Research Article

Photocatalytic Improvement under Visible Light in TiO_2 Nanoparticles by Carbon Nanotube Incorporation

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Photocatalytic activity of TiO_2 nanoparticles was successfully enhanced by addition of multiwall carbon nanotubes (MWCNT) to make CNT/ TiO_2 nanocomposites by sol-gel method at ambient temperature. CNT treated by HNO_3 : H_2SO_4 treatment (1 : 3 v/v) was mixed with TiO_2 nanoparticles at various molar ratios and calcination temperatures. The optimal molar ratio of CNT : TiO_2 was found at 0.05 : 1 by weight. The optimal calcination condition was 400°C for 3 h. From the results, the photocatalytic activities of CNT/ TiO_2 nanocomposites were determined by the decolorization of 1×10^{-5} M methylene blue (MB) under visible light. CNT/ TiO_2 nanocomposites could enhance the photocatalytic activity and showed faster for the degradation of MB with only 90 min. The degradation efficiency of the MB solution with CNT/ TiO_2 nanocomposite achieved 70% which was higher than that with pristine TiO_2 (22%). This could be explained that CNT prevents TiO_2 from its agglomeration which could further enhance electron transfer in the composites. In addition, CNT/ TiO_2 nanocomposites had high specific surface area ($202 \text{ m}^2/\text{g}$) which is very promising for utilization as a photocatalyst for environmental applications.

1. Introduction

Titanium dioxide (TiO_2) is an ideal photocatalyst for high photocatalytic activities. TiO_2 can accelerate removals of organic compounds with its high stability in a chemical point of view. It is relatively cheap and easily available. Although TiO_2 has several advantages, it has some hindrances to apply in the environmental field, that is, photocatalytic degradation of organic pollutants, because TiO_2 is limited to work under only UV radiation ($<387 \text{ nm}$) [1, 2]. The primary problem is the low concentration of pollutants which reduces the efficiency of TiO_2 . Another problem is the recombination of electron-hole pair. Therefore, many studies have been focused on how to improve the photocatalytic activity of TiO_2 under visible light ($>400 \text{ nm}$) [3–5].

Carbon nanotube (CNT) has been successfully used as catalyst supporting materials with properties superior to those of other regular catalyst supports like activated carbon, soot, or graphite. CNT was recently found to be able to excellently absorb some toxic gases because CNT provides large specific surface area [6–8]. Peining et al. [9], Cao et al. [10], and Shitole et al. [11] have reported the combined roles of CNT and TiO_2 . CNT and TiO_2 composites showed a synergistic effect on the efficient degradation of some organic compounds. This is closely related to the enhancement of pollutant adsorptions from air and water because of the extremely high surface area of CNT and high microporous volume of TiO_2 . However, in the composite preparation, pristine CNT tends to lack solubility and be difficultly manipulated in any solvents, which have imposed great limitations

TABLE 1: Several photocatalysts made of CNT/TiO₂ composites (prepared by sol-gel technique) for photocatalytic degradations of dyes or pollutant under UV and visible radiations from opened literatures.

Catalyst	Titanium precursor	Dye/pollutant*	Light source	Degradation efficiency	Reference
CNT/TiO ₂	TTIP	MO	UV	99%	Saleh and Gupta [16]
				99%	Shitole et al. [11]
		MB	Visible	99%	Xu et al. [19]
				50%	Guo et al. [17]
	TNB	Phenol	UV	60%	Yao et al. [18]
		MO	UV	99%	Hu et al. [20]
		MB	Visible	60%	Zhang et al. [23]
			UV	70%	Oh et al. [21]
				99%	Li et al. [25]

* MO = methyl orange; MB = methylene blue; TTIP = titanium tetraisopropoxide; TNB = titanium butoxide.

to the use of CNT as templates to assemble diverse functional components. Therefore, to efficiently fabricate CNT based nanohybrids, it is necessary to activate the graphitic surfaces of CNT [12, 13]. Functionalization of CNT remains one of the most studied areas in CNT research fields. The most common covalent functionalization involves the addition of carbonyl and carboxyl groups via an aggressive treatment with HNO₃ or a mixture of HNO₃/H₂SO₄ acid. Covalent functionalization of CNT has been shown to be an efficient method for increasing solubility and chemical reactivity of CNT. Composite of acid-treated CNT and TiO₂ was found to have higher photocatalytic activity than pristine CNT and pristine TiO₂. The composite also showed a decrease of charge recombination by trapping electron in the valence band and an increase of the visible light absorption [10, 14–17]. Visible light absorption of the composite could be achieved because of the reducing band gap energy of the composite [12, 17].

Typically, CNT and TiO₂ composites were fabricated by sol-gel method. Sol-gel method is the common technique to synthesize TiO₂ nanoparticle because it is easy to control the chemical composition and inexpensive. Sol-gel method also does not need complicated equipment [18–20]. In addition, other advantages of sol-gel method are high purity, homogeneity, controllable stoichiometry, and ambient temperature preparation [21–23].

Table 1 shows several photocatalysts fabricated by sol-gel technique, which were made of CNT/TiO₂ composites and applied for photocatalytic degradations of dyes under UV and visible light radiations from opened literatures [11–16, 18]. Most of the studies showed that the rate of photocatalytic activity for degradation of pollutants can be enhanced by CNT/TiO₂ nanocomposites. Although many researchers studied the synthesis of TiO₂ and doped it with CNT, they mostly reported the photocatalytic activities under UV light. There are very few reports studied on those photocatalytic activities under visible light with relatively low activities (degradations of dyes ~50%) [17, 18]. Thus, this study aims to improve photocatalytic activity of CNT/TiO₂ nanocomposites under visible light.

For this contribution, we reported the preparation and characterizations of CNT/TiO₂ nanocomposites at ambient

temperature using TiBu and MWCNT as precursors. This is the first report on the precursors and ambient temperature preparation for CNT/TiO₂ nanocomposites. The optimal molar ratio (CNT/TiO₂) and calcination temperature were studied. FTIR, XRD, UV-vis, BET surface area analysis, and SEM were used to characterize the composites. Additionally, the photocatalytic activity of the composite photocatalysts was determined by decolorization of MB under visible light.

2. Experimental

2.1. Materials. All chemicals used were of analytical grade. Titanium butoxide (97%, Fluka), MWCNT (Nanogeneration Company, purity > 90%, average diameter 9.5 nm, and length 1.5 μm), ethanol (96%, Merck), nitric acid (65%, Merck), sulfuric acid (95–97%, Merck), hydrochloric acid (37%, Merck), and deionizer water were used for the preparation of nanocomposites. MB (UNILAB) was used for the photocatalytic experiments.

2.2. Acid Treatment of CNT. In a typical acid treatment, MWCNT was treated by nitric/sulfuric-mixed acid following the methods reported in previous works [10, 11]. MWCNT (1g) was stirred for 10 min in HNO₃:H₂SO₄ mixture (1:3 (v/v), 40 mL). The solution was sonicated for 6 h at 70°C in an ultrasonic bath to completely disperse MWCNT in the acid solution. MWCNT was then washed with deionized water to remove any residual acid until its pH value was adjusted to be 7. Treated MWCNT was dried overnight at 100°C in an oven. Finally, the resulting carboxyl-functionalized MWCNT powders were obtained. This functionalization will enhance the solubility of MWCNT in solvents as well as the creation of chemical compatibility with TiO₂ surfaces.

2.3. Preparation of CNT/TiO₂ Nanocomposites. Saleh and Gupta [16] and Morales et al. [24] reported a method to prepare CNT/TiO₂ nanocomposites at relatively high temperature (70–80°C) with a long time process (typically 6–8 h). In this work, CNT/TiO₂ nanocomposites were synthesized by sol-gel method adapted from that method. Specially, the

preparation time was shortened to be only 3 h and the preparation temperature was reduced to be at room temperature. TiBu ($\text{Ti}(\text{OC}_4\text{H}_9)_4$) was used as a titanium precursor. TiBu, ethanol, H_2O , and HCl were sequentially mixed as a solution. The molar ratio of TiBu:ethanol: H_2O :HCl was 1:0.35:34:0.2. The mixture was stirred at ambient temperature for 1 h to complete the hydrolysis reaction. Acid-treated CNT was then dispersed in a solution. The solution was sonicated for 2 h at ambient temperature. The molar ratios of CNT: TiO_2 used in the sol were 0.1:1, 0.05:1, and 0.03:1 by weight. Finally, the mixture was dried overnight at 100°C and calcined at different temperatures (300, 350, 400, or 500°C) for 3 h.

2.4. Characterizations of CNT/ TiO_2 Nanocomposites. For physical properties, the crystallinity of CNT/ TiO_2 nanocomposites was studied by X-ray diffraction (XRD) (D8 Advanced Bruker Euler Cradle) using $\text{Cu K}\alpha$ ($\lambda = 0.1540\text{ nm}$) as the X-ray source. The accelerating voltage and the emission current were 40 kV and 40 mA, respectively. The diffractograms were recorded in the 2θ range from 20° to 80° with the rate of $0.01^\circ/1.5\text{ s}$. The crystallite size was calculated by using the Scherrer equation. Fourier transform infrared (FTIR) spectra were recorded by a PerkinElmer System 2000 FTIR spectrometer using KBr pellets over the range of wavenumbers of $400\text{--}4000\text{ cm}^{-1}$. Brunauer-Emmett-Teller (BET) surface areas were also measured using the nitrogen adsorption method (ASAP 2010, Micromeritics Company) at 77 K. The UV-vis absorption was examined by UV-vis spectrophotometer (diffuse reflectance mode) in a range of wavelengths of $200\text{--}800\text{ nm}$. Composition of CNT and TiO_2 in the obtained composites was calculated from the thermogravimetric analysis (TGA) thermograms. The TGA thermograms were investigated from a TGA equipment (Pyris 1 TGA, PerkinElmer, USA). Morphological appearance of the pristine TiO_2 , acid-treated CNT, and CNT/ TiO_2 nanocomposites was obtained by a field emission scanning electron microscope (FE-SEM) (JEOL JSM-7001F).

2.5. Photodecolorization of Methylene Blue. Photocatalytic activities of CNT/ TiO_2 nanocomposites were studied from the removal of MB in aqueous solution. The concentration of MB used was $1 \times 10^{-5}\text{ M}$. MB aqueous solution (50 mL) and CNT/ TiO_2 nanoparticles (0.05 g) were mixed and stirred (for 15 min) at room temperature in a reactor under a dark condition for 3 h. The decrease of MB concentration under the dark condition was then determined by UV-vis spectrometer (GENESYS 10-S, Thermo Electron Corporation) at the maximum wavelength (λ_{max}) of 664 nm. After completed adsorption, the sample was put inside the reactor again with a new MB aqueous solution (50 mL). The visible light source, a fluorescence lamp (15 W, Philip), was turned on to study the photocatalytic activity of photocatalysts under visible irradiation. Finally, the reduction of MB concentration was recorded at a fix time interval (every 30 min).

FIGURE 1: FTIR spectra of (a) pristine CNT, (b) acid-treated CNT, and (c) CNT/ TiO_2 -0.05:1 nanocomposites at wavenumbers $400\text{--}4000\text{ cm}^{-1}$.

The decolorization efficiency of MB was calculated by using [21]

$$\text{Percentage of degradation} = \frac{(C_0 - C)}{C_0} \times 100, \quad (1)$$

where C_0 and C are an initial concentration and a concentration at a measuring time, respectively.

3. Results and Discussion

3.1. Acid Treatment of CNT. As mentioned above, acid treatment is one of important processes for CNT functionalization. For the preparation of CNT/ TiO_2 nanocomposites, the functionalization facilitates the solubility of CNT in solvents. In the first step of work, carboxyl-functionalized CNT powders were fabricated by acidic oxidation in CNT prior to using in the preparation of CNT/ TiO_2 nanocomposites. FTIR spectra of pristine CNT and acid-treated CNT are shown in Figure 1 (lines (a) and (b)). A broad peak at $3,400\text{--}3,600\text{ cm}^{-1}$ can be assigned to the stretching vibration of OH group of the adsorbed water. This peak could be found in all samples tested. The oxidized (acid-treated) CNT showed peaks of carbonyl and carboxyl groups at $1,650\text{ cm}^{-1}$ and $1,710\text{ cm}^{-1}$, respectively. Furthermore, the carbonyl group was confirmed by a strong peak in the C-O stretching at $1,180\text{ cm}^{-1}$ (broad band at $1,100\text{--}1,300\text{ cm}^{-1}$) [16, 24]. These indicated the presence of chemically functional groups on CNT.

To confirm the characteristics of acid-treated CNT in CNT/ TiO_2 nanocomposites, the nanocomposites were preliminary fabricated (CNT/ TiO_2 ratio at 1:20, calcination temperature at 400°C). FTIR spectrum of CNT/ TiO_2 nanocomposites also assigned the peaks of carbonyl group at $1,650\text{ cm}^{-1}$ and found the titania (Ti-O or Ti-O-Ti) bonding at 550 cm^{-1} , as shown in Figure 1 (line (c)). This confirmed the functionalization of CNT and the functional groups remained in oxidized CNT in the obtained composites. The

FIGURE 2: XRD patterns of acid-treated CNT, TiO_2 nanoparticles, and CNT/TiO_2 -0.05:1 nanocomposites at various calcination temperatures.

functional groups in CNT play a role in creating chemical compatibility of CNT with TiO_2 surfaces [10, 14–17].

3.2. Preparation of CNT/TiO_2 Nanocomposites

3.2.1. Effect of Calcination Temperature. Acid-treated CNT was used to prepare CNT/TiO_2 nanocomposites by sol-gel method at ambient temperature. The molar ratio of CNT: TiO_2 was fixed at 0.05:1 (by weight). The composites were calcined in air at different temperatures (i.e., 300, 350, 400, and 500°C) to study the suitable calcination temperature for high-crystalline anatase titania and remained content of CNT.

XRD patterns of acid-treated CNT (heat-treated at 400°C), TiO_2 nanoparticles (calcined at 400°C), and CNT/TiO_2 nanocomposites (calcined at various calcination temperatures) are shown in Figure 2. It was observed that the strong peaks of CNT powders at angles (2θ) of 25.8° and 42.7° can be assigned to C(002) and C(100) diffractions [25]. For calcined TiO_2 nanoparticles and CNT/TiO_2 nanocomposites, the peaks appearing at 25.80°, 37.80°, 48.18°, 54.09°, 55.10°, and 62.70° can be assigned to crystalline planes of (101), (004), (200), (105), (211), and (204) which clearly confirmed the anatase TiO_2 phase [24]. These peaks correspond to the Joint Committee on Powder Diffraction Standards (JCPDS) Card File number 21-1272 [26, 27]. The peak of CNT/TiO_2 nanocomposites at 25.80°, which corresponds to the C(002) reflection of CNT, overlaps the anatase (101) TiO_2 reflection. Therefore, the anatase phase was the major crystal in CNT/TiO_2 nanocomposites.

For comparison of various calcination temperatures, it could be observed that the intensity and the sharpness peak were increased when the samples were calcined at higher temperatures. This indicates higher crystallinity of TiO_2 calcined at higher temperatures. Moreover, because the calcination was carried out in air, CNT can be easier oxidized at higher temperature [28–30]. The TGA thermogram of

TABLE 2: Effect of various calcination temperatures on nanostructure and band gap energy of CNT/TiO_2 nanocomposites at the ratio of 0.05:1.

Sample	Crystallite size (nm)	$\lambda_{\text{cut-off}}$ (nm)	Band gap energy (eV)
TiO_2	30.2	440	2.8
CNT/TiO_2 -300°C	22.2	760	1.6
CNT/TiO_2 -350°C	25.6	760	1.6
CNT/TiO_2 -400°C	27.7	755	1.6
CNT/TiO_2 -500°C	33.3	750	1.7

CNT (the result is not shown here), which was investigated under oxygen condition, revealed the significant weight loss around 500–600°C. This evidence also supports the increasing intensity and the sharpness of peaks at higher calcination temperature. Therefore, the calcinations at 500°C show the highest intensity.

The crystallite size of TiO_2 anatase in CNT/TiO_2 nanocomposites was estimated from Scherrer's equation which is shown in Table 2. It was observed that the crystallite size of TiO_2 nanoparticles calcined at 400°C was 30.2 nm which is larger than that of CNT/TiO_2 nanocomposites calcined at 400°C (27.7 nm). For CNT/TiO_2 nanocomposites, the crystallite size was found to increase with increasing calcination temperature (i.e., 22.2 nm at 300°C and 33.3 nm at 500°C).

UV-vis spectra of CNT, TiO_2 nanoparticles, and CNT/TiO_2 nanocomposites calcined at various temperatures were showed in Figure 3. TiO_2 shows light absorption under UV region (200–400 nm), while CNT can absorb light in both UV and visible regions (200–700 nm). For CNT/TiO_2 nanocomposites calcined at temperatures 300–400°C, the UV-vis absorption spectra are similar to CNT. The absorption intensities in the visible region of CNT/TiO_2 nanocomposites calcined at temperatures 300–400°C are lower than that of CNT. The higher calcination temperatures, the lower visible region intensity, could be observed. The absorption in visible region dramatically decreased when the composites were calcined at 500°C. This revealed the degradation of CNT, which corresponds to the result from XRD as explained above.

Band gap energy of CNT, TiO_2 nanoparticles, and CNT/TiO_2 nanocomposites calcined at various temperatures was estimated from the UV absorption edges from UV-vis spectra using cut-off adsorption edges [31, 32]. The results of calculation are shown in Table 2. It is well known that the band gap of TiO_2 is around 3.2 eV [25, 27, 28]; the band gap energy of TiO_2 shown in Table 2 is 2.8 eV. The lower band gap of TiO_2 is because some organic compounds did not completely burn out at the calcination temperature of 400°C. It was observed that the absorption wavelength of CNT/TiO_2 nanocomposites showed lower band gaps compared with pristine TiO_2 because of the presence of CNT. The composites which were calcined at different temperatures in the range of 300°C–400°C demonstrated similar UV absorption edge at 755–760 nm, equivalent to band gap energy of about 1.6 eV. The calcination temperature at 500°C showed

FIGURE 3: UV-vis spectra of acid-treated CNT, TiO_2 nanoparticles, and CNT/TiO_2 -0.05:1 nanocomposites at various calcination temperatures.

the absorption band edge at 750 nm (band gap = 1.7 eV). This is because of some degradation of CNT. This band gap of the composites obtained is narrower than the reported CNT/TiO_2 nanocomposites prepared by different sol-gel method (2.31 eV) [27] and hydrothermal (2.84 eV) [11]. The narrow band gap benefits to the composites that can absorb light in visible region make the photocatalyst able to be used in the visible irradiation.

3.2.2. Effect of CNT/TiO_2 Molar Ratio. CNT/TiO_2 nanocomposites with various molar ratios of CNT to TiO_2 were fabricated. The composites calcined at 400°C . CNT/TiO_2 molar ratio was varied at 0.10:1, 0.05:1, and 0.03:1. It should be noted that, in the preparation of the composite (61.5 mL), the weight of TiO_2 precursor (TiBu) was fixed at 6.5 g for all samples, while the amount of CNT added was varied corresponding to the molar ratios.

Figure 4 shows XRD patterns of the nanocomposites at various molar ratios compared with acid-treated CNT and TiO_2 nanoparticles calcined at 400°C . It was observed that, at the fixed amount of TiO_2 , increasing composition of CNT resulted in decreases of peak intensity and sharpness. This could be attributed to the obstruction in crystallization of TiO_2 if higher amount of CNT is added to TiO_2 precursor during sol-gel process.

The crystallite sizes of the composites at various CNT/TiO_2 molar ratios were estimated as shown in Table 3. It was obviously seen that, at the fixed amount of TiO_2 , increasing composition of CNT resulted in decrease of crystallite size of TiO_2 . This indicates the heterogeneous nucleation in CNT for the formation of anatase TiO_2 particles.

UV-vis spectra of samples are shown in Figure 5. All CNT/TiO_2 nanocomposites at various $\text{CNT}:\text{TiO}_2$ molar ratios could enhance the UV light sensitivity of anatase TiO_2 and increase the absorption capacity for visible light irradiation. At higher composition of CNT, relatively higher intensity of UV-vis spectra could be observed. For comparison, band gap energy of CNT/TiO_2 nanocomposites at various

TABLE 3: Effect of molar ratio on nanostructure and band gap energy of CNT/TiO_2 nanocomposites calcined at 400°C .

Sample	Crystalline size (nm)	$\lambda_{\text{cut-off}}$ (nm)	Band gap energy (eV)
TiO_2	30.2	440	2.8
CNT/TiO_2 -0.03:1	27.7	750	1.7
CNT/TiO_2 -0.05:1	25.6	755	1.6
CNT/TiO_2 -0.10:1	22.2	755	1.6

FIGURE 4: XRD patterns of acid-treated CNT, TiO_2 , and CNT/TiO_2 nanocomposites at various molar ratios of CNT to TiO_2 calcined at 400°C .

FIGURE 5: UV-vis spectra of CNT, TiO_2 nanoparticles, and CNT/TiO_2 nanocomposites at different molar ratios of CNT to TiO_2 calcined at 400°C .

CNT/TiO_2 molar ratios was calculated as shown in Table 3. It can be seen that higher composition of CNT resulted in lower band gap energy.

3.3. Morphology and Surface Properties of CNT/TiO_2 Nanocomposites. To investigate the morphology and surface properties of CNT/TiO_2 nanocomposites, the nanocomposites

FIGURE 6: FE-SEM images of (a) acid-treated CNT, (b) TiO_2 , and (c) CNT/TiO_2 -0.05:1 nanocomposites calcined at 400°C .

TABLE 4: BET surface area of TiO_2 , acid-treated CNT, and CNT/TiO_2 nanocomposites calcined at 400°C .

Sample	S_{BET} (m^2/g)
TiO_2	79
Acid-treated CNT	218
CNT/TiO_2 -0.05:1	202

at CNT/TiO_2 ratio of 0.05:1 were fabricated and calcined (400°C). Specific surface areas of CNT, TiO_2 nanoparticles, and CNT/TiO_2 nanocomposites were characterized by BET method, where the result is shown in Table 4. The surface areas of TiO_2 and CNT were 79 and $218 \text{ m}^2/\text{g}$, respectively. With adding small amount of CNT in TiO_2 as nanocomposites, the surface area of TiO_2 was increased to $202 \text{ m}^2/\text{g}$. This observation indicated that the composites have relatively high surface for chemical reactions.

Figure 6 depicts FE-SEM images showing the morphology and microstructure of CNT, TiO_2 , and CNT/TiO_2 nanocomposites. It could be observed that, in CNT/TiO_2 nanocomposites, even the weight ratio of CNT to TiO_2 is very low, but the characteristic morphology of CNT in nanocomposites was obviously observed (Figure 6(c)). The dispersion of TiO_2 nanoparticles on the surface of CNT could be confirmed in the image. However, some part of TiO_2 aggregates could be observed in the images, due to high composition of TiO_2 in the composites.

3.4. Photodecolorization of MB. The effects of calcination temperature and CNT/TiO_2 molar ratio of CNT/TiO_2 nanocomposites were confirmed by the photocatalytic activity for MB degradation under visible light irradiation.

3.4.1. Effect of Calcination Temperature. The photocatalytic activity of CNT/TiO_2 nanocomposites calcined at various temperatures is presented in Figure 7. In this experiment, the molar ratio of CNT/TiO_2 was fixed at 0.05:1. To eliminate the decolorization of MB by adsorption and study only the decolorization by photocatalysis, the adsorption of MB under a dark condition was carried out. The decrease of MB concentration under the dark condition was determined for 3 h. After completed adsorption, the sample was placed inside the reactor again with a new MB solution; then the photocatalytic activity of photocatalysts under visible light irradiation was performed.

The dye adsorption behavior of CNT/TiO_2 nanocomposites is shown in Figure 7(a). For comparison, the acid-treated CNT and TiO_2 nanoparticles with the equal amount of each component in the composites were also tested (e.g., CNT/TiO_2 composites = 0.05 g, CNT = 0.0024 g, and TiO_2 = 0.0476 g). Even CNT was used as less amount compared with TiO_2 ; the MB adsorption of CNT was higher than TiO_2 , because of remarkably higher surface of CNT. The MB adsorption of CNT/TiO_2 nanocomposites was higher than those of acid-treated CNT and TiO_2 , because of higher weight amount of composites compared with the pristine ones.

FIGURE 7: Photocatalytic degradations of acid-treated CNT, TiO_2 , and CNT/ TiO_2 nanocomposites (ratio at 0.05 : 1) at various calcination temperatures. The experiments were carried out under (a) dark condition and (b) visible irradiation (remark: CNT in (b) was acid-treated CNT after 12-h dye adsorption under dark condition to reach the adsorption equilibrium of dye on CNT).

From various calcination temperatures, it was found that composites calcined at lower temperatures showed higher MB adsorption. This result is in correspondence with TGA thermogram of CNT that shows decomposition at high temperature as described above.

In order to consider the decolorization of MB under visible irradiation by photocatalytic properties of CNT without any effect of adsorption, adsorption equilibrium of MB on CNT was studied. CNT has significantly high surface, so it takes longer time to reach the adsorption equilibrium of MB on CNT compared with TiO_2 [16]. It was found that the adsorption equilibrium of MB on CNT was 12 h (4 cycles of 3 h adsorption). Therefore, the photocatalytic performance of CNT was investigated under visible irradiation after the 12-h dye adsorption.

After 3 h adsorption of MB in dark condition (except for CNT, adsorption = 12 h), the photocatalytic degradation of MB under visible irradiation was studied (Figure 7(b)). Decolorization of MB with CNT showed different behavior from that in the adsorption step, because dye molecules were mostly adsorbed in dark condition after 12 h adsorption. TiO_2 nanoparticles showed photocatalytic behavior under visible light irradiation with higher decolorization of MB compared with that in the dark condition. The MB degradation on CNT/ TiO_2 nanocomposites (from all calcination temperatures) was higher than that on pristine TiO_2 particles. This is because of the advantage of CNT for visible light adsorption. In addition, the important role of CNT was as a transporting channel of electron to TiO_2 nanoparticles [26, 27, 29, 30].

For comparison of various calcinations, it can be observed that the photocatalytic activity increased with increasing calcination temperatures from 300°C to 400°C because of more crystallinity of TiO_2 (see Figure 2) with the presence of CNT (confirmed by TGA). At too high calcination temperature, that is, 500°C, the photocatalytic activity was the lowest compared with other CNT/ TiO_2 due to the degradation

of CNT during the calcination. From this result, the optimal calcinations temperature which provided the highest photocatalytic activity was 400°C. At this temperature, the composites have a good composition and interfacial contacts between CNT and anatase TiO_2 .

3.4.2. Effect of CNT/ TiO_2 Molar Ratio. Figure 8 shows photocatalytic degradations of CNT, TiO_2 , and CNT/ TiO_2 nanocomposites (calcined at 400°C) at various molar ratios of CNT : TiO_2 compared with a blank (MB without any photocatalyst). Figure 8(a) showed the dye adsorption in the dark condition. At CNT : TiO_2 ratio of 0.10 : 1, the highest adsorption performance was observed due to its high CNT content.

After reaching the adsorption equilibrium in dark conditions, the photocatalytic activity of MB degradation under visible light irradiation was examined in Figure 8(b). It was observed that CNT/ TiO_2 nanocomposites at CNT : TiO_2 ratio of 0.05 : 1 showed the highest photocatalytic activity efficiency (70% at 90 min) compared with other ratios as summarized in Table 5. The photocatalytic activity of the nanocomposites at CNT : TiO_2 ratio of 0.05 : 1 was also higher than pristine TiO_2 nanoparticles and CNT.

The composites with CNT/ TiO_2 ratio of 0.05 : 1 showed faster photodegradation than that of 0.03 : 1 because of higher composition of CNT for light adsorption. Addition of CNT to form the composites with higher ratio of CNT/ TiO_2 (0.10 : 1) did not further increase the MB degradation rate because too high content of CNT causes much light adsorption which could reduce the light intensity on the most composites in the deeper position of solution. This evidence was also reported in the literature [20].

Only a few researchers previously reported on the photocatalytic activity of organic pollutants under visible light irradiation [12, 17]. As shown in Table 1, the previously reported

FIGURE 8: Photocatalytic degradations of acid-treated CNT, TiO_2 , and CNT/ TiO_2 nanocomposites at various molar ratios of CNT to TiO_2 (calcined at 400°C) compared with a blank (MB without any photocatalyst). The experiments were carried out under (a) dark condition and (b) visible irradiation (remark: CNT in (b) was acid-treated CNT after 12-h dye adsorption under dark condition to reach the adsorption equilibrium of dye on CNT).

TABLE 5: Decolorization (adsorption) and photocatalytic degradation of MB under visible radiations of acid-treated CNT, TiO_2 , and CNT/ TiO_2 nanocomposites at various molar ratios of CNT to TiO_2 (calcined at 400°C).

Catalyst	Decolorization efficiency by adsorption (dark condition)	Photocatalytic degradation efficiency (visible irradiation)
CNT	19%	8%
TiO_2	10%	22%
CNT/ TiO_2 -0.03:1	57%	47%
CNT/ TiO_2 -0.05:1	63%	70%
CNT/ TiO_2 -0.10:1	65%	57%

efficiency of photocatalytic degradation under visible irradiation was not relatively high (60% within 120 min). In this work, CNT/ TiO_2 nanocomposites showed much better photocatalytic degradation efficiency (70% within 90 min) due to small band gap and high surface area of CNT, which could support photocatalytic reactivity of TiO_2 .

3.5. Mechanism of Photodecolorization of MB with CNT/ TiO_2 Nanocomposites. The reaction of the photodecolorization of MB under visible irradiation can be described as the schematic illustration in Figure 9. The mechanism in this illustration is quite different from previous reports [23, 30–32]. CNT/ TiO_2 nanocomposites were attacked by photon from visible light which are subjected to band gap excitation ($>380\text{ nm}$, visible region); they undergo electron-hole pair production and charge separation. Photoinduced electrons (e^-) from CNT are easily transferred to the conduction band of TiO_2 [29]. Detailed mechanism is shown in

Simultaneously, the positively charged hole (h^+) from CNT reacted with the adsorbed water (H_2O) and OH^- group and produced $\text{OH}^\bullet$ radicals. At the same time, electrons from TiO_2 reacted with O_2 and produce $\text{O}_2^{\bullet-}$ radical ions that are able to degrade MB. The reaction for describing the photoreduction of CNT/ TiO_2 nanocomposites can be summarized in

It can be proposed here that the role of CNT can be illustrated by injecting electrons into TiO_2 conduction band under visible irradiation, triggering their formation of very reactive radicals such as superoxide radical ion ($\text{O}_2^{\bullet-}$) and hydroxyl radicals ($\text{OH}^\bullet$), which are then responsible for the degradation of the organic compounds [26–29].

The mechanism of MB oxidation is that the excited state from visible light of MB injects an electron into the conduction band of TiO_2 as shown in (6) and (7). Consequently, MB is converted into a cationic dye radical ion ($\text{MB}^{\bullet+}$) that further takes part in the photodegradation reaction. MB is totally degraded and mineralized after the photodegradation reaction by $\text{OH}^\bullet$ and $\text{O}_2^{\bullet-}$ radicals as shown in the last two formulas

FIGURE 9: Schematic illustration of photocatalytic mechanism of CNT/TiO₂ nanocomposites (ratio at 0.05 : 1, calcined at 400°C) under visible irradiation (→ = charge transfer, →• = chemical reaction).

4. Conclusions

Photocatalytic activity of TiO₂ nanoparticle was successfully enhanced by addition of CNT to make CNT/TiO₂ nanocomposites. Acid-treated CNT was mixed with TiO₂ nanoparticles at various molar ratios and calcined at various temperatures. The optimal molar ratio of CNT : TiO₂ was 0.05 : 1 by weight. The optimal calcination condition was 400°C for 3 h. The degradation efficiency of the MB solution with CNT/TiO₂ nanocomposite under visible light irradiation achieved 70% within 90 min which was higher than that with pristine TiO₂. CNT has lower band gap compared with pristine TiO₂, resulting in better light absorption of the composites in visible region. In addition, CNT/TiO₂ nanocomposites had high specific surface area which is very promising for utilization as a photocatalyst for environmental applications. In comparison with the previous studies reported on fabrication of CNT/TiO₂ photocatalysts by sol-gel method, this work proposes a short time and low-energy preparation process which is in line with green chemistry concept. In addition, this work is the first report for highest degradation efficiency of MB under visible light irradiation until 70% within 90 min. These two important roles of CNT together lead to enhancing photocatalytic activity.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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