Fabrication of Hollow TiO\textsubscript{2} Nanotubes via a Simple Gas-Phase Process Using In-Flight Coating Followed by Heat Treatment

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As nanostructured materials with wide applicability, hollow TiO\textsubscript{2} nanotubes (HTNTs) were fabricated for the first time using an “in-flight” coating method. TiO\textsubscript{2} coating layers were deposited on the surface of carbon nanotubes (CNTs) suspended in gas, and the resulting products were then heat-treated. Depending on the annealing process, products with various morphologies, including HTNTs, were produced. Raman spectroscopy, scanning electron microscopy, and energy-dispersive X-ray spectroscopy analyses confirmed the absence of CNTs in the HTNTs. The obtained results will provide valuable information for controlling hollow nanostructured materials for a wide range of applications in fields including photocatalysis, gas sensors, and solar cells.

Introduction

Hollow TiO\textsubscript{2} nanotubes (HTNTs) are one of the most promising nanostructured materials for a wide range of applications owing to their three-dimensional structures and large specific surface areas (Eder et al., 2007, 2009; Deng et al., 2014; Song et al., 2016; Cheng et al., 2018). HTNTs can be fabricated in the liquid phase via anodic oxidation, sol-gel, hydrothermal, solvothermal, and template methods (Eder and Windle, 2008a, 2008b; Bouazza et al., 2009; Fang et al., 2011; Kim et al., 2012). Template synthesis using carbon nanotubes (CNTs) is preferred for HTNT fabrication because the CNTs help maintain the tubular morphology of TiO\textsubscript{2} during annealing to obtain the desired crystalline phases (Eder and Windle, 2008a; Bouazza et al., 2009). Subsequently, the CNTs can be removed by annealing in air.

Liquid-phase methods require the CNT surface to be functionalized with other chemical groups (as anchors) to allow interaction with metal oxides. Eder and Windle (2008b) used benzyl alcohol as a linking agent to enhance the interaction between CNTs and a titanium precursor without using covalent functionalization. However, sample preparation and treatment involves multiple processing steps. Furthermore, the fabrication of HTNTs using atomic layer deposition also involves several steps and requires expensive equipment that operates under low vacuum conditions with slow deposition rates (Chang et al., 2012; Borbón-Nuñez et al., 2017).

We have successfully fabricated metal–oxide-coated CNTs by in-flight coating (Kubo et al., 2015, 2016). Beneficially, this process reduces particle agglomeration and involves one step, a low temperature, and a relatively high deposition rate. It is possible for the CNT template to be removed by changing the annealing conditions, thus producing HTNTs. Hence, the objective of this study was to develop a new technique for HTNT fabrication via in-flight coating with subsequent heat treatment.

1. Experimental

A schematic of the HTNT fabrication process is shown in Figure 1. First, TiO\textsubscript{2} layers were deposited on the surfaces of CNTs (with diameter and length in the range of 110–170 nm and 5–9 µm, respectively) by an in-flight coating method. In this method, aerosolized CNTs prepared by spray-drying an aqueous suspension of CNTs were carried to a plasma-enhanced chemical vapor deposition (PECVD) reactor by He at a flow rate of 1500 sccm. Meanwhile, He at a flow rate of 5 sccm was fed through titanium tetraisopropoxide (TTIP) stored in a heated bubbler to vaporize the precursor. The flow rate of TTIP in the He stream was estimated from the consumption of TTIP as 0.104 sccm. Furthermore, this stream was added by He and O\textsubscript{2} at flow rates of 400 and 50 sccm, respectively. The aerosolized CNTs and TTIP vapor were fed simultaneously into a microwave PECVD reactor operated at 4 kPa. The products (CNTs with the as-deposited layer) were collected from the PECVD reactor on a silicon substrate. The details of the experimental setup are described elsewhere (Kubo et al., 2015, 2016). The products were annealed in air or N\textsubscript{2} followed by annealing in air. The annealing time for each annealing process was 12 h with
heating and cooling rates of 5°C/min. Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) line scanning, and Raman spectroscopy were used to characterize the products.

2. Results and Discussion

The SEM images in Figure 2 reveal the morphologies of the products obtained under different annealing conditions. The short, flaked-off section observed in the as-deposited (without annealing) coating layer (Figure 2(a)) shows that the surface of the CNT was coated sufficiently with the TiO2 layer. Moreover, the coating layer consisted of many aggregate particles adhered to the CNT to form a rough surface. The formation of this structure is attributed to the slow dissociation rate of the TTIP precursor in plasma fields, as explained in detail in our previous study (Kubo et al., 2016). The average thickness of the TiO2 layer was approximately 140 nm.

The EDS line profile of the as-deposited coating layer is shown in Figure 2(e). The red arrow in Figure 2(a) indicates the scanning profile direction. The C profile showed a signal with the maximum intensity (length: ~150 nm) at the center, which is in the range of the CNT diameter described above. Figure 2(b) shows the coating layer after annealing in air at 600°C. The presence of cracks in this layer clearly indicates collapse of the TiO2 coating layer. In this case, the CNTs are considered to undergo combustion (chemical reaction between C and O2), causing their removal from the product. Consequently, the burnt CNTs could not support the TiO2 structure, resulting in the formation of cracks. The absence of CNTs in the coating layer was confirmed by the SEM–EDS line profile (Figure 2(f)), where there are essentially only Ti and O signals. This result is in good agreement with those reported previously for the oxidative removal of CNTs in air at annealing temperatures of 500–800°C (Eder and Windle, 2008b).

A coating layer with a similar morphology was obtained by annealing first in N2, and then in air at 600°C (Figure 2(c)). However, the product had fewer cracks and reflected the shape of the CNT template more. The C, Ti, and O profiles from the SEM–EDS line analysis (Figure 2(g)) again indicate that the CNTs disappeared from inside the coating structure. The shapes of the profiles of Ti and O in Figure
2(g) appear rather flat and looks similar to those in Figure 2(e). For Figure 2(e) (for the product shown in Figure 2(a)), the profiles of Ti and O should theoretically show a decrease in their center because a CNT is present in the core. The reason for the rather flat shape, i.e., the absence of any distinct decrease in the center, is considered to be due to the scattered data of the EDS signals. The products in Figure 2(a) and 2(c) have cylindrical shape. Further, the EDS profiles of Ti and O in Figure 2(g) do not exhibit a distinct maximum nor dent in the center, like those in Figure 2(e). Therefore, the central part of the product in Figure 2(c) is considered to be hollow, indicating the successful fabrication of HTNTs via this process. By increasing the annealing temperature in air to 700°C (Figure 2(d)), the surface of the coating layer became smoother than that obtained by annealing at 600°C (Figure 2(c)). A cross-section of the coating layer revealed that the layer has a dense inner structure. Moreover, this cross-section in Figure 2(d) is for a bundle of HTNTs with three holes. The size of the holes is 110–190 nm, which is comparable to the diameter of the CNTs used here.

Additional experiments confirmed that CNTs were not removed by annealing in N₂ alone at temperatures up to 900°C (Figure 2(h)). Overall, these results indicate that the coating layer must be heat-treated first in the presence of CNTs as an interior support so that the layer maintains its tubular shape during the CNT removal. Annealing at 600°C caused the layer to undergo an amorphous-to-anatase phase transformation, as described below. Therefore, this transformation is thought to enhance the mechanical strength of the layer. The dense and smooth structure of Figure 2(d) is considered to form by sintering of the TiO₂ layer at higher temperatures.

**Figure 3** shows the Raman spectra of the products. For the product with as-deposited coating layers, the two peaks observed at 519 and 1583 cm⁻¹ are attributed to the Si substrate and the G band of sp²-hybridized carbon (Kubo et al., 2016), respectively, the latter of which indicates the existence of CNTs in the products. As there are no other distinct peaks, the coating layers are considered amorphous. However, the G band peak disappeared after annealing in air or annealing in N₂, followed by annealing in air, indicating the absence of CNTs in the products. Moreover, the appearance of peaks at 199, 398, and 636 cm⁻¹ indicated that the coating layers had undergone an amorphous-to-anatase phase transformation (Eder and Windle, 2008a; Borbón-Núñez et al., 2017).

Figure 3 also shows that the Raman peaks at 199, 398, and 636 cm⁻¹ for the sample of air 600°C were much stronger than those for N₂ 600°C–air 700°C and N₂ 600°C–air 600°C. This can be attributed to a competition between crystallization and densification of the TiO₂ layers. When the annealing was done at 600°C in air, the CNTs underwent combustion, i.e., oxidation due to the chemical reaction between C and O₂. This reaction releases heat energy to raise the temperature, and is thus considered to speed up the crystallization process. In contrast, when the product was annealed first in N₂, the coating structure became dense and less crystallized because the heat-releasing oxidation did not take place during the annealing in N₂.

The Raman peaks were weaker when the product was first annealed in N₂ at 600°C and then in air at 600°C and 700°C as shown in Figure 3. When annealed in air at 600°C, the TiO₂ layer on the product exhibits a loose structure with many granular materials. This result agrees well with the result reported by Keddie and Giannelis (1991). In contrast to this, a denser layer will be formed when the sintering of the layer occurs prior to extensive crystallization. Such a dense structure is reported to retard crystallization processes (Panda et al., 1989; Keddie and Giannelis, 1991). This is considered to be the reason for the weaker Raman peaks for the products annealed first in N₂.

**Conclusions**

We successfully fabricated HTNTs using an in-flight coating method, followed by annealing in N₂ and then in air. Annealing in N₂ first enhanced the mechanical strength of the coating layer and produced a denser and smoother structure. In contrast, the HTNT structure collapsed after annealing in air only. Annealing in air or N₂ also transformed the amorphous TiO₂ phase into the anatase phase. Finally, the absence of CNTs in the HTNTs was confirmed by Raman spectroscopy and SEM–EDS line analyses. We believe that our results will provide valuable information for the fabrication of HTNTs with wide applicability in various fields such as photocatalysis, gas sensors, and solar cells.

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**Literature Cited**


