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CNT/TiO_2 core-shell structures prepared by atomic layer deposition and characterization of their photocatalytic properties

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ABSTRACT

TiO_2 film was coated on acid-treated and pristine multiwall carbon nanotubes (CNTs) with different thicknesses by atomic layer deposition at 100 °C to form a CNT/TiO_2 core-shell structure. The relationship between oxygen-containing functional groups on the surface of CNTs and growth rate of TiO_2 film was studied. The saturation growth rate of TiO_2 was 0.55 Å/cycle for acid-treated CNTs with sufficient durations of pulse time for the precursors of $TiCl_4$ and H_2O. The as-prepared TiO_2 film was amorphous, and the anatase and rutile phases of TiO_2 were obtained by heating to 300 °C and 800 °C, respectively. The shell thickness of anatase TiO_2 on CNTs was a key factor to determine the efficiency of methylene blue (MB) degradation. The thickness of 22 nm exhibited the best efficiency of MB degradation due to lower electron-hole recombination rate and higher amount of hydroxyl group generated on the surface of TiO_2 after UV irradiation.

1. Introduction

Photocatalytic oxidation and reduction of heterojunction catalysts for pollutant degradation and hydrogen generation are the subjects of extensive investigation [1–3]. Since Fujishima and Honda discovered the first TiO_2 (rutile phase) electrode that caused water decomposition into oxygen and hydrogen after absorption of UV light in 1972 [4], a lot of effort has been made in understanding the fundamental process and enhancing the photocatalytic efficiency of semiconductors. Carbon nanotubes have many unique properties and are commonly used as a support material for many catalysts [5]. For example, the specific surface area, electric conductivity, thermal stability, and adsorption capacity of CNTs are better than those of activated carbon. The different semiconducting, semimetallic, or metallic properties of CNTs determine the characteristics of heterojunction of catalyst-support interface [6]. Gao et al. have used a modified sol-gel method to deposit a uniform film of TiO_2 on CNTs to form a composite structure for enhanced photocatalytic activity [7,8]. Compared with sol-gel and other traditional processes such as hydrothermal, physical vapor deposition, and chemical vapor deposition (CVD) [9], atomic layer deposition (ALD) produces highly conformal film and allows atomic-scale thickness control. Although the effects of process parameters such as substrate temperature, cycle number, and anchor sites on functionalized CNTs [10–13] on the properties of the heterojunction of CNT/TiO_2 core-shell structure fabricated by ALD have been reported by several groups, there are few studies to examine the effects of pulse time of precursors on growing TiO_2 on CNTs and film thickness on the photocatalytic efficiency.

In the present study, the photocatalytic degradation of MB by a CNT/TiO_2 structure was examined. The composite structure was fabricated by ALD with various parameters, including the surface functionalization. Note that there are several approaches for surface functionalization of CNTs, including gas phase treatment [14], photo-oxidation [15], oxygen plasma [16], and other chemical methods [17]. However, surface functionalization of CNTs with controllable amount of functional groups and lower damage for further reaction are difficult to achieve. For instance, in the gas phase treatment method the sidewall of CNTs may exfoliate in the reducing atmosphere at high temperatures. Formation of uniform functional groups on the surface of CNTs is unpredictable in the photo-oxidation and oxygen plasma methods. In chemical methods, such as esterification or amidization, the treated CNTs are not easy to purify and collect in the solution. In the present study, acid-treatment was employed because it offers advantages of low cost and easy to control in comparison to the above mentioned methods. Nitric acid was used for surface treatment at a moderate temperature. The degree of surface functionalization of CNTs could be controlled by the concentration of acid, reaction temperature, and duration of treatment and the treated-CNTs could be easily collected by filtration using deionized water.

2. Experimental procedures

Multiwalled CNTs (90% purity, 20–40 nm in outer diameter, 3–12 μm in length) were obtained from Powertip Technology Corporation. The pristine CNTs (p-CNTs) were immersed in HNO_3 (65% purity) and

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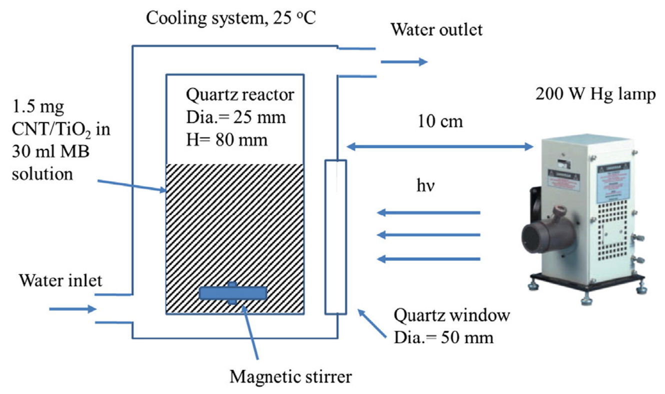

Fig. 1. Schematic configuration of the photoreactor setup.

Table 1
Relative percentages of the seven types of carbon atoms in CNTs with different durations of acid treatment time.

Treatment time (h)	Carbide	sp^2 C=C	sp^3 C—C	—C—O	>C=O	—COO	π-π*
Pristine	4.7	54.1	12.1	14.3	6.7	3.9	4.2
3	4.2	50.2	13.4	15.3	8.6	4.0	4.3
6	4.8	46.4	13.7	17.5	9.1	4.4	4.1
9	4.6	38.4	14.4	23.8	11.3	5.0	2.5

refluxed at 140 °C for 3, 6, or 9 h, hereafter named as acid-treated CNTs (a-CNTs). The a-CNTs were washed with deionized water and alcohol, collected by centrifuge, and then dried at 80 °C for 24 h. Both a-CNTs and p-CNTs were used as a support for coating with TiO_2 by ALD. Firstly, 10 mg of CNTs were sonicated in 20 ml acetone for 90 min to get good dispersion on a 4-inch Si wafer. The dispersed CNTs were then deposited with TiO_2 by ALD using $TiCl_4$ and H_2O as the precursors for 100 to 800 cycles at 100 °C. Both precursor tanks of $TiCl_4$ and H_2O were kept at room temperature, and the vapor delivery lines connected to the reactor were maintained at 80 °C. The working pressure was 1 Torr, and nitrogen with a purity of 99.999% was used as a purge gas. The durations of pulse-purge-pulse-purge time were controlled at several values to achieve precise thickness control of TiO_2. The CNT/TiO_2 composite was then annealed in N_2 atmosphere from 200 °C to 1000 °C for 2 h to get the crystalline anatase and rutile TiO_2 shell.

The CNT/TiO_2 composites prepared with a-CNTs and p-CNTs as the template were examined by field-emission scanning electron microscopy (FESEM, JEOL 6500F) and transmission electron microscopy (TEM, JEOL 2100F) equipped with energy-dispersive X-ray (EDX) spectroscopy. The structural analysis was performed by X-ray diffraction (XRD, Shimadzu 6000) with the Cu K_α radiation. The surface chemistry was analyzed by X-ray photoelectron spectroscopy (XPS, PHI 1600). The background signal was subtracted by Shirley's method. All binding energies were calibrated with the graphite C 1s peak at 284.5 eV. The values of FWHM of all deconvoluted peaks were from 1.2 to 2.4 eV. The photocatalytic activity was examined by studying the decomposition of MB by irradiation with a 200 W Hg lamp (Model No. 6283, Newport Corp.) whose spectral irradiance ranges from UV to IR [18]. The distance between the photoreactor and lamp was 10 cm. The schematic configuration of the photoreactor is shown in Fig. 1. Before the mercury lamp was turned on, 1.5 mg of CNT/TiO_2 composite was added to 30 ml of MB solution with ultrasonic treatment for 10 min and was then magnetically stirred in a dark condition for another 10 min to achieve adsorption-desorption equilibrium. The initial concentration of MB solution was 20 ppm. The absorbances of MB solution and CNT/TiO_2 samples were recorded by a UV–vis spectrometer (Hitachi U-3010) with absorption mode and reflection mode, respectively. The UV–vis spectrometer was equipped with an integrated sphere, and Al_2O_3 was used as a standard reference. According to Beer's law, the MB solution was firstly diluted to fit the linear calibration curve derived from the relationship between the concentration of MB and the strongest peak of absorbance of MB at 664 nm before photodegradation of MB was conducted [19]. The absorption of MB solution at 664 nm was recorded every 10 min until 60 min.

3. Results and discussion

3.1. Modification of CNTs

XPS provides the information of functional groups of CNTs. As shown in Fig. 2 (a) and (b), the C 1s spectra are deconvoluted to seven Gaussian components, and the following bonds are assigned: carbidic carbon

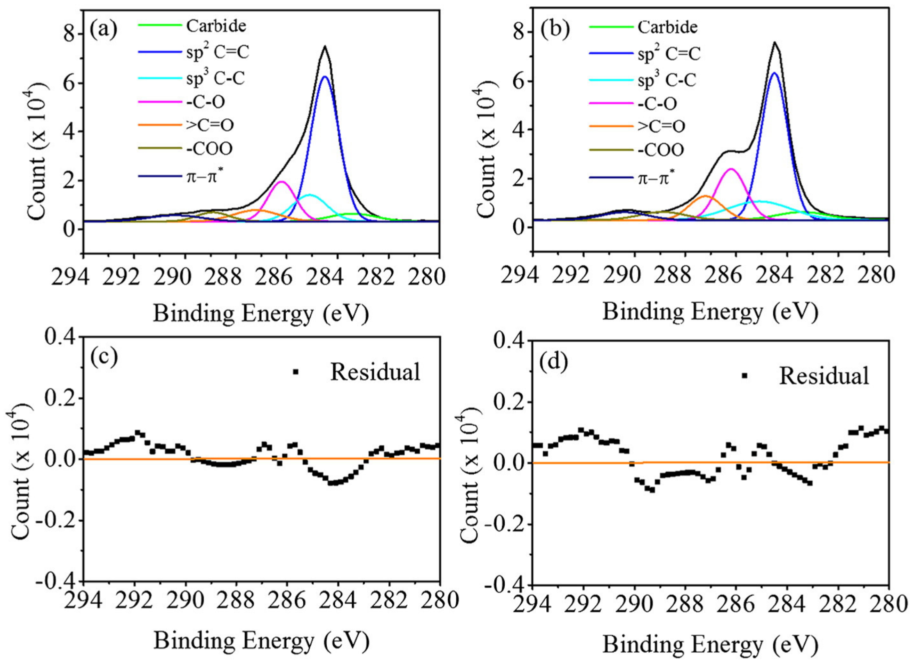

Fig. 2. XPS C 1s spectra of (a) p-CNTs and (b) a-CNTs treated for 6 h. The curve fitting suggests the existence of seven species. (c) and (d) are residual functions of (a) and (b), respectively.