

For comparison, the sheet resistances of a mesoporous TiO₂ material without CNT-implanting and a physical mixture of CNT and mesoporous TiO₂ were also obtained under the same conditions. The results show that the CNT/meso-TiO₂ composite material exhibits much lower sheet resistance than those of other materials (Fig. 4). These results may be due to a strong connection between the implanted-CNT and mesoporous TiO₂ framework. The strong interaction and the extensive interface between them are expected to cause a convenient transferring of electrons between each other. The sheet resistance values in Fig. 4 do not indicate the actual resistance of those materials because the resistances can be changed by the preparation conditions of the disc such as pressure and size, but the present data helps to reveal the relative resistance of each material under same conditions.

In conclusion, the mesoporous TiO₂ material embedding CNT has been successfully synthesized by the nanocasting method using the CNT/meso-SiO₂ template. The CNT/meso-TiO₂ composite material shows ordered mesostructure, high surface area, large pore volume and low sheet resistance. The present material is expected to provide potentials for several applications which need well-defined mesopores as well as fast electron transfer.

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