Simultaneous Control of Phase Transformation and Crystal of Amorphous TiO_2 Coating on MWCNT Surface

Yoo Lim Cha*, Il Han Park**, Kyung Hwan Moon**, Dong Hwan Kim**, Seung Il Jung†, and Young Soo Yoon‡

*Department of Chemical and Biological Engineering, Gachon University, Seongnam 13120, Korea
**Future Industry R&D Center, DH Holdings Co., LTD, Seoul 14322, Korea
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ABSTRACT

We developed a mass production method that simultaneously controls the phase transformation and crystal size of TiO_2 coatings on multwalled carbon nanotubes (MWCNTs). Initially, MWCNTs were successfully coated with amorphous 15–20-nm-thick TiO_2 by an in-situ sol–gel method. As the calcination temperature increased in both air and argon atmospheres, the amorphous TiO_2 was gradually transformed into the fully anatase phase at approximately 600°C, a mixture of the anatase and rutile phases at approximately 700°C, and the fully rutile phase above approximately 800°C. The crystal size increased with increasing calcination temperature. Moreover, above 600°C, the size of crystals formed in air was approximately twice that of crystals formed in argon. The reason is thought to be that MWCNTs, which continuously supported the stresses associated with the reconstructive phase transformation, disappeared owing to complete oxidation in air at these high temperatures.

Key words : Chemical properties, Microstructure, TiO_2 Fuel cells

1. Introduction

Carbon nanotubes (CNTs) have attracted much attention because of their unique electronic structure, large surface area, good chemical and thermal stability, and excellent mechanical properties. Further, the semiconducting oxide TiO_2 has been widely studied for its distinctive chemical and physical properties, which make it suitable for application in various fields. TiO_2 has two main phases: anatase, which is the kinetically favored phase, and rutile, which is the thermodynamically stable phase. It has been shown that the crystal structure strongly affects the performance of TiO_2. Anatase TiO_2 is more suitable for catalysis applications than rutile TiO_2 owing to its higher specific area. The photocatalytic activity of TiO_2 follows the order rutile < anatase < anatase/rutile mixture, whereas rutile TiO_2 has been shown to be preferable in terms of the selectivity and improved kinetics in photocatalytic reactions and the dielectric constant. Consequently, composite materials containing CNTs and TiO_2 are believed to have many potential applications and exhibit cooperative and synergetic effects between the metal oxides and carbon phases. Many researchers have found that TiO_2/CNT composites showed excellent performance in a wide variety of applications such as optoelectronics, supercapacitors, electrocatalysts, batteries, and photocatalysts. In particular, multiwalled CNTs (MWCNTs) coated with metal oxides such as TiO_2 have been receiving considerable attention for application as a catalyst-supporting material for fuel cells, as the coating can improve the surface properties of MWCNTs and cause high dispersion/distribution of the catalyst material. In addition, their superior electrochemical properties and physical properties have been demonstrated in many articles. To increase the applicability of these promising TiO_2/CNT composites, we should overcome the disadvantages of conventional synthetic processes such as low yields and low productivity. An in-situ sol–gel process is economically efficient, repeatable, and convenient, which makes it a suitable alternative to traditional methods. In addition, the sol–gel process provides particularly good control, from the molecular precursor to the final product, as well as allowing high purity and homogeneity. For TiO_2 synthesis, it has already been demonstrated that the sol–gel method yields smaller particles and better crystallinity, despite its lower process cost, than the hydrothermal method, hydrolysis method, etc.

In the present study, we describe our successful attempt to achieve a high yield of a homogeneously coated TiO_2/MWCNT composite via a sol–gel method. In addition, we identify the suitable conditions for obtaining rutile TiO_2, anatase TiO_2, and an anatase/rutile mixture. Benzyl alcohol (BA) is added as a surfactant, which can improve the coating of pristine CNTs with TiO_2 and act as an excellent tool...
to control the size of the deposited TiO$_2$ particles upon crystallization and phase transformation$^{20}$ Calcination in air and argon is performed to investigate the effect of the atmosphere on the phase transformation and size of the crystals. The structure and morphology of the synthesized TiO$_2$/CNT composites are characterized by scanning and transmission electron microscopy (SEM and TEM, respectively), X-ray diffraction (XRD) analysis, and thermogravimetric analysis (TGA).

2. Experimental Procedure

2.1. Material preparation

An (Fe–Mo/Mg)O catalyst was prepared according to the following procedure. A mixture of Fe(NO$_3$)$_3$·9H$_2$O (99%, Aldrich) and molybdenum solution (Aldrich, ICP/DCP standard, 9.8 mg/mL in H$_2$O) was dissolved in deionized (DI) water under stirring for 30 min. In addition, Mg(NO$_3$)$_2$·6H$_2$O (99%, Aldrich) and citric acid were dissolved in DI water under stirring for 30 min. The mixed Fe–Mo nitrate solution was then introduced into the Mg nitrate–citric acid solution under stirring for 30 min. Next, the pH of the final catalyst solution was adjusted to 7 using an ammonia solution. In our experiment, the molar ratio of the catalyst was 1 : 0.1 : 1 : 0.5 (Fe/Mo/Mg/citric acid). After mixing at room temperature, the catalyst solution was carefully poured into an alumina boat. The combustion and synthesis processes were conducted sequentially in a quartz tube reactor (i.d., 100 mm and length, 1000 mm) mounted in a furnace. The alumina boat containing the catalyst solution was placed at the center of the reactor tube. The quartz tube was rapidly heated to 550°C in an argon atmosphere and maintained at this temperature for 5 min in an argon atmosphere. Without any pause, the quartz tube was then heated to 700°C in an oxygen atmosphere and kept at this temperature for 2 min. Then, a mixture of argon (200 sccm) and acetylene (100 sccm) was introduced into the reactor for 30 min. After the reaction, the reactor was rapidly cooled to room temperature in an argon atmosphere. Finally, we obtained pristine MWCNTs with a diameter of approximately 30 nm.$^{20}$

2.2. MWCNTs coated with TiO$_2$

To prepare the composite materials, 2 g of the prepared MWCNTs were dispersed in 0.4 kg of ethanol and sonicated for 30 min at room temperature. Subsequently, a solution obtained by dissolving 43 g of BA in 11.91 g of water was added. The mixture was dispersed by ultrasonic vibration for another 30 min and then transferred to the reactor, which was kept at 0°C at a stirring speed of 350 rpm in a nitrogen atmosphere. In the next step, 60 mL each of titanium butoxide (TNBT, Sigma Aldrich) and ethanol were introduced into the solution slowly at the same rate of 30 mL/h through a feeder machine. The final molar ratio of the mixture of TNBT : BA : EtOH : H$_2$O was 1 : 3 : 76 : 5. Finally, after the reaction was complete, the suspension was filtered using a membrane with a 1 μm pore size and washed by

![Fig. 1. (a) SEM, (b) TEM, (c) XRD, and (d) TGA data of as-synthesized CNT-TiO$_2$. Insets in (b) are a high-resolution TEM image and diffraction pattern.](image-url)
ethanol, followed by vacuum drying at 60°C for 12 h. Calcination of the obtained TiO$_2$/MWCNT composites in air or argon was performed for 2 h at temperatures of 500, 600, 700, and 800°C.

2.3. Characterization of composite materials
The characteristics of these samples were analyzed using the following equipment. The morphology of the catalyst was observed by SEM (JSM-6701F, JEOL, Japan) and TEM (Tecnai G2 F20, FEI, USA) using both low- and high-resolution images. The elemental composition of the composite powder was investigated by an energy-dispersive X-ray spectroscopy (EDX) instrument attached to the TEM equipment. XRD analysis was performed using a Rigaku X-ray diffractometer with a Cu Ka source. Angular regions of 2θ between 20° and 90° were explored at a scan rate of 6°/min with a step size of 0.02°. The thermal behavior of the composite material was analyzed using a Q500 instrument (TA Instruments, USA) under heating to 900°C at 10°C/min under air flow (60 mL/min).

3. Results and Discussion
Figure 1(a) and 1(b) show SEM and TEM images, respectively, of the as-synthesized TiO$_2$/CNT composite material before calcination. The SEM images present an overall view of the TiO$_2$/CNT composite material. Homogeneous coating of TiO$_2$ on the MWCNTs without apparent agglomeration of TiO$_2$ particles is observed. From the high-resolution TEM image [inset, Fig. 1(b)], the MWCNTs in the as-prepared TiO$_2$/MWCNT composite material have diameters of approximately 60 nm and are homogeneously covered by a layer of TiO$_2$ with a thickness of approximately 10–15 nm. The presence of occasional fractures is attributed to the vacuum-assisted drying process. The diffraction pattern in the inset confirms that the phase of the TiO$_2$ coating is amorphous, which is further verified by the XRD analysis shown in Fig. 1(c). There have been many studies of CNTs coated with TiO$_2$; however, most of them obtained a thin layer of TiO$_2$ by using a relatively high concentration of CNTs. Eder and Windle analyzed the thickness of the TiO$_2$ coating by varying the concentration of CNTs and found that the thickness decreased from 95 to 20 nm with increasing CNT concentration from 0.5 wt% to 50 wt%. In this study, the concentration of MWCNTs is calculated to be 0.36 wt%, which is much lower than those in previous studies. Despite the low concentration, a relatively thin TiO$_2$ coating is successfully obtained. The TGA results of the as-synthesized composite material in Fig. 1(d) show three weight loss steps. The first one, between 30 and 180°C, with an approximate weight loss of 10%, is assigned to the removal of absorbed water and/or solvent. The second one, with an approximate weight loss of 5%, corresponds to the removal of structural water and occurs between 180 and 460°C. The last one, with

![Fig. 2. SEM images of the samples after calcination at 800°C in (a) air, (b) argon. (c) and (d) are high-resolution images of (a) and (b), respectively.](image-url)
an approximate weight loss of 15% due to MWCNT combustion, occurs between 460 and 660°C.

Eder and Windle adopted a very similar synthesis method and assumed a coating mechanism in which the TiO₂ coating is formed via interaction between the aromatic CNT surface and the benzyl ring of BA. The hydroxyl groups of BA then coordinate with the titanium and may further induce condensation to form a Ti–O–Ti network via the so-called BA route.¹⁹Calcination in ambient air or argon at various temperatures is performed to investigate the crystallization performance of TiO₂. Fig. 2(a) and 2(c) show low- and high-resolution SEM images, respectively, of the samples calcined at 800°C in air. Little tubular structure is observed, and large bulk crystals break the initially continuous smooth surface. Fig. 2(b) and 2(d) are SEM images of the samples calcined at 800°C in argon. The tubular structure is roughly preserved owing to the presence of MWCNTs, and discrete, relatively small spherical crystals are agglomerated. Fig. 3 shows TEM images corresponding to the SEM images in Fig. 2. Tubular structure can be seen in Fig. 3(b) but is hardly identifiable in Fig. 3(a). Crystals with diameters of approximately 25 nm on the surface of the MWCNTs can be observed in Fig. 3(d). However, the diameter of the crystals formed in air is approximately 45 nm according to Fig. 3(c), which is almost twice that of crystals formed in argon. SEM and TEM images and diffraction patterns of the samples after calcination at other temperatures in air and argon are presented in the supplementary material. Increases in crystal size with increasing temperature can be observed for both atmospheres, where small crystals are formed at 500 and 600°C, and significantly larger crystals appear at 700 and 800°C. The diffraction patterns prove that the TiO₂ coating is in the anatase phase at 500 and 600°C, whereas the rutile phase appears at 800°C, and a mixture of the two may be present at 700°C. Moreover, the crystals formed in air atmosphere are much larger than those formed in argon atmosphere at the same temperature. However, the MWCNTs may have been oxidized at high temperatures in air; therefore, EDX analysis was performed. Fig. 4 shows the EDX results of the samples calcined at 500 and 800°C in air and in argon. Only O and Ti can be detected for the samples calcined in air. However, in addition to O and Ti, C is also detected for the sample calcined in argon. Therefore, instead of remaining present, as they did in argon, the MWCNTs were completely oxidized in air above 500°C, resulting in TiO₂ nanotubes or nanowires.²¹⁻²⁵ In fact, CNTs have been used as templates to syn-

Fig. 3. TEM images of the samples after calcination at 800°C in (a) air, (b) argon. (c) and (d) are high-resolution image of (a) and (b), respectively. Insets show the diffraction patterns.
thesize various nanostructured materials.

To confirm the phase composition and compare the crystal size, XRD analysis was performed. Fig. 5 verifies the result that only anatase was formed at 500 and 600°C, whereas anatase was partially and fully transformed into rutile at 700 and 800°C, respectively. To evaluate the effect of MWCNTs on the crystallization of TiO$_2$, the TiO$_2$ crystal sizes were estimated from the line broadening via Scherrer’s equation: 

$$d = \frac{0.89\lambda}{\beta\cos(\theta)}$$

where $\lambda = 1.5406$ Å, and $\beta$ is the full width at half-maximum. The results are summarized in Table 1. The crystal size of anatase and rutile TiO$_2$ obtained in air were both observed to increase considerably with temperature. However, the crystal size of anatase and rutile TiO$_2$ obtained in argon did not exhibit a continuous rapid increase. An obvious increase was observed from 500 to 600°C for the anatase phase, whereas a slight increase appeared from 600 to 700°C for the anatase phase and from 700 to 800°C for the rutile phase. The reason is still under investigation. Rutile crystals were found to be significantly larger than anatase crystals in both atmospheres. Interest-

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**Fig. 4.** EDX results of the samples after calcination (a) in air at 500°C, (b) in air at 800°C, (c) in argon at 500°C, and (d) in argon at 800°C.

**Fig. 5.** XRD data of the samples after calcination at different temperatures in (a) air and (b) argon.
ingly, the crystal size obtained in argon was much smaller than that obtained in air at the same temperature. Moreover, the crystal size obtained in argon at 500°C was found to be even smaller than that obtained in air at 350°C. The reason could be that CNTs stabilize small crystals during crystallization and phase transformation in the calcination process. In addition, the amount of rutile transformed in argon (70%) is larger than that transformed in air (57%). This result suggests that argon atmosphere favors formation of rutile compared to air atmosphere.

Finally, the thermal behavior and stability of the composite materials were investigated by TGA using the data shown in Fig. 6(a) and 6(b). All of the samples calcined in air exhibited no weight loss, as the MWCNTs and absorbed water/surfactant were removed during calcination. However, all the samples calcined in argon showed a considerable weight loss of approximately 10 wt% between 460 and 630°C owing to oxidation of the MWCNTs, and an additional exothermal contribution between 300 and 460°C accompanied by further weight loss. Eder and Windle showed that BA was not removed upon heating in argon at 600°C owing to evaporation, but rather remained, presumably as a polymerized carbon, on the TiO$_2$ surface. Hence, the weight loss of approximately 10% in this range is attributed to oxidation of residual carbon species.

4. Conclusions

In summary, we successfully obtained a high yield of homogeneously coated TiO$_2$ with a thickness of 10–15 nm, which is relatively thin, on the surface of MWCNTs via a sol–gel method, despite using a quite low concentration of CNTs (0.36 wt%) compared to other studies. Apparent agglomeration of TiO$_2$ nanoparticles was not observed in SEM and TEM images. Through calcination in air and argon, amorphous TiO$_2$ was transformed into the anatase phase at 500 and 600°C, which was then partially and fully transformed into the rutile phase at 700 and 800°C, respectively. MWCNTs were oxidized in air above 500°C, although they remained present in argon. The crystal size increased as the temperature increased; moreover, the crystals formed in air were significantly larger than those formed in argon. The reason could be the absence of MWCNTs, which can continuously support the stresses associated with phase reconstruction, owing to collapse of the tubular structure caused by complete oxidation of MWCNTs at high temperatures in air.

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