

# Photocatalytic Carbon-Nanotube–TiO<sub>2</sub> Composites

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The literature and advances in photocatalysis based on the combination of titania (TiO<sub>2</sub>) and carbon nanotubes is presented. The semiconductor basis for photocatalysis is introduced for anatase and rutile. Furthermore, the proposed mechanisms of catalytic enhancement resulting from the pairing of the titania semiconductor with either metallic, semiconducting, or defect-rich carbon nanotubes (CNT) is discussed. Differences are apparent for the mixtures and chemically bonded CNT–TiO<sub>2</sub> composites. The article then highlights the recent advances in the synthesis techniques for these composites and their photocatalytic reactions with organic, inorganic, and biological agents. Finally, various applications and challenges for these composite materials are reported.

## 1. Introduction

Carbon nanotube-anatase titanium dioxide (CNT–TiO<sub>2</sub>) composite systems are currently being considered for many applications including their potential use to address environmental problems. TiO<sub>2</sub> 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. Two TiO<sub>2</sub> polymorphs are typically being used—anatase and rutile, with the anatase phase exhibiting a significantly higher photocatalytic activity than the rutile phase. Although the reasons are not yet fully understood, it is speculated that the higher charge-carrier mobility of 80 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in anatase,<sup>[1]</sup> which is 89 times faster than in rutile,<sup>[2]</sup> causes their superior photocatalytic properties. However, the mixture of the two polymorphs yields even higher photocatalytic activity at specific ratios, as exhibited by the commercially available AEROXIDE TiO<sub>2</sub> P25. The enhancement is attributed to the special electronic states of the two crystal structures, which allow for a semiconductor–semiconductor junction. The details of such mechanisms will be explained later.

The mixture of two types of semiconductor particles, semiconductor particles with metal particles, and recently carbon particles with anatase, showed photocatalytic enhancements in many cases to be described later. This concept can then be extended to defined carbon structures with tailored electronic properties. Fullerenes and CNTs are excellent candidates to allow

deeper insight into the semiconductor junction of titania with metallic or semiconducting carbons. Furthermore, CNTs have excellent mechanical properties and a large specific surface area (>150 m<sup>2</sup> g<sup>-1</sup>).<sup>[3]</sup> They also allow for surface chemical modifications to control the type of bonds that can be formed with titania, be it chemically bonded or van der Waals bonded. The mixture of titania and CNT also has a large area where pollutants (organic or inorganic reactants) can adsorb. Adsorption is a key process in the photocatalytic destruction of pollutants, as will be discussed later. Thus, CNT–TiO<sub>2</sub> mixtures and composites are able to achieve photocatalytic activities well beyond the anatase/rutile composites.

This article highlights the literature on the synthesis of CNT–titania composite structures, and addresses the enhancement mechanism of the anatase–rutile composite and the CNT–TiO<sub>2</sub> systems. The flexibility to tailor the CNT electronic properties are discussed next, followed by proposed mechanisms for photocatalysis. Furthermore, the recent publications for CNT–TiO<sub>2</sub> composites in photocatalytic degradation studies are examined with focus toward understanding the activity enhancement. Finally, a discussion of the various applications and the materials science challenges are presented.

## 2. Background

### 2.1. Anatase–Rutile Composite System

One of the commercially available forms of TiO<sub>2</sub> often used as a standard for photocatalytic studies is AEROXIDE TiO<sub>2</sub> P25. This is a mixed particle system of approximately 75–80% anatase and 25–20% rutile with a specific surface area of about 50 m<sup>2</sup> g<sup>-1</sup> and synthesized by the Aerosil (flame pyrolysis) process. Anatase has a higher photocatalytic activity than rutile for several reasons. One of them is the size of the band-gap, where anatase has a larger band-gap than rutile, 3.2 eV versus 3.0 eV, respectively. This provides anatase with a higher redox potential. Another reason is that anatase has a higher area density of surface hydroxyls, which slows the recombination of photogenerated electron–hole pairs. In 1991, Bickley initially proposed that the enhancement of the photocatalytic properties in P25 stemmed from a space-charge region formed at the rutile–anatase interface where band bending occurred due to the difference in the band-gap of the two phases. The charge carriers generated were thought to form in the anatase particles, and then the holes migrate into the rutile particles.

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Bickley also noted that the actual mechanism remains unclear, and might be more complex.<sup>[4]</sup>

In 2002, Kawahara et al.<sup>[5]</sup> devised a model system to mimic the mixed-particle system by patterning a photocatalyst film consisting of anatase and rutile regions with varying widths and depths. Silver was photodeposited on top of the thin film. Kawahara et al. concluded that photoexcitation generates electrons that are then transferred from the conduction band of the anatase phase into rutile. Furthermore, the excess silver that was found on top of rutile is seen as evidence for a surface redox process based on holes in anatase and electrons in rutile. As an explanation for why the holes and electrons do not readily combine, the conduction band edges were considered. Anatase has a 0.2 eV higher band edge than rutile. This may result in the facilitation of interfacial electron transfer and the suppression of recombination. However, this explanation of the anatase–rutile mixture is not without opposition from other groups. An alternative interpretation regarding the interfacial charge-transfer process is that photo-generated electrons transfer from the rutile phase to anatase, even though anatase itself has a larger band-gap energy.<sup>[2,6–8]</sup> Hurum et al. used a band-gap illumination process, performed electron paramagnetic resonance (EPR) measurements, and stated that the enhancement of P25 is attributed to the presence of lattice, interfacial, and surface-trapping sites as well as the charge-transfer process across the interface from rutile to anatase. A possible mechanism suggests that anatase has trapping sites that have energies of 0.8 eV less than the anatase conduction band. Thus, the rutile conduction band actually has a higher energy than the anatase trapping sites, and electrons are able to transfer. Hurum et al.<sup>[7]</sup> noted that rutile itself may have photocatalytic properties similar to anatase when recombination-preventing dyes are used. Furthermore, since rutile has a lower band-gap than anatase, it is photocatalytically active at longer wavelengths, and an enhancement may be observed depending on lighting conditions. Hurum's analysis is supported by the observation that the signal generated by the rutile trapping sites decreases while the signal generated by the anatase and surface sites increases once illumination is terminated on the colloidal suspension of P25 in methanol. This method provides the best support thus far in discerning the mechanism of photocatalytic enhancement of the anatase–rutile mixture.

## 2.2. Activated Carbon

Activated carbon was initially used as a support for TiO<sub>2</sub> in photodegradation studies.<sup>[9]</sup> It has a very large specific surface area that is typically more than one order of magnitude larger than P25. The main photocatalytic degradation process is best modeled by the Langmuir–Hinshelwood mechanism. This mechanism requires the adsorption of species before the species begin to degrade. Therefore, it can be expected that increasing the specific surface area yields an increase in adsorbed amounts of pollutants and thus enhances photocatalytic activity. Matos et al.<sup>[10]</sup> determined that there is a synergistic effect when using AEROXIDE TiO<sub>2</sub> P25 mixed with activated carbon having a surface area of 775 m<sup>2</sup> g<sup>-1</sup>. The phenol degradation enhancement was attributed to the strong adsorption of phenol and its

intermediate species on the activated carbon followed by subsequent mass transfer of the species to the photocatalytically active TiO<sub>2</sub>.

## 2.3. CNTs and TiO<sub>2</sub> Photocatalysis

Aside from introducing various surface irregularities to provide trap states for electrons, another more effective method of increasing recombination times for electron–hole pairs is to form a semiconductor–metal junction called a Schottky barrier, where there is a space-charge separation region. At the interface of the two materials, electrons flow from one material to the other (from the higher to lower Fermi level) to align the Fermi energy levels. In the case of a metal with a higher work function than the n-type semiconductor, such as TiO<sub>2</sub>, electrons will flow from the semiconductor into the metal to adjust the Fermi energy levels. This formation of a Schottky barrier results in the metal having an excess negative charge and the semiconductor an excess positive charge. In between is a depletion layer that maintains charge separation. Traditionally, this method of extending recombination times was established with platinum and other noble metal interfaces. The interested reader is referred to the review paper by Linsebigler et al.<sup>[11]</sup> for more details on the photocatalytic properties of TiO<sub>2</sub> and the electronic modification when there is an interface of TiO<sub>2</sub> and a metal.

CNTs have a variety of electronic properties. Similar to the metals above, they may also exhibit metallic conductivity as one of the many possible electronic structures. CNTs have a large electron-storage capacity (one electron for every 32 carbon atoms),<sup>[12]</sup> and therefore may accept photon-excited electrons in mixtures or nanocomposites with titania, thus retarding or hindering the recombination. Photon-generated electron–hole pairs have a recombination time on the order of 10<sup>-9</sup> s, however, the chemical interaction with adsorbed pollutant species has a time scale of 10<sup>-8</sup>–10<sup>-3</sup> s. These characteristic times were measured using laser flash photolysis and are consolidated for a variety of processes as described by Hoffmann et al.<sup>[13]</sup> The CNT–TiO<sub>2</sub> Schottky barrier junction is an effective method of increasing recombination time, as was demonstrated by a variety of publications based on dye degradation. CNTs also provide a larger specific surface area similar to activated carbon and thus enhance the photocatalytic degradation as explained above.

Beyond the surface area, CNTs may be tailored to enhance specificity toward adsorbents through the modification of their surface groups. When purified via acid treatment, CNTs formed alcohol, keto, and acid moieties on their surfaces. These groups can be further modified to improve adsorption of specific species, an advantage over activated carbons that are typically nonselective and have a lower pollutant-degradation rate due to the degradation of all species (benign and pollutant) present.<sup>[14]</sup>

Wang et al.<sup>[15]</sup> proposed that CNTs may also enhance the TiO<sub>2</sub> photocatalytic efficiency by acting as a photosensitizer. Anatase TiO<sub>2</sub> requires UV light in order to excite an electron with enough energy to overcome the band-gap. The UV spectrum represents only 5% of the total sunlight spectrum. Being able to use a larger portion of the spectrum of natural sunlight for photocatalysis is an important aspect for commercialization, for the use of

photocatalyst systems in self-sustaining environmental waste cleanup, or for water purification. Also, CNTs may exhibit photosensitizing properties, thus extending photocatalysis into the visible spectrum.<sup>[15,16]</sup>

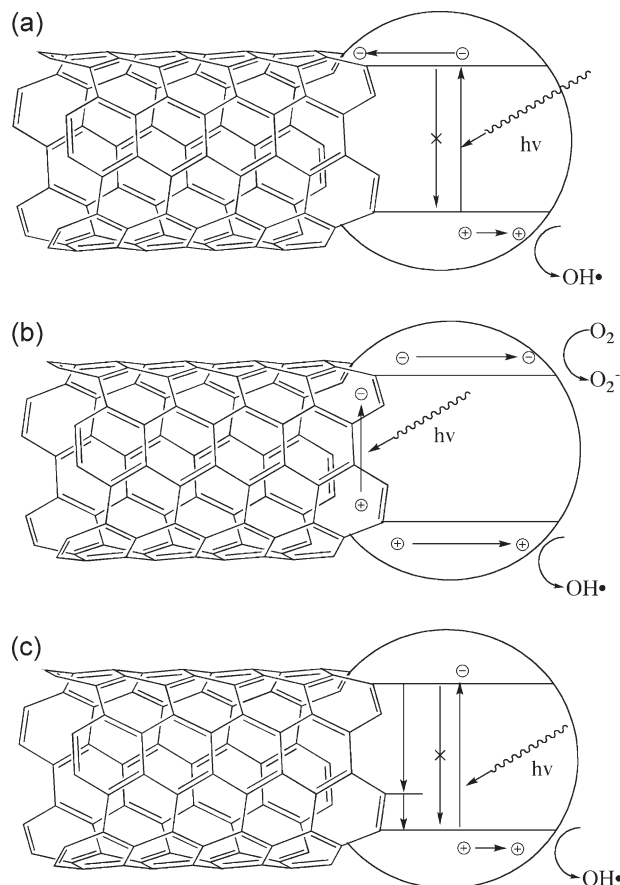
Two problems that need to be addressed with nanosize photocatalysts is the difficulty in distributing single particles and collecting them after use. Support structures are needed. Two approaches are possible: i) embedding them into a matrix or ii) attaching them to magnetic particles. The first approach can be achieved by electrospinning nanofibers containing titania and CNTs. This yields nanofiber mats that immobilize the materials.<sup>[17]</sup> In the second approach, CNT-TiO<sub>2</sub> composites could be made magnetic by using iron-filled CNTs. Magnetic particles can also be dispersed with a magnetic fluidized bed.<sup>[18]</sup>

#### 2.4. Mechanisms of Photocatalysis Enhancement in CNT-TiO<sub>2</sub> Composites

Two mechanisms are being discussed to explain the enhancement of the photocatalytic properties of CNT-TiO<sub>2</sub> composites. The first is a modified mechanism proposed by Hoffmann et al.<sup>[13]</sup> Here, a high-energy photon excites an electron from the valence band to the conduction band of anatase TiO<sub>2</sub>. Photo-generated electrons formed in the space-charge regions are transferred into the CNTs, and holes remain on the TiO<sub>2</sub> to take part in redox reactions. A schematic of this mechanism is shown in Figure 1a.

The second mechanism was proposed by Wang et al.,<sup>[15]</sup> whereby the CNTs act as sensitizers and transfer electrons to the TiO<sub>2</sub>. The photogenerated electron is injected into the conduction band of the TiO<sub>2</sub>, allowing for the formation of superoxide radicals by adsorbed molecular oxygen. Once this occurs, the positively charged nanotubes remove an electron from the valence band of the TiO<sub>2</sub> leaving a hole. The now positively charged TiO<sub>2</sub> can then react with adsorbed water to form hydroxyl radicals. The proposed mechanism is provided in Figure 1b.

However, the CNT-TiO<sub>2</sub> nanocomposite system proves to be more complex. Pyrgiotakis et al.<sup>[19]</sup> reported two distinct contributions from the CNT-TiO<sub>2</sub> composite. One is the carbon-oxygen-titanium bond that extends the light absorption to longer wavelengths, that is, similar to carbon-doped titania, thus potentially leading to the improvement of the photocatalytic activity. The second is the electronic configuration of the CNTs. Arc-discharge grown and CVD-grown CNTs were coated with TiO<sub>2</sub> via sol-gel processes. Although both nanocomposites were structurally similar, the photocatalytic dye degradation rate for the arc-discharge CNTs was ten-fold higher than for the CVD-grown CNT nanocomposite. X-Ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR) were used to confirm the presence of Ti-O-C bonds in both types of nanocomposites, see Figure 1c. The difference in activity is therefore attributed to the electronic nature of the CNTs. Raman spectroscopy indicated that arc-discharge-synthesized CNTs must have a higher electrical conductivity and fewer defects. This is also supported by transmission electron microscopy (TEM) images of the nanocomposites. Arc-discharge-synthesized CNTs were found to retain their straight walls without major defects in



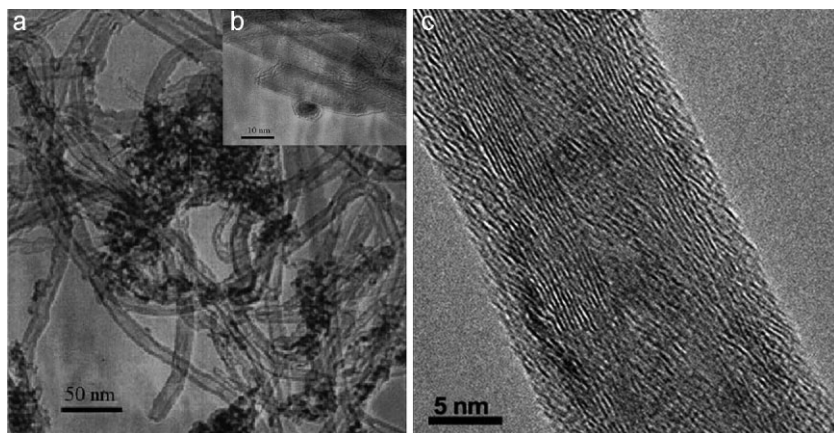
**Figure 1.** The proposed mechanisms for the CNT-mediated enhancement of photocatalysis. a) CNTs act as an electron sinks, and scavenge away the electrons hindering recombination. b) Mechanism proposed by Wang et al. [15], where the photon generates an electron-hole pair in the CNT. Based on the relevant positions of the bands, an electron (or the hole) is injected in the titania generating a O<sub>2</sub>•<sup>-</sup> or a OH• species. c) The nanotubes can act as impurity through the Ti-O-C bonds.

the inner multiwall tubes. With regard to photocatalysis, the electronic-band structure of the CNT is a more important factor than the chemical bond between the CNT and TiO<sub>2</sub>. It is important to note that during photocatalytic degradation studies some degree of CNT oxidation is expected to occur, though this has not been well characterized in the literature. The oxidized portions of the CNTs may initially exhibit opportunities for defect states allowing for enhanced photogeneration of electron-hole pairs; however, the long-term effects, that is, complete degradation of the CNTs, is expected to diminish the photocatalytic ability of the composite system.

### 3. Literature Highlights

#### 3.1. Synthesis of CNT-TiO<sub>2</sub> Composites

CNTs can be turned into nanocomposites with titania in several ways. The chemical pathway and the nanocomposite configuration



**Figure 2.** Two different configurations of the CNT–TiO<sub>2</sub> composite. a) Particle nucleation on the surface of the CNTs. b) High-magnification image of the particles (scale bar: 10 nm). c) Complete coating as layer on the surface of the CNTs by the authors' group. Figure 2a and b adapted and reprinted with permission from Ref. [21]. Copyright 2005 Elsevier.

can be varied. Although the most common method is the sol–gel route,<sup>[15,20–33]</sup> there are reports where the coating has been accomplished by the hydrothermal method.<sup>[20,26,27,32,34,35]</sup> One of the most published configurations has titania nanoparticles bounded to the surface of the CNTs. This is typically achieved by nucleating and growing titania on dispersed CNTs in a liquid medium. Alternative configurations include a complete coating of the CNTs with TiO<sub>2</sub> and the embedding of CNTs in a TiO<sub>2</sub> matrix (see Fig. 2). The following paragraphs will give a more detailed description of the synthesis routes of the nanocomposites that are published to date.

The sol–gel coating of CNTs is performed in a liquid medium. Therefore, the biggest challenge is the dispersion of the CNTs in mediums like alcohol (ethanol or isopropanol)<sup>[15,21,23,28]</sup> containing the TiO<sub>2</sub> precursor. The most common precursors are various metal alkoxides, (R–O)<sub>4</sub>Ti. The common characteristic of the titanium alkoxide precursors is their reactivity with water to yield TiO<sub>2</sub>, which in general is amorphous at room temperature with small seeds of the anatase phase. The most common precursor is titanium isopropoxide,<sup>[15,21,30]</sup> since it combines several desirable characteristics. It readily dissolves in alcohols and is not overly sensitive to humidity. An alternative is titanium butoxide,<sup>[23,26,28,31,32]</sup> which is even less sensitive to humidity; however, its higher viscosity may cause problems when dissolving it in ethanol at high concentrations. There are also reports where titanium ethoxide was used.<sup>[20]</sup> The reactivity of the alkoxide with water is important, since it decides between homogenous nucleation in solution or heterogeneous nucleation on the CNT. Furthermore, the growth of the nanoparticles is influenced. Fast condensation rates usually result in large particle-size distributions of the primary particles. The addition of acids or bases is one possibility to change the reaction rate.<sup>[15,21,23,26,28]</sup>

Alternatives to the titanium alkoxides in sol–gel are titanium tetrachloride<sup>[27,31]</sup> and titanium oxy sulfate (TiOSO<sub>4</sub>)<sup>[32]</sup> which have been used in the past for the synthesis of TiO<sub>2</sub> particles. These precursors can be used in water, but this requires the CNTs to be dispersed in water as well, which can be challenging since unmodified CNT are hydrophobic (they typically form large

agglomerates that will settle to the bottom of the container, where they get coated instead of the individual tubes). Sun and Gao<sup>[36]</sup> developed a method to renders CNTs dispersible in water via heating in an ammonia atmosphere at 600 °C. However, most publications use surface charges stemming from acid groups that were introduced by treatments in hot oxidizing mineral acids.<sup>[23,26,28,30,31]</sup>

Recently, CNTs have also been coated via hydrothermal methods.<sup>[20,26,27,32,34,35]</sup> Hydrothermal processes use mostly titanium tetrachloride<sup>[27,31]</sup> and TiOSO<sub>4</sub>.<sup>[32]</sup> Regardless of the chosen conditions and chemistry, the final material is mostly amorphous TiO<sub>2</sub> with seeds of anatase. To fully crystallize the coating, a heat treatment is required that usually occurs at 300–500 °C in air to avoid the burnout of the CNTs and avoid the phase transformation from anatase to rutile.<sup>[3,28,31]</sup>

It is worth mentioning that the coating of single-wall nanotubes was reported only recently.<sup>[37,38]</sup> Single-wall CNT coatings are of importance since the electronic properties of tubes are better defined than in multiwalled CNTs. This will allow for better experiments to verify the proposed mechanisms. A relatively new method of preparing such composites is the filter-mat or fiber-form via the electrospinning method.<sup>[25,30,39]</sup> Such methods produce mm to m long fibers with 40–100 nm in diameter. Typically, a fiber mat is formed, which is currently explored for a variety of catalytic applications. Such methodologies again involve chemistries very similar to the sol–gel route. One of the major differences is the addition of a polymer to form the backbone of the structure. Lee and Sigmund<sup>[17]</sup> have measured the mechanical properties of such fibers. The modulus of elasticity was found to be above 250 GPa for the CNT reinforced anatase nanofibers, which is significantly higher compared to less than 100 GPa, which was found for the electrospun pure-anatase nanofibers.

### 3.2. Photocatalytic Activity

CNT–TiO<sub>2</sub> nanocomposites are novel, and there are only few publications on their photocatalytic activity to date. Additionally, the comparison of photocatalytic activities from lab to lab is very challenging, due to a variety of methodologies for testing. The most common method of assessing the activity of a nanocomposite photocatalyst is by measuring the time dependence of the concentration loss of an organic compound under UV irradiation. This can be done with a dye<sup>[32,34,35,40–42]</sup> or, alternatively, with potential pollutants, such as phenol.<sup>[15,21,35]</sup> Recently, there have also been reports of degrading toxic gases such NO<sub>x</sub>.<sup>[32]</sup> The degradation usually follows the Langmuir–Hinshelwood reaction kinetics, which predicts an exponential decay of concentration as a function of time. However, there are many experimental parameters that control the reaction rate and kinetics. These experimental parameters include the concentration of the targeted organic compound, the surface area and amount of

**Table 1.** Photocatalytic properties of CNT/TiO<sub>2</sub> in comparison to pure TiO<sub>2</sub>.

Reference	Mass fraction CNT	Reference material; reaction rate [min <sup>-1</sup> ]	TiO <sub>2</sub> solids loading [10 <sup>-2</sup> mg mL <sup>-1</sup> ]	UV intensity at (wavelength) [mW cm <sup>-2</sup> ] at [nm]	Degraded material; concentration [mg L <sup>-1</sup> ]	Enhancement factor over TiO <sub>2</sub>
Yu et al. [43]	0.97	TiO <sub>2</sub> ; 2.693 × 10 <sup>-3</sup>	1.43	Not mentioned	Acetone; 400	1.5
	0.95					1.6
	0.91					0.85
	0.85					0.62
	0.75					0.51
Yu [42]	0.75 [a]	P25; 0.0351	50.0	0.37 (365)	Procion Yellow HE4R; 100	1.64
	0.75[a] (AC)[b]					1.98
Wang et al. [15]	0.954	TiO <sub>2</sub> ; 1.8 × 10 <sup>-3</sup>	1.43	Not mentioned (366, 456, 546)	Phenol; 50	1.10
	0.922					1.80
	0.836					4.10
	0.729					3.00
	0.800					1.80
Pyrgiotakis et al. [19]	0.50[a]	TiO <sub>2</sub> ; 0.019	6.00	2.0 (305)	Procion Red MX-5B; 5	1.93
	0.33[a]					0.98
	0.25[a]					0.63
	0.85	TiO <sub>2</sub> ; 0.005	1.70	2.0 (350)	Procion Red MX-5B; 5	10.47
	0.9997	TiO <sub>2</sub> ; 7.3 × 10 <sup>-3</sup>	2.00	8.6 (350)	Procion Red MX-5B 5	0.91
	0.9990					2.50
	0.9980					1.67
0.9950					0.99	

[a] CNT/particle mixture. [b] AC: activated carbon.

the photocatalytic particles, the UV intensity, the UV frequencies, diffusion or convection control, and secondary parameters such as temperature, the chemical structure of the organic compound, and more. Therefore, the most relevant way of representing photocatalytic activity is as relative numbers in comparison to a standard, which could be P25. Table 1 summarizes some of the recently synthesized composites and their photocatalytic data. In most cases, enhancement of the catalysis was observed with increasing percentage of CNT with maximum activity at around 85 mass% CNT before a decline at higher percentages of the CNT.

### 3.3. Applications

Many exciting new technologies can be realized through the use of CNT–TiO<sub>2</sub> composites, extending the already extensive range of applications of photocatalytic TiO<sub>2</sub>. The most recognized application that the photocatalyst system may be incorporated into is for treatment of various biological, organic, or inorganic hazardous pollutants in both water and air streams. Furthermore, the composite may be utilized in the passive decontamination of surfaces.

With regard to biological pollutants, bacterial endospores contain three distinct layers of thick protein coatings surrounding the nucleus, which prevent decontamination by harsh chemicals, thermal treatments, and/or irradiation. Lee et al.<sup>[3]</sup> was able to destroy more than 99.9% of gram-negative bacterial endospores within 2 h using the CNT–TiO<sub>2</sub> composite system coupled with

UV irradiation. This is the first report that photocatalysts can effectively destroy spores. Furthermore, the results showed significant improvements over AEROXIDE TiO<sub>2</sub> P25. In a similar manner, Krishna et al.<sup>[44]</sup> used the same particles to inactivate *Escherichia coli* bacteria. The most important characteristic of those results is that although *E. coli* has a simpler structure easily destroyed by UV alone, it was shown that the photocatalytic destruction with the anatase-coated CNTs was lower than AEROXIDE TiO<sub>2</sub> P25, and even lower than the use of UV irradiation alone. The authors have attributed this phenomenon to the adsorption issues associated with dense surface fimbriae of the bacteria cell membrane preventing the adsorption of the CNT–TiO<sub>2</sub>.

In fluid streams, the incorporation of the CNT–TiO<sub>2</sub> photocatalysts may be an attractive addition or alternative to the various disinfection techniques currently used. Chlorination, ozonation, and UV irradiation are some of the commonly used forms of disinfection in the treatment of water. These systems all generate strongly oxidizing agents that eliminate microorganisms rapidly. However, the systems require high energy usage and constant monitoring. CNT–TiO<sub>2</sub> systems may provide a robust system requiring little or no maintenance. The development of electrospun CNT–TiO<sub>2</sub> fibers addresses the previous complex issue of reclaiming small TiO<sub>2</sub> particles. With electrospun fibers, the TiO<sub>2</sub> particles are bonded to long strands of CNTs that can be easily isolated. In many wastewater facilities, ozone systems already exist and use UV to generate disinfecting reactive ozone from the dissolved oxygen. The incorporation of fibers of CNT–TiO<sub>2</sub> may utilize already existing UV lamps in

order to effectively remove unwanted chemical or biological hazards.<sup>[45]</sup> See Hoffman et al.<sup>[13]</sup> for an extensive list of organic and inorganic substances that can be addressed using photocatalysts.

As mentioned earlier, electrospun nanofibers of CNT–TiO<sub>2</sub> photocatalysts may also be produced into mats that can be used in air purification systems. Current high-efficiency particulate air (HEPA) glass-fiber filters are effective at removing small contaminants in the air stream; however, the use of photocatalytically active fiber systems could potentially extend the life of filters and prevent secondary reaerosolization of organic contaminants or biological organisms during maintenance of the filters. A UV illumination system could be implemented to decompose organic or biological hazards, thus regenerating the filters and decreasing the need for replacements.

Another exciting implementation is the passive decontamination, or self-cleaning, of surfaces. TiO<sub>2</sub>-nanoparticle photocatalysts have already been incorporated onto surfaces.<sup>[46]</sup> However, this coating requires the use of UV lamps to incite photocatalytic degradation of surface dirt or microbes, and thus would not be a feasible system for general use. Since the use of CNTs may enhance the photocatalytic properties of TiO<sub>2</sub> into the visible spectrum, current illumination systems may potentially be used to decontaminate harmful microbes or inorganic stains passively and continuously.

#### 4. Challenges and Conclusions

In summary, the photocatalytic properties of TiO<sub>2</sub> at room temperature may be enhanced by: i) slowing the recombination of photogenerated electron–hole pairs due to a semiconductor–semiconductor junction, ii) extending the excitation wavelength, and iii) increasing the surface-adsorbed amount of reactant species. The first two mechanisms of enhancement were demonstrated by the example of AEROXIDE TiO<sub>2</sub> P25. The particle mixture transfers electrons or holes from one phase to the other. Rutile extends the excitation wavelength, and anatase surface sites trap electrons to slow recombination. The third route to enhance photocatalysis is demonstrated by the activated carbon–TiO<sub>2</sub> system. All three mechanisms of enhancement are exploited in novel CNT–TiO<sub>2</sub> mixtures and nanocomposites.

The primary materials science challenge is to fully understand the underlying mechanisms of the photocatalytic enhancement by the CNT–TiO<sub>2</sub> composite system. The mechanisms can be evaluated through the development of single-walled CNTs, whose well-defined electronic structures may provide research opportunities to explore the proposed mechanisms. Coupled with the EPR technique to elucidate the finer mechanisms in the anatase/rutile composite, the effects of the electronic structure, such as variation in band-gap of the CNTs on the CNT–TiO<sub>2</sub> composite, may be determined. Whether the CNTs act predominantly to retard the recombination of photogenerated electron–hole pairs or as sensitizers from which photogenerated charged species are produced at longer wavelengths determines what structural developments are needed to optimize the composite. In the former, a structure which exposes the TiO<sub>2</sub> to the most light would optimize the photocatalytic enhancement, as achieved through nucleation of the TiO<sub>2</sub> on CNTs; in the latter, a structure

emphasizing the interaction of incident photons with the CNTs would be favored, such as in the case of coating TiO<sub>2</sub> with CNTs. In both cases, the use of pristine CNTs is extremely important when synthesizing the composite structures.

CNTs are increasingly being examined for upscale and industrial synthesis by a variety of companies, such as the Bayer Corporation. However, the processing has not yet matured, and quality-control issues need to be addressed. High-yield synthesis techniques, such as combustion chemical-vapor deposition or chemical-vapor deposition using metal catalysts still exhibit issues such as nonuniform or uneven product properties, leading to less than optimal enhancement of photocatalytic activity. Furthermore, residual catalyst materials tend to remain in the products, and post-production treatments may be necessary to further purify the nanotubes. Other synthesis techniques that result in higher purities, such as arc-discharge and laser ablation, have low yield and are therefore unfeasible for industrial implementation.<sup>[47]</sup>

Research and discovery opportunities exist for the CNT–TiO<sub>2</sub> composite systems. Being able to tailor and synthesize high quantities of uniform composite and further research into catalytic activity and its standardization is necessary. Especially, a more thorough understanding, perhaps by the use of EPR measurements, of the actual mechanisms of how CNTs enhance the photocatalytic properties of TiO<sub>2</sub>-based systems needs to be undertaken. Nevertheless, CNT–TiO<sub>2</sub> composites are expected to be developed as a robust means to address various environmental and self-cleaning issues.

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