

# TiO<sub>2</sub>/CNT coaxial composite array with visible-light absorption

C.-C. Chang and C.-C. Chen\*

Chaoramics Laboratory, Department of Chemical Engineering, National Chung Cheng University  
Chia-Yi 621, Taiwan, \*[chmccc@ccu.edu.tw](mailto:chmccc@ccu.edu.tw)

## ABSTRACT

Titania (TiO<sub>2</sub>)/carbon nanotube (CNT) composite array was successfully prepared by growing TiO<sub>2</sub> on every CNTs of the CNT array. The sample preparation included 3 steps. First, CNT array on Si substrate was prepared by flowing acetone vapor through Co-deposited Si wafer at 850 °C heating temperature under argon and ammonia in a tube oven. Next, Ti was deposited on the CNT array using a DC sputter, where the thickness of deposited titanium could be adjusted. The final step involved oxidation of titanium in air under 400°C heating temperature. The resulted morphology was of coaxial structure, where TiO<sub>2</sub> layer wrapped the inner CNTs. The TiO<sub>2</sub> layer was of anatase phase from the SAED analysis. Adsorption spectrum reveals the TiO<sub>2</sub>/CNT composite array have both the UV and vis.-light absorptions. The ratio of UV/vis.-light absorption increased with the increasing thickness of TiO<sub>2</sub> (using CNT/Ti, thickness ratio, as an index). However, if the TiO<sub>2</sub> thickness was too large, the ratio of UV/vis.-light absorption cannot be furthered increased. The vis.-light absorption of TiO<sub>2</sub>/CNT composite array is resulted from the change of electron density of Ti due to the metal-support interactions between TiO<sub>2</sub> and CNT.

**Keywords:** titania, titania nanotube, carbon nanotube, nano composite array, visible-light absorption

## 1 INTRODUCTION

Titania is well known for its photocatalytic capability in the UV range, due to the corresponding band gap. In order to increase the absorption range, particularly in vis. light, titania capable of visible-light absorption has been prepared by doping of light elements such as C, N, F, P and S [1, 2]. To increase the surface area, titania nanotubes were synthesized by template synthesis [3, 4] and hydrothermal reaction [5]. Recently, titania nanotubes can be readily obtained by soaking the titanium substrate in hot NaOH solution [6]. In this study, the coaxial TiO<sub>2</sub>/CNT nanotube array is prepared in order to have the visible-light absorption, large surface area and the confinement effect from the organized array as well.

## 2 EXPERIMENTAL

A layer of Co film, served as catalyst to grow CNT, was deposited on the Si substrate by a DC sputter and the film thickness was around 7 nm. The as-deposited substrate was

placed in a tube furnace set at a temperature of 850 °C. Acetone was the carbon source and acetone vapor was brought into the furnace by the carrier gas of nitrogen at a rate of 200 sccm, after the furnace reached the setting temperature. Prior to the introduction of acetone vapor ammonia was fed into furnace at a rate of 100 sccm. CNT array with good alignment was grown on the substrate. The as-grown CNT array was placed in the sputter to coat a layer of Ti film with various thickness on individual CNTs. Then, the Ti film outside of CNT was heated in air at a temperature of 400 °C to oxidize the Ti film, allowing the formation of TiO<sub>2</sub>/CNT coaxial composite array on the Si substrate. The above procedures were schematically shown in Fig. 1. The products in each steps were analyzed by scanning electron microscopy (SEM, Jeol, JSM-5410), filed-emission scanning electron microscopy (FESEM, Hitachi, s-4800), transmission electron microscopy (TEM, Hitachi, s-2400FK), energy dispersive spectrum (EDS, Oxford, Link ISIS 300), X-ray photoelectron spectroscopy (XPS, VG ESCA AE-085), UV-visible spectroscopy (Jasco FTIR-430).

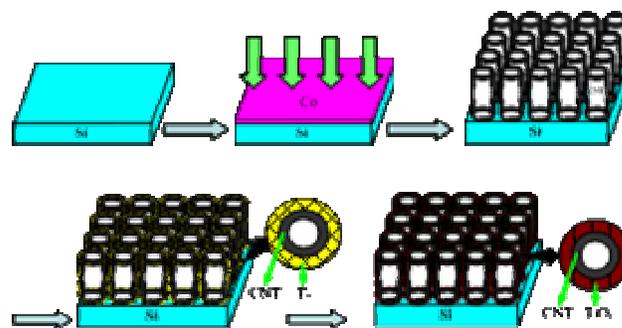


Fig. 1: Schematic of experimental procedures

## 3 RESULTS AND DISCUSSIONS

### 3.1 Preparation of CNT array

The preparation of CNT array on Si substrate is the fundamental infrastructure for the desired TiO<sub>2</sub>/CNT coaxial composite array. Fig. 2 shows the SEM image of as-grown CNT array on the Si substrate, indicating good alignment of CNTs and low density nature of CNT array. TEM image in Fig. 3 shows the CNT was multi-walled and the length was about 3 μm. The inner and outer diameters

were respectively 14 and 30 nm. SAED pattern indicates the (002), (101) and (112) planes of CNT.

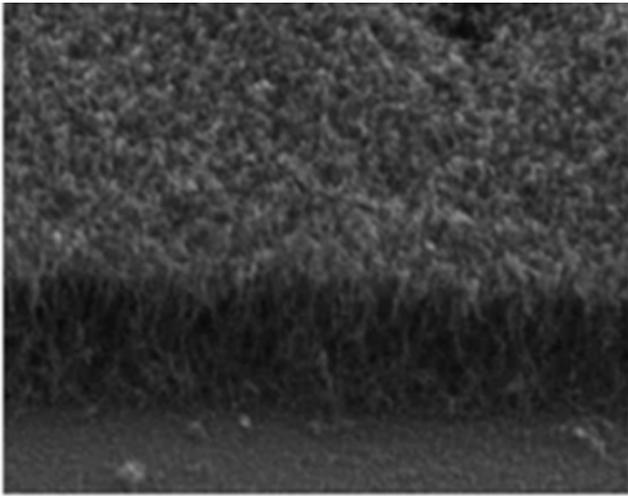


Fig. 2: SEM image of CNT array

coating. Thus, the density of CNT array should be neither too high nor too low.

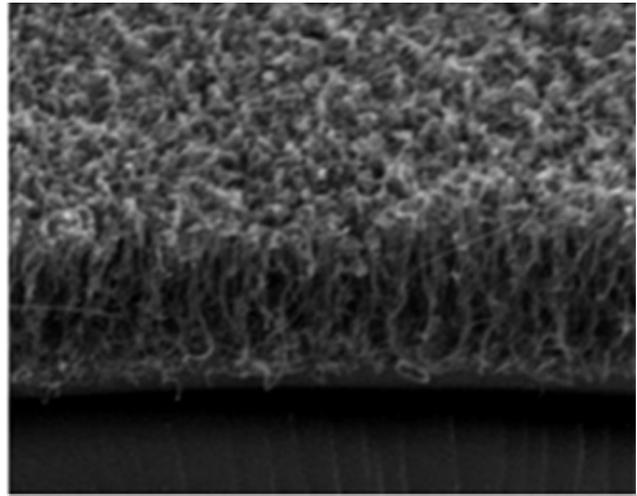


Fig. 4: SEM image of Ti-coated CNT array.

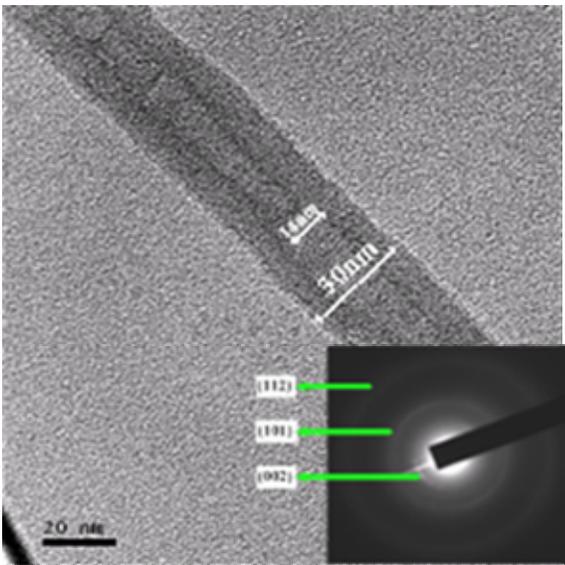


Fig. 3: TEM image of CNT. Inset is the SAED pattern.

### 3.2 Ti-coated CNT array

Due to the low density of CNT array, Ti film was successfully deposited on every CNTs, as shown in Fig. 4. The array structure remained in tact. TEM image of Ti-coated CNT was shown in Fig. 5. EDS spectrum pointed out the coated layer was Ti. The diameter of Ti-coated CNT was around 64 nm, indicating the coated thickness of Ti is about 17 nm. The thickness of Ti layer can be readily adjusted. The morphology of Ti-coated CNT was brush-like, with hairs uniformly pointing outwardly. It is noted that the density of CNT array is crucial to the deposition of Ti

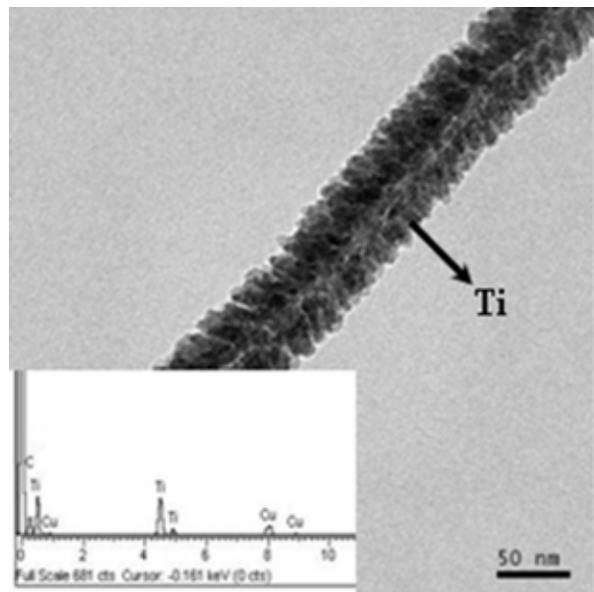


Fig. 5: TEM image of Ti-coated CNT. Inset is EDS spectrum.

### 3.3 TiO<sub>2</sub>/CNT coaxial composite array

The layer of Ti coating outside of CNT transforms to TiO<sub>2</sub> by oxidation in air at the elevated temperature. Figure 6 shows the TEM image of CNT coated with TiO<sub>2</sub>. The diameter of the TiO<sub>2</sub>/CNT coaxial nanotube was about 84 nm, increasing from the 64 nm of Ti/CNT coaxial nanotube. The increase of diameter is due to the participation of oxygen atoms in Ti-O bondings. SAED pattern in Fig. 6 shows the coexistence of CNT (002) and TiO<sub>2</sub> (101) planes, and shows the TiO<sub>2</sub> is of anatase phase. Comparing to the

brush-like morphology of Ti/CNT nanotube, the surface of TiO<sub>2</sub>/CNT nanotube is much smoother. This may be due to the nucleation and annealing of TiO<sub>2</sub> during the oxidation treatment to smooth out the rough Ti grains. Nevertheless, the outer surface of TiO<sub>2</sub> still shows the wavy signature of Ti film. Fig. 7 shows the FESEM image of TiO<sub>2</sub>/CNT coaxial array, where the alignment was slightly deteriorated. The possible cause for the deterioration is the large variation of oxidation rate throughout the entire array.

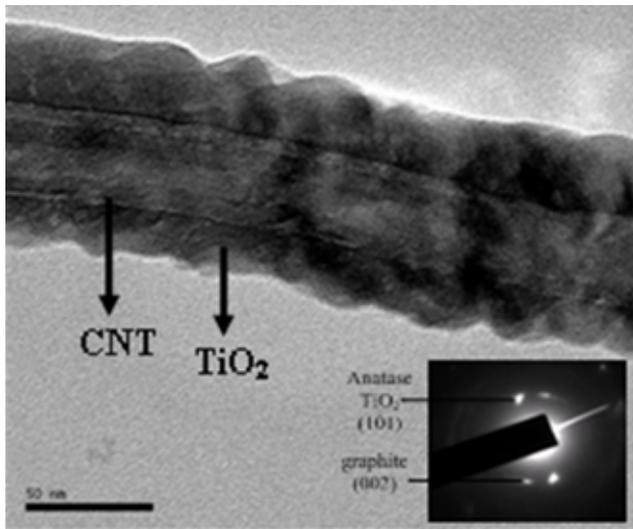


Fig. 6: TEM image of TiO<sub>2</sub>/CNT coaxial nanotube. Inset shows the (101) plane of anatase TiO<sub>2</sub> and (002) plane of CNT.

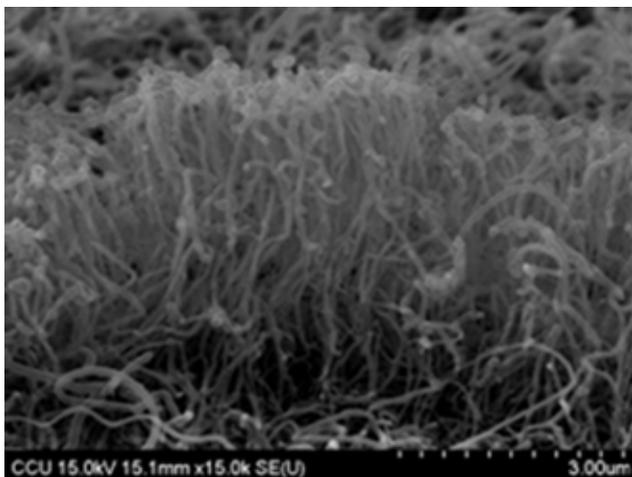


Fig. 7: SEM image of TiO<sub>2</sub>/CNT coaxial array.

### 3.4 Absorption spectrum

TiO<sub>2</sub>/CNT coaxial arrays with different TiO<sub>2</sub> thickness were prepared by controlling the thickness of Ti coated layer. Absorption spectra of these samples were given in Fig. 8, showing the emergence of visible-light absorption besides the UV one. This indicates the shift of absorption from UV to visible-light range. Moreover, also given in Fig. 8, when the TiO<sub>2</sub> thickness increased, the intensity of visible-light absorption increased accordingly, along with the decrease of UV absorption. However, if the TiO<sub>2</sub> thickness was too large, the ratio of UV/vis.-light absorption cannot be further increased. The underlying causes for the appearance of visible-light absorption and the shift of absorption should be due to the coaxial structure between TiO<sub>2</sub> and CNT. It is well known that the surface of CNT is apt to bonding to the -OH or -COOH functional groups. During the growth of TiO<sub>2</sub>, Ti atoms at the CNT-TiO<sub>2</sub> interface bond with the oxygen atoms of -OH and -COOH functional group. Fig. 10 shows the XPS spectrum, where C-O and C-O-C bondings indicate the functional groups at the CNT surface. In addition, most of the Ti is in the form of Ti<sup>4+</sup> (TiO<sub>2</sub>) and the rest is in the form of Ti<sup>3+</sup> (Ti<sub>2</sub>O<sub>3</sub>) and Ti<sup>2+</sup> (TiO). Because the electron density readily influences the bandgap, the changing electron density of Ti results in the appearance of visible-light absorption. The intensity of absorption shift depends on the degree of increasing electron density of Ti, which is proportional to the relative content of carbon in the interface. It is worthy to note that this change of Ti's electron density is due to the metal-support interactions [7, 8] taking place at the TiO<sub>2</sub> and CNT interface, which is different from the doping effect [1].

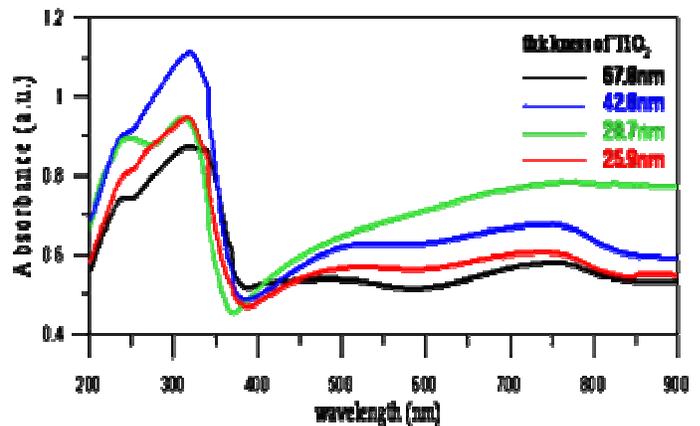


Fig. 8: Absorption spectra of TiO<sub>2</sub>/CNT coaxial array with various TiO<sub>2</sub> thickness.

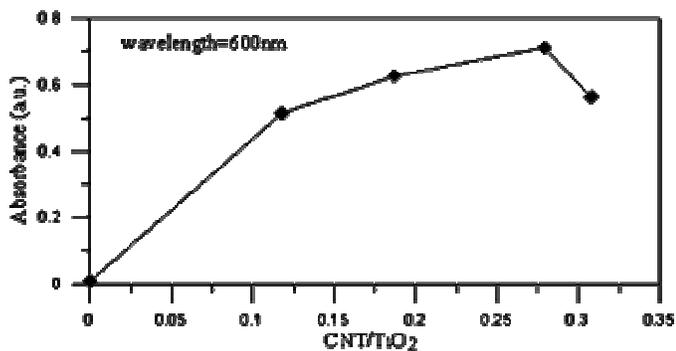


Fig. 9: Visible-light Absorption intensity varies with the ratio between CNT and TiO<sub>2</sub>.

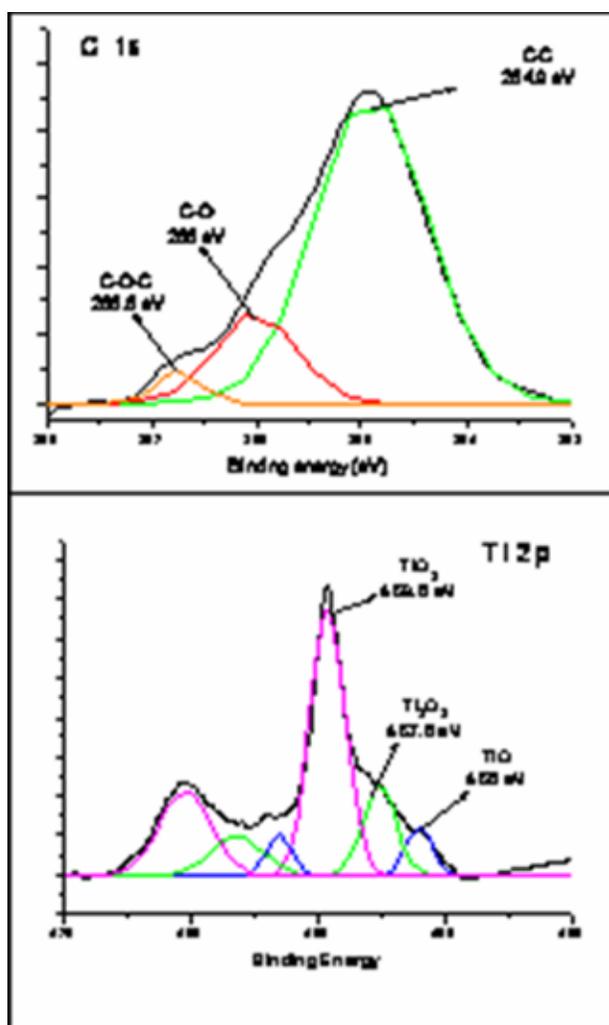


Fig. 10: A typical XPS spectrum of TiO<sub>2</sub>/CNT coaxial array.

## 4 CONCLUSIONS

Titania (TiO<sub>2</sub>)/carbon nanotube (CNT) composite array was successfully prepared by growing TiO<sub>2</sub> on every CNTs of the CNT array. The resulted morphology was of coaxial structure, where TiO<sub>2</sub> layer wrapped the inner CNTs. The TiO<sub>2</sub> layer was of anatase phase. Adsorption spectrum reveals the TiO<sub>2</sub>/CNT composite array have both the UV and vis.-light absorptions. The ratio of UV/vis.-light absorption increased with the increasing thickness of TiO<sub>2</sub> (using CNT/Ti, thickness ratio, as an index). However, if the TiO<sub>2</sub> thickness was too large, the ratio of UV/vis.-light absorption cannot be furthered increased. The vis.-light absorption of TiO<sub>2</sub>/CNT composite array is resulted from the increase of electron density of Ti due to the metal-support interactions between TiO<sub>2</sub> and CNT.

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