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# *In-situ* coating of MWNTs with sol-gel $TiO_2$ nanoparticles

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## ABSTRACT

Multi-walled carbon nanotubes (MWNTs) were *in-situ* coated with anatase $TiO_2$ via sol-gel process followed by annealing of the composites using infrared (IR) lamp. SEM results showed that MWNTs were coated with 15-45nm thick $TiO_2$ layer depending on the composite ratios. Based on the XRD results, MWNTs were found to show heterogeneous nucleation for anatase $TiO_2$ and promote the formation of larger anatase $TiO_2$ crystalline particles with higher crystalline degree. The UV-Vis-NIR characterization indicated the MWNTs also enhanced the sensitivity of $TiO_2$ matrix for both UV and visible light, and the bond edge absorption position of the $TiO_2$ composites shifted toward higher wavelengths with the decrease of MWNTs content. The method could be utilized to fabricate MWNTs /$TiO_2$ composites conveniently. Copyright © 2010 VBRI press.

**Keywords:** Carbon nanotubes; $TiO_2$ ; nanocomposites; sol-gel method

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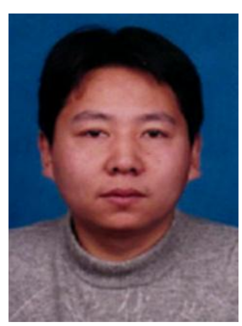

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## Introduction

Since the discovery of carbon nanotubes(CNTs), polymer-based composites including CNTs have attracted considerable attention in the research and industrial communities, due to their good electrical conductivity, high stiffness and high strength at relatively low CNTs content [**1-6**]. In the meanwhile, researchers also found that CNTs could form composites with many inorganic materials. For examples, Ma et al. [**7**] have prepared CNT–SiC composites by hot-pressing the mixture of large multi wall carbon nanotubes (MWNTs) and SiC powder. $SiO_x$ coated CNTs [**8**] have been fabricated through a sol-gel technique at room temperature. Besides that, CNTs composite containing metal, metal oxide or metal salts were also reported, e.g. CNT-Fe/Co-$MgAl_2O_4$, CNT-Co-MgO and CNT-Fe-$Al_2O_3$ have also been synthesized [**9-13**]. Chen et al. [**14**] fabricated SnO-CNT composites by a sol-gel method as anode actively material for lithium-ion batteries. Han and Zettl [**15**] have coated single-walled carbon nanotubes (SWNTs) with a thin $SnO_2$ layer by a chemical solution route. The MWNTs-$SnO_2$ composites [**16**] were synthesized by a new and simple one-step wet chemical method.

Because of the higher photocatalytic efficiency, $TiO_2$ nano particles, especially anatase phase, have become more and more popular in related fields such as optics, microelectronics and photocatalysis. MWNTs could act as a good support for photocatalytic $TiO_2$ due to their high mechanical and chemical stability, larger specific area and the mesoporous character, a dispersion of $TiO_2$ on MWNTs surface could create more active sites for the photocatalytic reactions [**17**]. So the CNTs–$TiO_2$ composites could be utilized in treating various biological, organic, or inorganic hazardous pollutants in water or air, and even the passive decontamination of surfaces. Wang et al. [**18**] synthesized anatase $TiO_2$-CNTs nanocomposites through a nanocoating-hydrothermal process, and the composites showed enhanced photocatalytic activity for photodegradation reaction of methylene blue under visible-light irradiation. Dong et al. [**19**] attached $TiO_2$ nanoparticles onto shortened CNTs by electrostatic attraction. Jitianu et al. [**20**] also reported the anatase-type $TiO_2$ coating of MWNTs by a sol–gel method using classical alkoxides as $Ti(OEt)_4$ and $Ti(OPri)_4$ and by hydrothermal hydrolysis of $TiOSO_4$ in sulfuric acid under elevated pressure at 120$^o$C.

This paper reports the coating of MWNTs with anatase $TiO_2$ nano particles through a simple sol-gel process. The MWNTs/$TiO_2$ composite powder was characterized by techniques such as Field emission-scanning electron microscopy (FE-SEM), Fourier transform infrared (FTIR), X-ray diffraction (XRD) and UV-Vis-NIR spectroscopy.

## Experimental

### *Materials*

MWCNTs prepared from catalytic decomposition of $C_2H_2$ or $CH_4$ over the pre-reduced $LaCoO_3$ [**21**] were provided by CNTs R&D Center of Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences. The MWNTs received had a purity of 85% and length of 5-15um, and were further purified with dilute hydrochloride acid at room temperature.

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Some $Ti(OBu)_4$ were dissolved into some absolute alcohol to form uniform solution, and MWCNTs were dispersed into some absolute alcohol by sonication. Then the MWCNTs dispersion were mixed with the $Ti(OBu)_4$ solution and homogenized by sonication for 20 min. Finally, the mixture was kept standing until the volatilization of alcohol, the grey MWCNTs/$TiO_2$ composite powder could be obtained by annealing the resultant gel fully under infrared (IR) lamp in air atmosphere.

### *Characterizations*

The morphology of the MWCNTs/$TiO_2$ composite powder was observed under field emission scanning electron microscopy (FE-SEM) by using a JSM-6700F instrument. All the surfaces were examined after being gilded to avoid electrostatic charging and poor image resolution. The crystalline types and sizes of the $TiO_2$ crystals in MWNTs/$TiO_2$ composites were analyzed using D/MAX-2500PC XRD (Cuk$\alpha_1$ radiation with Nickel filter). The functional groups on purified MWNTs, $TiO_2$ and the MWNTs/$TiO_2$ composites were determined by Fourier transform infrared (FTIR) spectrum using Bruker VERTEX70. The diffuse reflection spectrum (DRS) was determined in the range of 200-800 nm to characterize the UV light sensitivity of the resultant $TiO_2$ composites by using UV-Vis-NIR spectrophotometer (Cary 500 scan).

## Results and discussion

**Fig. 1** shows SEM images of purified MWNTs and MWNTs/$TiO_2$ composites. Purified MWNTs in **Fig. 1a** with an average diameter of about 20 nm were very clean and intertwined with each other. The MWNTs composites containing 85 wt.% $TiO_2$ in **Fig. 1b** showed that the diameters of MWNTs were about 30-60nm thicker than those of purified MWNTs, i.e., MWNTs were coated with a 15-30 nm thick $TiO_2$ layer. Some $TiO_2$ agglomorates of about 230 nm could be found. For MWNTs composite containing 95 wt.% $TiO_2$ in **Fig. 1c**, almost all MWNTs were coated with 25-45 nm $TiO_2$ layer and the largest $TiO_2$ agglomerate was about 290 nm. With MWNTs content in composites decreasing, the $TiO_2$ coating on MWNTs became thicker, and the $TiO_2$ particles tended to have larger sizes. Based on the SEM images, without or with insufficient MWNTs, newly formed $TiO_2$ particles were subject to agglomerate due to the IR annealing and the interactions among the –OH groups on $TiO_2$. MWNTs were supposed to play a role in absorbing and assembling $TiO_2$ particles along the tubes, which in turn would enhance the photocatalysis efficiency of $TiO_2$.

The FTIR spectrum of purified MWNTs (**Fig. 2a**) shows the characteristic peaks of some polar groups, i.e., the stretching vibration of O-H bond at 3670 cm$^{-1}$, the wagging vibration of O-H bond near 682 cm$^{-1}$, the stretching

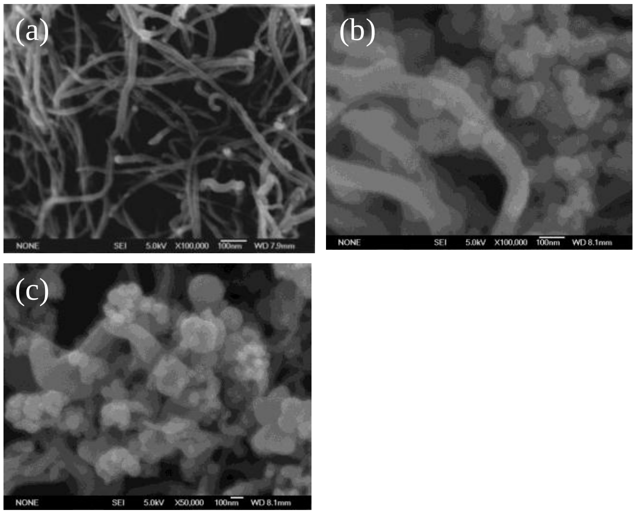


**Fig. 1.** SEM images: (a) MWCNTs; (b) and (c) MWCNTs composites containing 85 wt.% and 95 wt.% $TiO_2$, respectively.

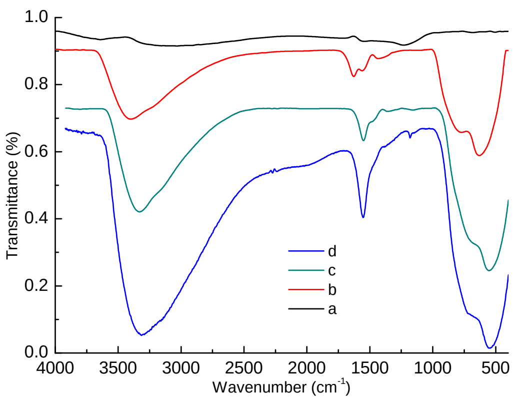


**Fig. 2.** FTIR spectra: (a) MWCNTs; (b) and (c) MWCNTs composites containing 85 wt.% and 95 wt.% $TiO_2$; (d) $TiO_2$.

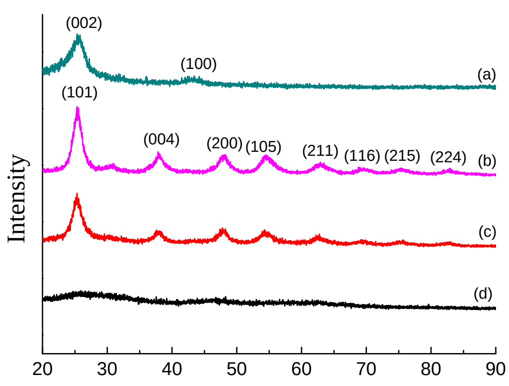


**Fig. 3.** XRD spectra: (a) MWCNTs; (b) and (c) MWCNTs composites containing 85 wt.%, and 95 wt.% $TiO_2$; (d) $TiO_2$.

vibration of C=O bond near 1690 $cm^{-1}$, and the stretching vibration of C-O bond near 1231 $cm^{-1}$. These results agreed well with XPS studies about CNTs [**22, 23**]. FTIR spectrum of neat $TiO_2$ (**Fig. 2d**) fabricated as a reference sample in a similar way to MWNTs/$TiO_2$ shows the three obvious peaks, which correspond to the Ti-O bond near 550 $cm^{-1}$, the H-O bond near 1550 $cm^{-1}$ and the H bond near 3330 $cm^{-1}$ might come from intermolecular condensation of $TiO_2$, respectively. Besides, the IR spectra of MWNTs composites containing 95 wt.% $TiO_2$ show three similar broad IR adsorption peaks at similar positions to that of $TiO_2$, and with the decrease in MWNTs content, the IR spectrum of $TiO_2$ composite became more similar to that of neat $TiO_2$, while the three IR adsorption peaks of the MWNTs composites containing 85 wt.% $TiO_2$ shifted towards higher wavelengths due to the stronger interactions between the polar groups on $TiO_2$ and MWNTs.

The XRD patterns of the samples are given in **Fig. 3**. The two peaks in **Fig. 3a** corresponded to the (0 0 2) and (1 00) reflections of MWNTs. The $TiO_2$ without MWNTs in **Fig. 3d** showed three wide, dispersive and weak bands indicating the smaller anatase particles with lower crystalline degree. All the diffractograms of MWNTs/$TiO_2$ appeared characteristic peaks of the anatase $TiO_2$, and both the intensity and the width at half height of anatase diffraction peaks varied with the composition of MWNTs/$TiO_2$ composites. The increase in both the intensity and sharpness of the diffraction peaks of MWNTs/$TiO_2$ composites indicated the heterogeneous nucleation of MWNTs for $TiO_2$ and the formation of larger anatase $TiO_2$ crystalline particles with higher crystalline degree in composite. It could also be found that the (0 0 2) reflection of MWNTs overlaps the (1 0 1) reflection of anatase $TiO_2$ [**24**] in **Fig. 3b** and **Fig. 3c**.

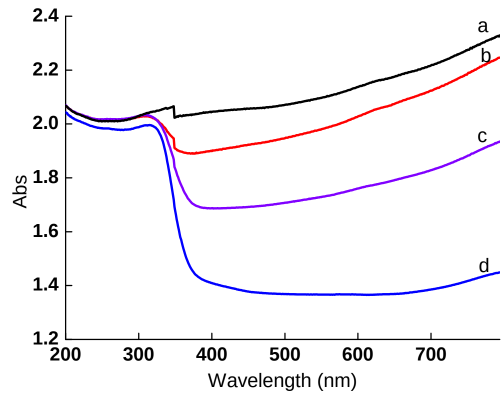


**Fig. 4.** DRS spectra by UV-Vis-NIR characterization: (a) MWCNTs; (b) and (c) MWCNTs composites containing 85 wt.% and 95 wt.% $TiO_2$; (d) $TiO_2$.

**Fig. 4** shows DRS of MWCNTs, MWCNTs/$TiO_2$composites and $TiO_2$ by UV-Vis-NIR technique. It could be found MWNTs have strong absorption for the light with wavelength ranging from 200 nm to 800 nm. Except for purified MWCNTs, neat $TiO_2$ and the MWNTs composites containing 85 wt.% and 95 wt.% $TiO_2$ all demonstrated the UV absorption bond edges at 338 nm, 339 nm and 347 nm, respectively. The result indicated the MWNTs/$TiO_2$ composites were UV light sensitive semiconductor, and the incorporation of MWNTs could not only enhance the UV light sensitivity of anatase $TiO_2$, but also increase the absorption capacity for visible light. What's more, with the decrease in MWNTs content, the absorption bond edge position of the $TiO_2$ composites shifted toward higher wavelengths, which implied the increase in the particle size of anatase $TiO_2$. The result is consistent with the SEM observation and XRD results. Besides, according to related theory, the blue shift of the absorption bond wavelength of the $TiO_2$ in composites also indicates higher bandgap as well as higher photo-oxidation and photo-reduction ability of anatase $TiO_2$ in MWNTs composites.

Due to the semiconducting properties of $TiO_2$, the MWNTs/$TiO_2$ composites could be applied in photo catalytic decomposition of aromatic pollutants in aqueous medium under UV light [**25**]. MWNTs having very large specific surface area could act as adsorbent to increase the target pollutant concentration to a high level around the TiO2 and achieve a high photo decomposition rate [**26**]. Wang et al. [**27**] proposed that CNTs might act as a photosensitizer, thus enhanced the photocatalytic efficiency of $TiO_2$ and extended photocatalysis into the visible spectrum [**28**], e.g., Chen et al. [**29**] found that visible light induced photoelectrocatalytic degradation of phenol by carbon nanotube-doped $TiO_2$ electrodes is enhanced. Kuo et al. [**30**] found the electron transfer in the $TiO_2$/CNTs composites reduced the electron/hole recombination and increased the photon efficiency. Besides, due to addition of MWNTs, $TiO_2$ displays remarkably higher efficiency of photocatalytic reduction of $CO_2$ with water [**31**].

## Conclusion

MWNTs-$TiO_2$ composites were fabricated successfully by a sol-gel process. With the MWNTs content in composites decreasing, the $TiO_2$ coating on MWNTs became thicker, and the $TiO_2$ particles tended to have larger sizes due to the heterogeneous nucleation of MWNTs for anatase $TiO_2$. The interactions between the polar groups on both $TiO_2$ and MWNTs were regarded to stimulate the combination of $TiO_2$ with MWNTs. Besides, the addition of MWNTs enhanced both the UV and visible light sensitivity of $TiO_2$. With the decrease in the MWNTs content the UV absorption bond edge position of the $TiO_2$ composites shifted toward higher wavelengths. The method is a convenient route to fabricate UV sensitive $TiO_2$/MWNTs composites.

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