

Microstructures and photonic effects of titania dispersed inside/outside carbon nanotube composites derived from different titanium alkoxide precursors

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The comparative microstructures and photonic effects of CNT/TiO₂ composites which were derived from pre-oxidized carbon nanotubes and different titanium alkoxide precursors (titanium (IV) n-butoxide (TNB), titanium(IV) isopropoxide (TIP) and titanium(IV) propoxide (TPP)) by a sol-gel method. The composites were characterized by their Brunauer-Emmett-Teller surface areas, transmission electron microscopy, X-ray diffraction, and UV-vis absorption spectroscopy. The photoactivity of the prepared materials under UV irradiation was tested using methylene blue (MB) in an aqueous solution. The CNT/TiO₂ composites derived from the TIP precursor only existed in an anatase state with a very strong intensity, while the CNT/TiO₂ composites derived from TIP and TPP precursors included a mixed structure of anatase and rutile. The TiO₂ particles were embedded into the tubes of CNTs for the CNT/TiO₂ composites derived from the precursors with TNB and TIP, while for the CNT/TiO₂ composites from TPP the TiO₂ particles were only distributed outside the surfaces of the CNTs and partially aggregated. The CNT/TiO₂ composites derived from TPP have a higher degradation effect on the MB solution more than that of TNB and TIP as titania precursors. A mechanism of TiO₂ particles dispersing inside or outside of the CNT is proposed.

Key words: CNT, TiO₂, titania precursor, comparative microstructure, photocatalytic effect.

Introduction

Since the discovery of photoelectrochemical water splitting by chemically modified titanium dioxide (TiO₂) by Fujishima and Honda in 1972 [1], TiO₂ has always been one of the best candidate materials due to its photocatalytic properties, its relative nontoxicity, and long-term thermodynamic stability. Several groups managed to enhance the photocatalytic properties and optimized titania's use to degrade various organic and inorganic pollutants [2]. On the other hand, carbon nanotubes (CNTs) have excellent mechanical properties and a large specific surface area ($> 150 \text{ m}^2\text{g}^{-1}$) [3, 4]. They allow for surface chemical modifications to control the type of bonds that can be formed with titania, which are chemically bonded or van der Waals bonded. A mixture of titania and CNT also has a large area where pollutants (organic or inorganic reactants) can be adsorbed. Adsorption is an important process for the photocatalytic destruction of pollutants. Therefore, chemically modified CNTs are interdependent dopants and supports for titanium dioxide to be used as photocatalysts.

Recently, CNT/TiO₂ composites have been expected to be a robust means to address various environmental and self-cleaning issues. Up to now, several groups reported on how to enhance their photocatalytic properties and

optimized titania's use to degrade various organic and inorganic pollutants in several ways such as by sol-gel [5-10], hydrothermal [11] and electrospinning [12] methods. An *et al.* [5] studied the photocatalytic activity for anatase TiO₂ deposited onto CNT via hydrolysis of titanium isopropoxide in supercritical ethanol in terms of its ability to mediate the degradation of phenol under visible light. CNTs have been coated via hydrothermal methods [11]. A relatively new method for preparing such composites is a filter-mat or fiber-form via an electrospinning method [12]. It plays a very significant role for the photocatalytic activity that TiO₂ particles are dispersed homogeneously on the surfaces of CNTs. However, little attention has been paid to systems of TiO₂ particles dispersed inside or outside of CNTs as photocatalysts.

In this study, we used the sol-gel method to prepare the CNT/TiO₂ composites. Three types of classical alkoxides: titanium(IV) n-butoxide (TNB, $\text{Ti}\{\text{OC}(\text{CH}_3)_3\}_4$), titanium(IV) isopropoxide (TIP, $\text{Ti}\{\text{OCH}(\text{CH}_3)_2\}_4$) and titanium(IV) propoxide (TPP, $\text{Ti}(\text{OCH}_2\text{CH}_2\text{CH}_3)_4$) were employed as precursors to form TiO₂ and the CNTs was pre-oxidized with m-chloroperbenzoic acid (MCPBA), resulting in CNT/TiO₂ composites. We focused on the comparative microstructures of the CNT/TiO₂ composites and studied the photocatalytic efficiency of TiO₂ particles dispersed inside or outside of the CNTs. The resultant CNT/TiO₂ composites were characterized by their Brunauer-Emmett-Teller (BET) surface areas, transmission electron microscopy (TEM), and X-ray diffraction (XRD). The photocatalytic activity of the as-prepared CNT/TiO₂ com-

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posites for methylene blue (MB, $C_{16}H_{18}N_3S \cdot Cl \cdot 3H_2O$) degradation under the UV light irradiation was investigated. Subsequently, a mechanism of TiO_2 particles dispersing inside or outside of the CNTs is proposed.

Experimental

Materials

Crystalline MWCNTs (diameter: ~ 20 nm; length: ~ 5 μm) powder was obtained from Carbon Nano-material Technology Co., Ltd, Korea. The TNB (99%), TIP (97%) and TPP (98%) as titanium alkoxide precursors to form the TiO_2 were purchased from Acros Organics (New Jersey, USA), Kanto Chemical Company (Tokyo, Japan) and Aldrich Chemical Company, respectively. The structures of TIP, TPP and TNB are displayed in Fig. 1. For the oxidation of the surfaces of CNTs, m-chlorperbenzoic acid (MCPBA) was chosen as the oxidizing agent which was purchased from Acros Organics, New Jersey, USA. Benzene (99.5%) was used as the organic solvent purchased from Samchun Pure Chemical Co., Ltd, Korea. MB was the analytical grade solvent used, and it was purchased from Dukan Pure Chemical Co., Ltd.

Synthesis of CNT/ TiO_2 composites

To prepare the oxidizing agent, ca 1.0 g MCPBA was melted in 60 ml benzene. Then ca 0.2 g CNTs was put into the oxidizing agent, refluxed at 353 K for 6 h until solid precipitates were formed and dried at 363 K. Titanium alkoxide precursors were dissolved separately in benzene at a ratio of 50 : 50. The solution was stirred magnetically for 30 minutes to obtain a titanium alkoxide precursor/benzene solution. Subsequently, the pre-oxidized CNTs were introduced into the titanium alkoxide precursor/benzene solutions. The mixtures were loosely covered and kept stirred by a magnet at 343 K for 5 h, until a homogenous CNTs-containing gel formed. The gel was heat treated at 973 K for 1 h with a heating rate of 279 K/minute to obtain CNT/ TiO_2 composite catalysts. By changing the titanium alkoxide precursors, different samples were obtained. The preparation conditions and code of samples are listed in Table 1. The CNT/ TiO_2 composite derived from titanium (IV) *n*-butoxide (TNB) has the nomenclature CNT/TNB, while from titanium (IV) isopropoxide (TIP) and titanium(IV) propoxide (TPP) have the nomenclature CNT/TIP and CNT/TPP, respectively.

Characterization of CNT/ TiO_2 composites

BET surface area was measured using a Quantachrome Surface Area analyzer (MONOSORB, USA). XRD (Shimata XD-D1, Japan) was used for crystal phase identification and estimation of the anatase-to-rutile ratios which were obtained at room temperature. Transmission electron microscopy (TEM, JEOL, JEM-2010, Japan) was used to observe the surface state and structure of the CNT/ TiO_2 composites. TEM at an acceleration voltage of 200 kV was used to investigate the size and

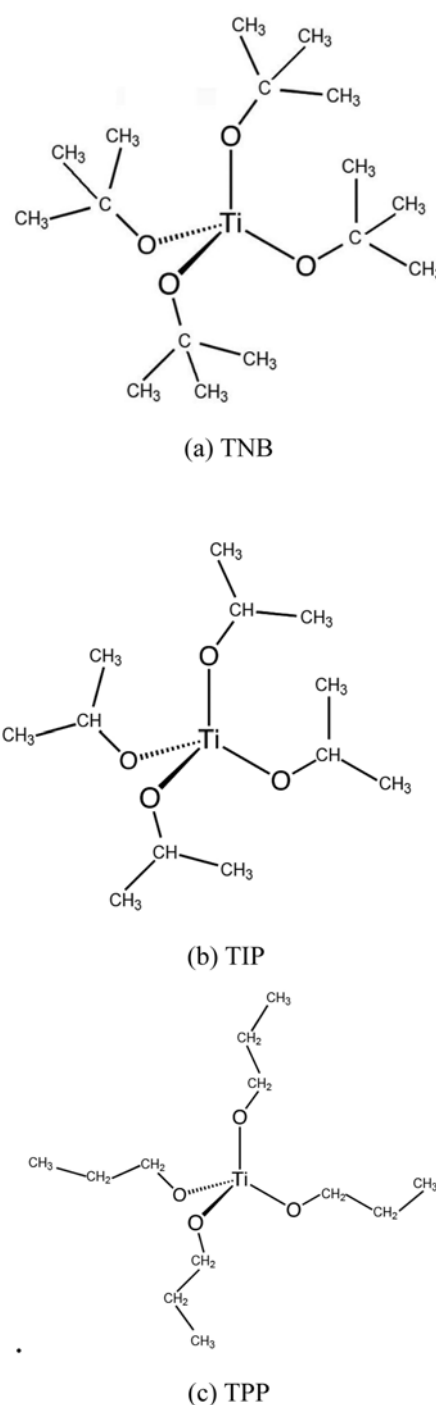


Fig. 1. The structures of (a) TNB, (b) TIP, and (c) TPP.

Table 1. Nomenclatures of CNT/ TiO_2 composite samples

Samples	Nomenclatures
CNT + Titanium(IV) <i>n</i> -butoxide (TNB)	CNT/TNB
CNT + Titanium(IV) isopropoxide (TIP)	CNT/TIP
CNT + Titanium(IV) propoxide (TPP)	CNT/TPP

distribution of the titanium particles deposited on the CNT surfaces of various samples. TEM specimens were prepared by placing a few drops of the sample solution on a carbon

grid. Finally, UV-vis spectra for the MB aqueous solution degraded by CNT/TiO₂ composites under UV light irradiation were recorded using a Genspec (Hitachi, Japan) spectrometer.

Photocatalytic activities CNT/TiO₂ composites

The photocatalytic effect of CNT/TiO₂ composites was determined using MB decomposition in an aqueous solution under a UV lamp (356 nm, 1.2 mW/cm²). The initial MB concentration chosen was 1.0×10^{-5} mol/l. The amount of suspended composites was kept at 1 g/l in 50 ml MB solution. Prior to illumination, the photocatalysts were impregnated in the pristine MB solution in a dark box for 60 minutes needed to achieve adsorption/desorption equilibrium. Then, the solution was irradiated with UV. The first sample was taken out at the end of the dark adsorption period (just before the light was turned on), in order to determine the MB concentration in solution, which was hereafter considered as the initial concentration (c_0) after dark adsorption. Samples were then withdrawn regularly from the reactor in the following order 10, 20, 30, 40, 50 and 60 minutes, and immediately centrifuged to separate any suspended solid. The spectra for each sample were recorded and the absorbance was determined at a characteristic wavelength 660 nm for each MB solution degraded.

Results and Discussion

Characterization of the CNT/TiO₂ composites

Table 2 shows the BET surface area of the CNT/TiO₂ composites. The BET surface area of CNT/TNB, CNT/TIP and CNT/TPP are 17.52, 27.58 and 26.64 m²/g, respectively. It is noted that the surface area of the composite catalysts is much lower than that of neat TiO₂ (123 m²/g) and CNTs (299 m²/g). It seems that the Ti content is much more than the C content in all of the composite catalysts, and TiO₂ is embedded into the CNT particles with the TiO₂ particles agglomerated together, thus the surface area of composites was further decreased.

The XRD results for the catalyst samples are shown in Fig. 2. Diffraction peaks corresponding to anatase and rutile phases are marked with 'A' and 'R', respectively. Generally, the crystal structure of titanium dioxide is mainly determined by the heat treatment temperature, in our case, all of the composites were heat-treated at 973 K for 1 h. The CNT/TIP composites in Fig. 2(b) had peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 which are the diffractions from the (101), (004), (200), (105), (211) and (204) planes of anatase without any other peaks, indicating the CNT/TIP only existed in an anatase state with a very strong intensity.

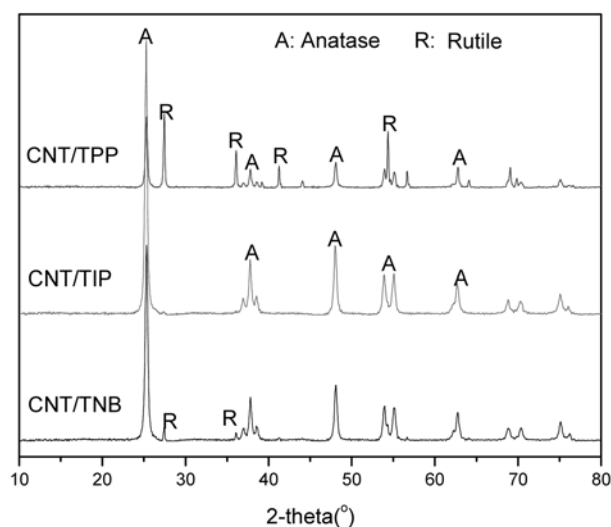


Fig. 2. XRD patterns of CNT/TiO₂ composites showing the diffraction peaks corresponding to anatase and rutile phases which are marked with 'A' and 'R', respectively; (a) the CNT/TiO₂ composites derived from TIP precursor only existed in an anatase state with a very strong intensity, while (b) the CNT/TiO₂ composites derived from TNB and TPP precursors included a mixed structure of anatase and rutile.

However, the CNT/TNB in Fig 2(a) and CNT/TPP in Fig. 2(c) not only had peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 which are the diffractions from the (101), (004), (200), (105), (211) and (204) planes of anatase, but also had peaks at 27.4, 36.1, 41.2 and 54.3 belonging to the diffraction peaks of (110), (101), (111) and (211) planes for rutile, indicating the CNT/TNB and CNT/TPP included a mixed structure of anatase and rutile. We also observed that the CNT/TNB composite had a stronger intensity from anatase and a relatively weaker intensity from rutile, while the CNT/TPP composite had stronger intensity of rutile and relatively weaker intensity of anatase. As the three types of titanium alkoxides precursors lead to different structures, when they are heat-treated at 973 K for 1 h, these titanium sources would form TiO₂ with different crystal structures. On the other hand, the characteristic peaks from CNTs could hardly be identified from the XRD patterns of the CNT/TiO₂ composites. It seemed that the small C content in the composites and the absence of CNTs aggregated in pores were supported by the disappearance characteristic peaks from CNTs in the XRD patterns.

The morphology of CNT/TiO₂ composites prepared with the CNTs and different titanium alkoxide precursors were examined by TEM. Fig. 3 shows the TEM images of the CNT/TiO₂ composites. It shows that TiO₂ particles were coated on the surface of CNTs and the CNT particles were dispersed homogeneously with apparent agglomeration of the TiO₂ particles. For the CNT/TiO₂ composites derived from different titania precursors of TNB in Fig. 3(a) and TIP in Fig. 3(b), it was interesting to note that some of the TiO₂ particles were embedded into the tubes of CNTs in this present study. On the other hand, for the titania precursor of TPP in Fig. 3(c), the TiO₂ particles were only

Table 2. The BET surface area of the CNT/TiO₂ composites

Samples	S _{BET} (m ² /g)
CNT/TNB	17.52
CNT/TIP	27.58
CNT/TPP	26.64

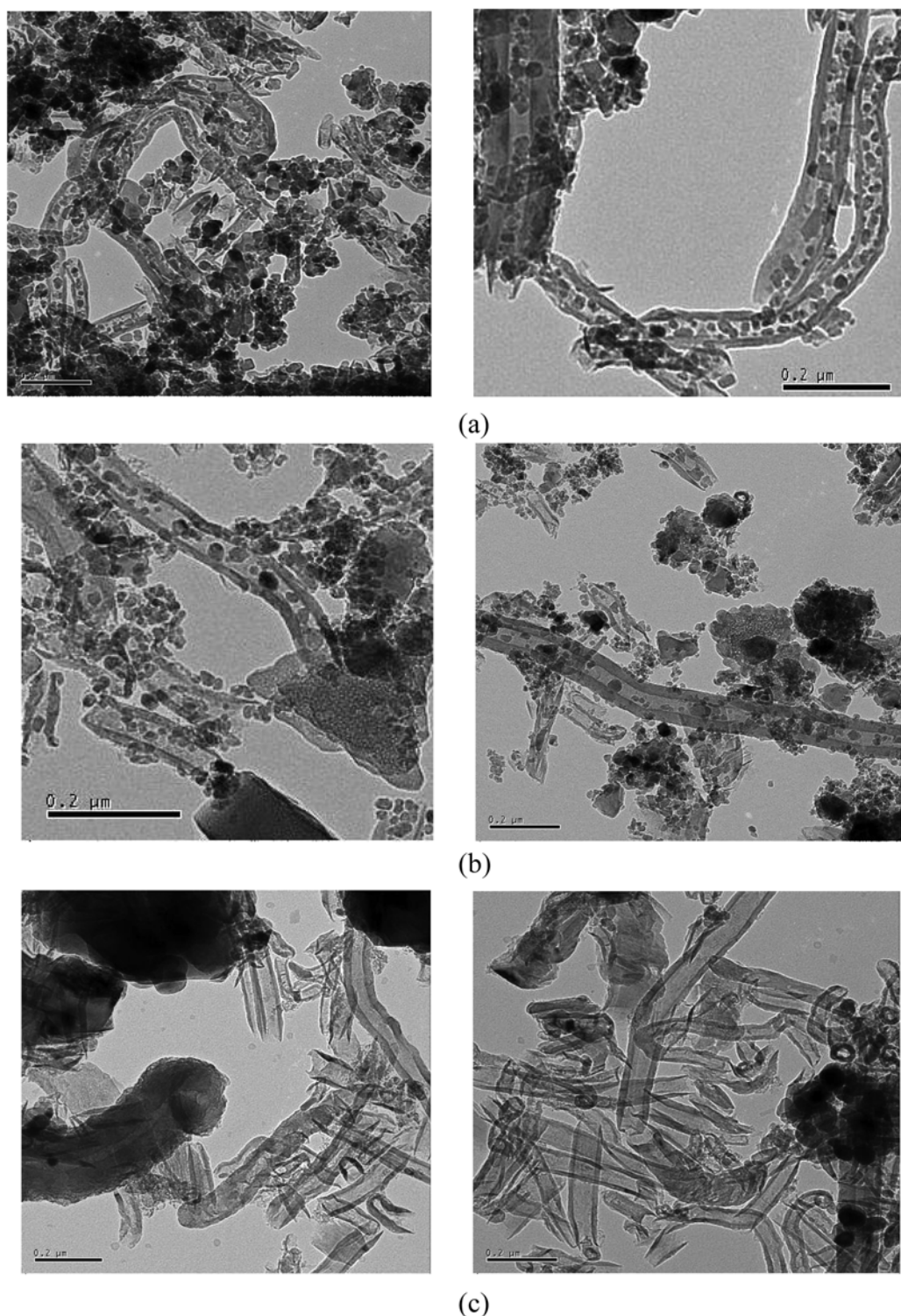


Fig. 3. TEM images of the CNT/TiO₂ composites derived from different titania precursors; (a) TNB, (b) TIP and (c) TPP; the TiO₂ particles were embedded into the tubes of CNTs for the CNT/TiO₂ composites derived from the precursors of (a) TNB and (b) TIP, while for the CNT/TiO₂ composite from (c) TPP the TiO₂ particles were only distributed on the outside surfaces of the CNTs and partially aggregated.

distributed on the outside surfaces of the CNTs and partially aggregated. A sol-gel method usually leads to a heterogeneous, non-uniform coating of CNTs by TiO₂, showing bare CNTs and random aggregation of TiO₂ onto the CNT surfaces [13-15], which is agreement with our result.

Photocatalytic activity of CNT/TiO₂ composites

The photocatalytic removal of MB aqueous solutions was investigated using a source of UV light irradiation. Fig. 4 shows the changes in relative concentration (c/c_0) of MB in the aqueous solutions on UV irradiation time

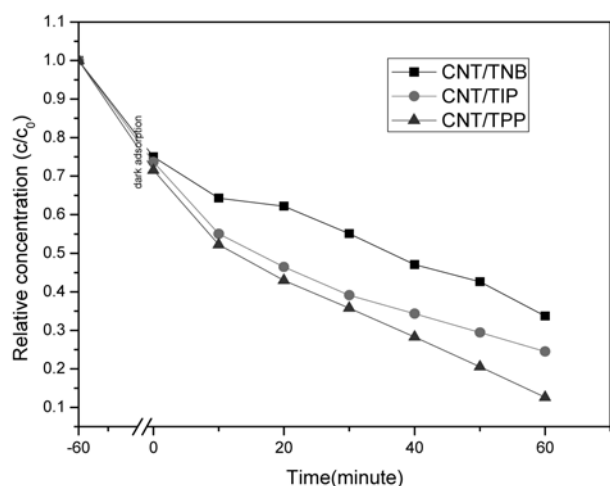


Fig. 4. Dependence of the relative concentration (c/c_0) of MB in the aqueous solutions on time of UV irradiation for the CNT/TiO₂ composites; the concentration of MB solution: 1.0×10^{-5} mol/l.

for the CNT/TiO₂ composites prepared with CNTs and different titanium alkoxide precursors. After 60 minutes of UV irradiation, it could be observed that the CNT/TPP in Fig. 4(c) has the highest degradation of MB solution of which 88% was almost removed. The MB degradation of the CNT/TNB in Fig. 4(a) and CNT/TIP in Fig. 4(b) also achieved 76% and 67%, respectively. From the data

of the BET surface area, the composites would have a low adsorption ability because they had a very low surface area. Consequently, it is emphasized that the MB degradation effect was mainly caused by the photocatalytic effect of TiO₂, so that the MB degradation effect of TiO₂ particles distributed uniformly on the outside surfaces of the CNTs was better than that of the inside and outside surfaces of the CNTs for the CNT/TiO₂ composites. The TiO₂ particles distributed inside the CNTs for the CNT/TiO₂ composites was due to the capillary effect [16, 17], leading to a poor synergic effect of the CNT/TiO₂ composites.

Mechanism of TiO₂ particles dispersing inside or outside of the CNTs

Under the same experimental conditions, for different titania precursors, the distribution state of TiO₂ particles is different. We considered that TiO₂ particles attached on the outside or inside of the CNTs depend on the chemical scission of the different titania precursors during the formation of CNT/TiO₂ gels. In order to describe the difference of different titania precursors, a scheme of the proposed chemical scission between the [TiO₄]⁻ group and [C₃H₇]⁺ or [C₄H₉]⁺ group is presented in Fig. 5. According to Solomons' organic chemistry [18], alkyl radicals are classified as being 1°, 2°, or 3° on the basis of the carbon atom that has the unpaired electron. More energy must be supplied to produce a 1° alkyl radical (the

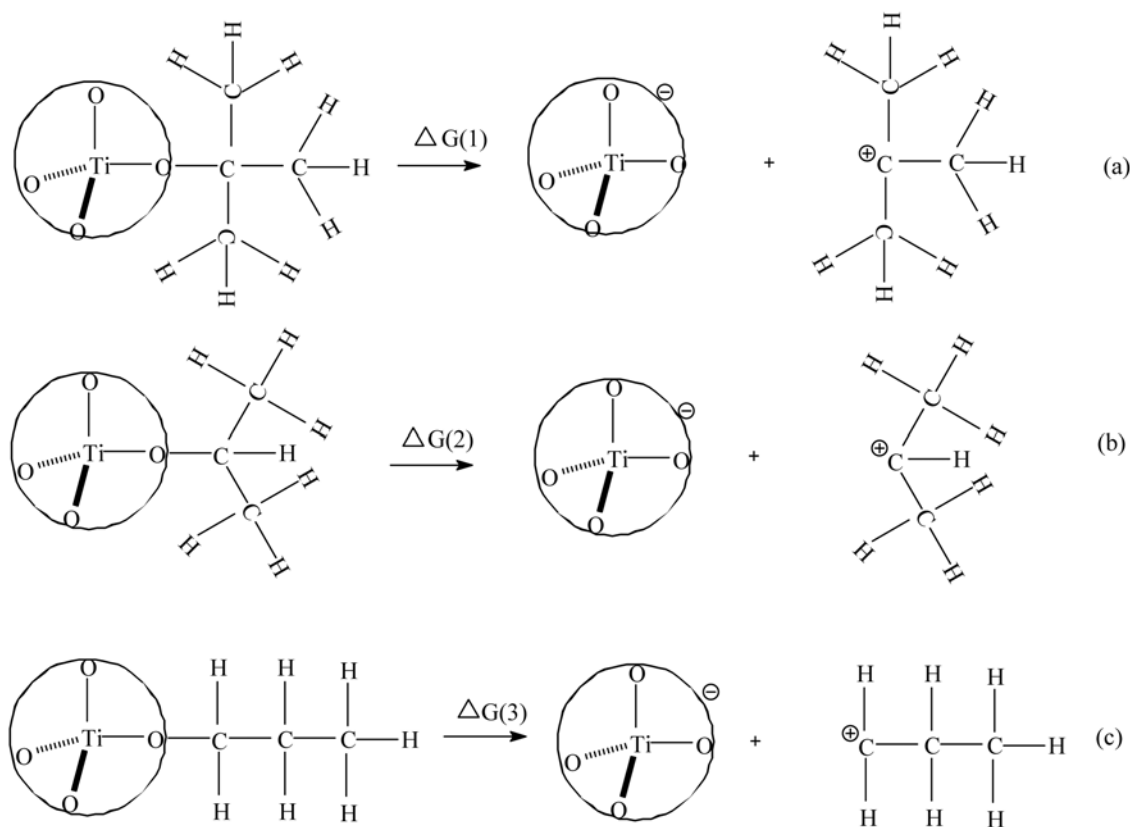


Fig. 5. The proposed chemical scission of different titania precursors during the formation of CNT/TiO₂ gels; (a) TNB, (b) TIP and (c) TPP ($\Delta G(\text{TNB}) < \Delta G(\text{TIP}) < \Delta G(\text{TPP})$).

propyl radical) from propane than is required to produce a 2° carbon radical (the isopropyl radical) from the same compound. Similarly, it needs a lower energy to produce a 3° carbon radical from the same compound. Thus, the free-energy order for the formation of carbocations from the protonated tertiary, secondary, and primary is $\Delta G(\text{TNB}) < \Delta G(\text{TIP}) < \Delta G(\text{TPP})$. With the same conditions, when the free-energy is lower, the formation of carbocations is easier. Therefore, among the three types of titania precursors, TPP in Fig. 5(c) is the most difficult to crack the bond of the $[\text{TiO}_4]^-$ group and the $[\text{C}_3\text{H}_7]^+$ group compared to the TNB in Fig. 5(a) and TIP in Fig. 5(b). Combining the results of TEM in Fig. 3(c), only with TPP as the titania precursor, TiO_2 particles coated the outside of the tubes and even covered all the surface of the CNTs. It is noted that there was a chemical scission between the $[\text{TiO}_4]^-$ group and the $[\text{C}_3\text{H}_7]^+$ or $[\text{C}_4\text{H}_9]^+$ group for the TIP and TNB, but not for the TPP. The diameter of the $[\text{TiO}_4]^-$ group for TIP and TNB is smaller than that for TPP molecule. It is proposed that the $[\text{TiO}_4]^-$ group for the TNB and TIP in Fig. 3(a) and (b) more easily permeated into the tubes than the original titania precursors. Therefore, the TiO_2 particles only attached outside the tubes for TPP in Fig. 3(c).

Conclusion

In this study, we present the comparative microstructures and photocatalytic effects of CNT/ TiO_2 composites prepared with pre-treated MWCNTs and different titanium alkoxide precursors in benzene solvent. Very small BET surface areas were obtained in our case for all of the composites. The CNT/ TiO_2 composites derived from the TIP precursor only existed in an anatase state with a very strong intensity, while the CNT/ TiO_2 composites derived from the TNB and TPP precursors included a mixed structure of anatase and rutile. The TiO_2 particles were embedded into the tubes of CNTs for the CNT/ TiO_2 composites derived from the precursors of TNB and TIP, while for the CNT/ TiO_2 composites derived from the TPP the TiO_2 particles were

only distributed on the outside surface of the CNTs and partially aggregated. The CNT/ TiO_2 composite derived from TPP had a higher degradation effect of a MB solution more than that of TNB and TIP as the titania precursors. Whether the TiO_2 particles are attached on the outside or inside of the CNTs depend on the free-energy for the formation of carbocations.

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