# Core–shell-structured carbon nanofiber-titanate nanotubes with enhanced photocatalytic activity

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## ARTICLE INFO

## ABSTRACT

Core–shell materials have been developed extensively because of their advanced properties and multifunctionality. Many approaches involving different synthesis techniques have been used for the preparation of various core–shell nanostructures. In this study, we synthesized core–shell-structured carbon nanofiber (CNF)-titanate nanotubes (TiNT) by electrospinning, carbonization, and subsequent alkaline hydrothermal treatment. The CNF core could act as a support, and the $TiO_2$-decorated TiNT shell could act as a photocatalyst. TiNT shells with diameters of several hundreds of nanometers and composed of 10-nm-diameter nanotubes are formed on the CNF surface. The formation of TiNTs on the CNF surface was observed using SEM, HR-TEM, XRD, and XPS analyses. Core–shell-structured CNF-TiNTs exhibited efficient photocatalytic activities for $CH_3CHO$ oxidation, which was attributed to the existence of photocatalytically active $TiO_2$-TiNT composites on the CNF surface, which could easily absorb UV light. Additionally, the surface area increase as a result of the alkaline hydrothermal treatment may also be responsible for the efficient photocatalytic activity of core–shell-structured CNF-TiNTs.

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## 1. Introduction

$TiO_2$ photocatalysts have been intensively studied for application to the remediation of polluted water and air [1–3]. The photocatalytic reactions are initiated by the absorption of UV photons. The valence band (VB) electrons are excited into the conduction band (CB), simultaneously generating holes in the VB. Subsequently, the photogenerated electrons and holes initiate reduction and oxidation reactions at the surface, respectively. The electrons are consumed by electron acceptors, such as oxygen, and the holes react with electron donors, such as $H_2O$ or hydroxyl groups, and produce hydroxyl radicals. However, some limitations of $TiO_2$ make it less efficient and hinder its more widespread application. One drawback is electron–hole recombination. The charge recombination and interfacial charge transfer rates depend on the surface properties of $TiO_2$. Therefore, to improve the photocatalytic activities of $TiO_2$ photocatalysts, many groups have tried to modify the $TiO_2$ surface by such approaches as noble metal deposition, inorganic anion adsorption, and surface charge modification [4].

For the practical application of $TiO_2$ photocatalysts, a number of studies have attempted to immobilize $TiO_2$ on different substrate materials, such as glass, zeolites, polymer fibers, and carbon materials [5–11]. Among these materials, carbon materials, such as activated carbon [12,13], carbon nanotubes [14–16], and carbon

nanofibers (CNF) [17–19], have been frequently used as a support material. Recently, Ouzzine et al. investigated the photocatalytic activities of $TiO_2$ deposited on CNFs using a sol–gel method based on the properties of the CNFs and reported that it was difficult to deposit a homogeneous $TiO_2$ layer on CNFs [19]. Previously, we reported that $TiO_2$-particle-embedded CNFs prepared by electrospinning exhibited efficient photocatalytic activities [17]. Although the photocatalytic activity for gaseous acetaldehyde oxidation was efficient, $TiO_2$ was not homogeneously embedded. On the other hand, $TiO_2$ nanoparticles homogeneously embedded on CNFs could be obtained using non-aggregated nanosized $TiO_2$ particles prepared by the sol–gel method instead of pre-aggregated commercial Hombikat $TiO_2$ nanoparticles [20]. However, the photocatalytic activities were limited because the photoactive $TiO_2$ nanoparticles were entirely embedded in the CNFs and could not directly absorb UV light. Therefore, we tried to cover the CNF surface with photocatalytically active nanostructured $TiO_2$ materials, which has not been achieved via deposition by coating.

Core–shell materials have attracted much attention because they are expected to have advanced properties. ZnO nanowires have been grown radially on the fiber surface using a hydrothermal approach, and this microfiber–nanowire hybrid structure was used for energy scavenging [21,22]. Guo et al. have recently investigated core–shell CNF-$TiO_2$ nanosheets [18]. The $TiO_2$ nanosheets were grown directly on the CNFs by hydrothermal treatment in a solution containing fluorine ions. Recently, we investigated the formation of $TiO_2$-decorated titanate nanotubes (TiNTs) from $TiO_2$ nanoparticles under alkaline hydrothermal conditions [23,24]. Tang et al.

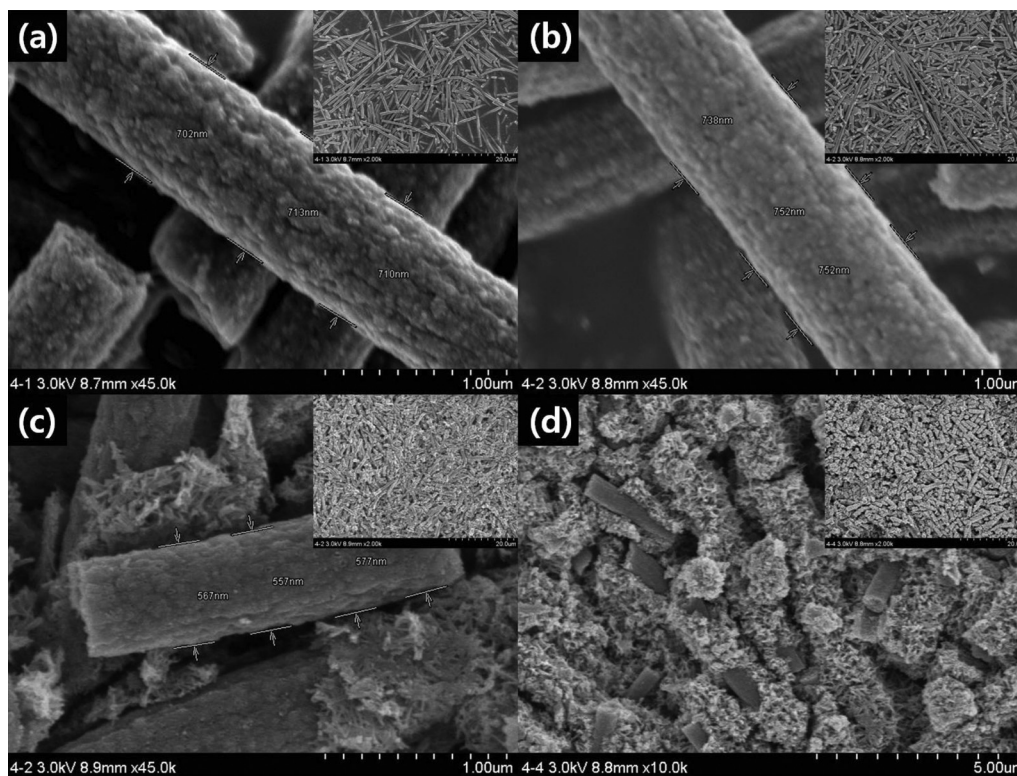**Fig. 1.** FE-SEM images of (a) TiO$_x$/CNF, (b) TiO$_2$/CNF, (c) TiNT/CNF, and (d) TiO$_2$-TiNT/CNF.

also showed that TiNTs could be formed at the surface of the TiO$_2$ sphere template [25]. Based on these results, we expected TiNTs to form on the CNF surface by alkaline hydrothermal treatment.

In this study, we combined the electrospinning and hydrothermal methods to fabricate core–shell-structured CNF-TiNT composite nanostructures. First, a TiO$_2$-containing PAN solution was electrospun, and the obtained nanofiber webs were carbonized to produce CNFs with TiO$_x$ nanoparticles. Second, the CNFs were hydrothermally treated with alkaline solution, after which TiNTs could form on the CNF surfaces. The obtained core–shell-structured CNF-TiNTs were characterized, and their photocatalytic activity for the oxidation of gaseous acetaldehyde was determined.

## 2. Experimental

### 2.1. Preparation of core–shell-structured carbon nanofiber-titanate nanotubes

TiO$_x$/CNFs were prepared by electrospinning/carbonization, as previously reported [17]. Nanosized TiO$_2$ synthesized by the sol–gel method was dispersed in 10 wt% polyacrylonitrile (PAN)/N,N-dimethylformamide (DMF) solution by stirring, and the mixture was sonicated to ensure good dispersal. The mass ratio of TiO$_2$ to PAN was 1:1. A yellow viscous TiO$_2$/PAN gel was electrospun, and the TiO$_2$/PAN nanofiber webs were collected. To obtain TiO$_x$/CNFs, the webs of TiO$_2$/PAN nanofibers were placed in a tube furnace, stabilized in air at 250 °C for 30 min, carbonized at 750 °C for 1 h, and then heated at 1400 °C in an N$_2$ atmosphere for an additional 1 h. The ramp rate was 5 °C/min between the 250, 750, and 1400 °C plateaus. TiO$_2$/CNFs could be obtained by the oxidation of TiO$_x$/CNFs by calcining at 400 °C for 3 h in air.

TiNT/CNFs were prepared by alkaline hydrothermal treatment, which is a typical method for synthesizing TiNTs from TiO$_2$ nanoparticles, as previously reported [23,24]. TiO$_x$/CNF were added

to 200 ml of 10 M NaOH solution, hydrothermally reacted at 150 °C for 24 h, and then washed with 0.1 M HCl and distilled water. The obtained samples were denoted TiNT/CNF. The TiNT/CNFs were further calcined at 400 °C for 3 h in air. The calcined samples were denoted TiO$_2$-TiNT/CNF.

### 2.2. Characterization

The surface morphology images were obtained using a field emission scanning electron microscope (FE-SEM, Hitachi S-4200, Japan). Transmission electron micrographs were obtained on a high-resolution transmission electron microscope (HR-TEM, JEM-2200FS, Japan). The cross-sectional images of the samples were analyzed with a scanning transmission electron microscope (STEM, HD-2300, Hitachi, Japan). The samples were embedded in epoxy resin, cut into thin sections using an ultra-microtome, placed on Cu grids, and then analyzed. EDS X-ray diffraction (XRD) patterns were obtained with an X-ray diffractometer (Rigaku D/MAX-2500, 18 kV) using Cu-$K_{a1}$ radiation. The oxidation states of C, Ti, O, N, and Na atoms were determined by X-ray photoelectron spectroscopy (XPS) (Kratos XSAM 800pci) using the Mg-K$_\alpha$ line (1253.6 eV) as the excitation source. The Brunauer–Emmett–Teller (BET) surface areas were determined from the nitrogen adsorption–desorption isotherms at 77 K (ASAP 2020 Micromeritics). The effective surface areas were estimated at a relative pressure ($P/P_0$) ranging from 0.01 to 0.1.

### 2.3. Photocatalytic activity measurements

The photocatalytic oxidation of gaseous CH$_3$CHO was determined in a closed circulated stainless steel reactor (volume, 150 cm$^3$) that could be divided into two parts (upper and bottom) by a control valve, similar to a previously reported experiment [17]. The gases used were CH$_3$CHO (300 ppmv N$_2$) as a CH$_3$CHO standard,