The Effects of Single-Walled Carbon Nanotubes on the Catalytic Properties of Titanium Dioxide

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Abstract

Concern about maximizing and improving heterogeneous catalysis has grown because it is used in a variety of applications. This study focused on the effect single-walled carbon nanotubes (SWNTs) had on titanium dioxide (TiO_2) catalysis. Two different forms of TiO_2, rutile and anatase, were combined with SWNTs in heterogeneous mixtures and turned into films. The properties of these films were explored through their conductivity measurements, ability to degrade Methylene Blue (MB) when exposed to UV and visible light, and Raman spectroscopy. The data suggest that interactions with SWNTs increase the catalytic properties of TiO_2 and extend the photoresponse range into the visible region of light.

Introduction

A great deal of work is being done to improve heterogeneous catalysis. In particular, researchers have been focusing on the catalytic properties of titanium dioxide (TiO_2) because it can be used in numerous applications. Studies have found that TiO_2 photocatalysts can purify water by degrading pharmaceuticals1 and aid in other environmental purifications.[2] However, TiO_2 has a slow reaction rate[3] and must be exposed to UV light to act as a photocatalyst.[2] Since UV light makes up only a small percentage of the entire light spectrum, TiO_2 lacks solar efficiency. In order to take full commercial advantage of the photocatalytic properties of TiO_2, its efficiency must be improved.

This study hoped to enhance the efficiency of TiO_2 by mixing it with SWNTs. Since their discovery in 1991, carbon nanotubes have fascinated researchers from various fields of science.[4] Carbon nanotubes are hollow tubes made of hexagons of sp^2-hybridized carbon atoms.[5] When they are made of only one sheet of carbon, they are known as single-walled carbon nanotubes (SWNTs). These types of nanotubes can be either metallic or semiconducting, depending on the alignment of the carbon hexagons.[6] The SWNTs can also interact electronically with other molecules in their environment. According to Britz and Khlobystov, “Molecules that affect nanotube properties are also altered in the presence of the nanotube.”[6] Thus, changes in the electronic and catalytic properties of nanotubes and other molecules can be observed when the two are mixed together and in close contact. This study focused on how SWNTs interact with TiO_2 when mixed nanoscopically in a heterogeneous film. In particular, it examined how the presence of the SWNTs affects the catalytic properties of TiO_2 during exposure to UV light and visible light.

Background

Many studies have explored how carbon nanotubes affect TiO_2 molecules. Kongkanand and Kamat, for instance, investigated the electronic interactions between TiO_2 nanoparticles and SWNTs. They discovered that when the TiO_2 nanoparticles are irradiated, they transfer electrons to the SWNTs, which accept and store them.[7] Therefore, there is some electronic coupling occurring between the TiO_2 and the SWNTs.

Studies have also examined the photocatalytic properties of TiO_2 under various wavelengths of light. For example, Zhang et al. chemisorbed a monolayer of polyaniline (PANI) onto TiO_2 photocatalysts, irradiated the photocatalysts with UV light and visible light, and used them to degrade MB. They found that the combination of PANI and TiO_2 degraded MB when exposed to UV light and visible light.[3] Thus, with the use of PANI, Zhang et al. were able to extend the photoresponsiveness of TiO_2 into the visible spectrum of light.

Approach

Nanotube Preparation

Before the SWNTs can be mixed with other particles, they must be put into solution form. In this study, solutions were created with nanotubes and an ionic surfactant, 1% sodium dodecyl sulfate (SDS). The SWNTs were produced through the CoMoCat process[8] (purchased from SouthWest NanoTechnologies Inc.). The solutions had 1 mg of SWNTs for every 1 mL of surfactant. The surfactant coats the SWNTs and prevents them from bundling together, but it must be thoroughly mixed with the SWNTs to do so. The solutions of SWNTs and surfactant were mixed thoroughly using ultrasonication and then centrifuged. During centrifugation the purer nanotubes stay at the top of the tube, while the less pure ones and the other materials in the mixture sink to the bottom. Since they are heavier than the pure nanotubes, the impure nanotubes and the junk material are pulled down by the centrifugal force. For this study only the SWNTs from the top portion of the tubes were used because they were cleaner and purer. (For more information on this process, please see reference 9.)

Film Preparation

After the nanotubes were put into solution form, they were mixed with two types of TiO_2: anatase and rutile. The two types have different crystal structures and sizes. The anatase particles were less than 25 nm in size, while the rutile particles were less than 100 nm. Prior to mixing the TiO_2 was also sonicated in a 1% SDS solution, which contained

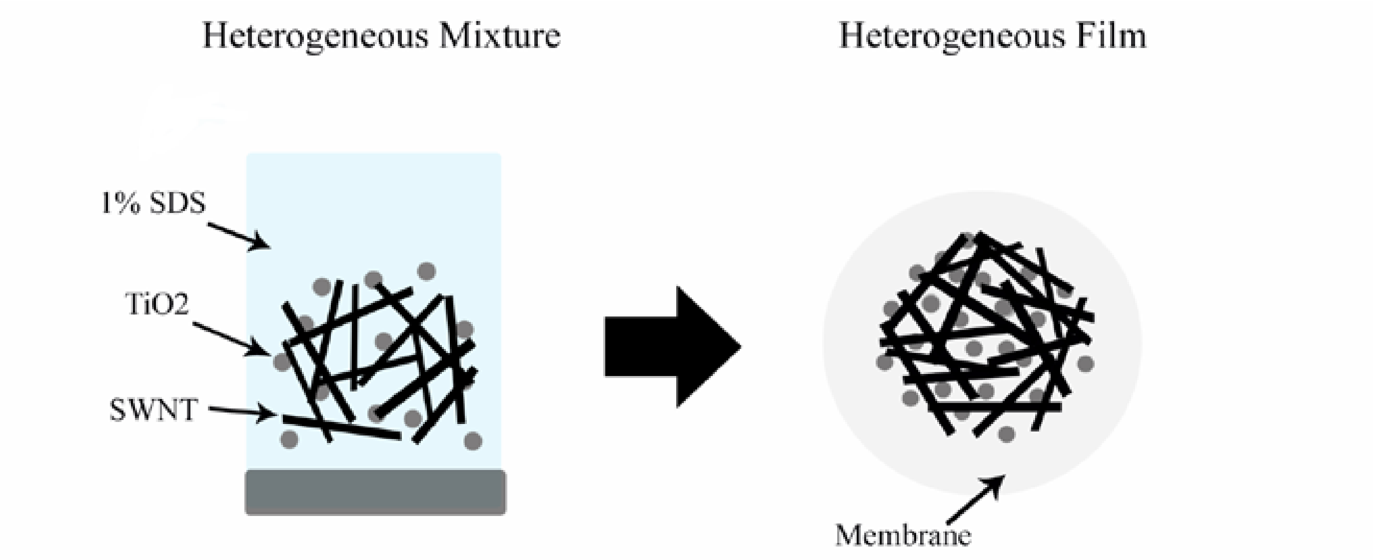

Figure 1. A scheme showing the SWNTs and TiO_2 in heterogeneous mixture and film form.

0.5 mg of TiO_2 per 1 mL of solution, to decrease the bundling of the TiO_2 particles. Initially, they were turned into heterogeneous mixtures. The mass ratios of TiO_2:SWNTs were 1:5, 1:1, and 5:1. Films labeled Rutile 1 and Anatase 1 had a 1:5 ratio, Rutile 2 and Anatase 2 had a 1:1 ratio, and Rutile 3 and Anatase 3 had a 5:1 ratio. The mixtures were diluted with 1% SDS to prevent the nanotubes from bundling together and to produce even films. Then these mixtures were turned into films using vacuum filtration (Figure 1). The films were created on porous 0.02 μm anodized alumina Anodisc membranes (Whatman) with 25 mm diameters. Control films that contained only TiO_2 and no SWNTs were made in the same manner. Similarly, a control film was made with only SWNTs and labeled SWNT.

Conductance

This study explored how the current and resistance of the films with TiO_2 and SWNT changed as the films were exposed to UV light to see if the two materials were interacting electronically. The change in current and resistance was monitored with a four-point probe during UV light exposure to determine the effect of the charge carriers in the TiO_2 while a bias of 0.15 V was applied to the sample. A 4 W handheld UV lamp (UVP, LLC) that emitted 365 nm light was used to illuminate the films.

To test the change in current and resistance, the film samples were placed under the four electrodes of the four-point probe, and the probe was run for two minutes to determine the resistance of the films. Then, the UV lamp was carefully held about 3 cm above the sample and turned on for 5 min while the probe continued to record current and resistance. Finally, the UV lamp was turned off and the samples were allowed to recover for 10 min while the probe continued to run. Throughout this entire time, the film was not moved or disturbed in any way.

UV Exposure

To explore the catalytic properties of the films, this study focused on their ability to degrade MB. When exposed to UV light, TiO_2 can degrade MB by breaking it down and altering its absorbance. This change in absorbance can be easily observed and recorded by a spectrophotometer. In this study the films were exposed to UV light and MB solution to see how the presence of SWNTs affected the TiO_2's ability to break down MB. The films were put into small petri dishes filled with a diluted MB solution. They were then exposed to UV light for 7 hr using a 4 W compact UV lamp (UVP, LLC) that emitted at 365 nm. Every hour the optical absorbance of 1 mL of MB solution from each petri dish was recorded using a UV-VIS-NIR spectrophotometer (Varian Cary 500) to observe any changes. To improve consistency and evaluation, each film was tested simultaneously with its respective control. Some of the films were exposed to UV light for less than 7 hr because, once they became saturated and stopped degrading the MB, the exposure was stopped.

Visible Light Exposure

The films were also exposed to visible light. Since TiO_2 alone should not react to visible light, the films were exposed to a visible wavelength of light to explore if the presence of SWNTs had increased the photoresponsiveness of the TiO_2 into the visible spectrum. One-fourth of the Anatase 3 and Rutile 3 films and their control films were placed into cuvettes filled with MB solution and exposed to an ion laser with a wavelength of 514 nm for 2 hr. After every hour of exposure, the optical absorbance of the MB solution in each cuvette was recorded using the UV-VIS-NIR spectrophotometer (Varian Cary 500).

Absorbance of TiO_2

To explore the differences between rutile and anatase TiO_2, this study looked at their absorbance spectra. The control films with the highest amount of anatase and rutile were put into the UV-VIS-NIR spectrophotometer (Varian Cary 500) and exposed to various wavelengths of light ranging from 250 nm to 700 nm. As the films were exposed, the percent of light being reflected was measured. The percent absorbance could then be determined from the percent of light being reflected.

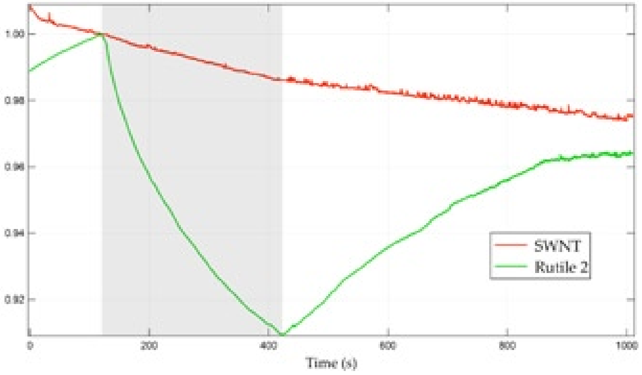

Figure 2. The current of the SWNT and Rutile 2 films before, during, and after UV exposure. The UV exposure is shown by the shaded region. The values have been normalized to the current at the start of UV exposure.

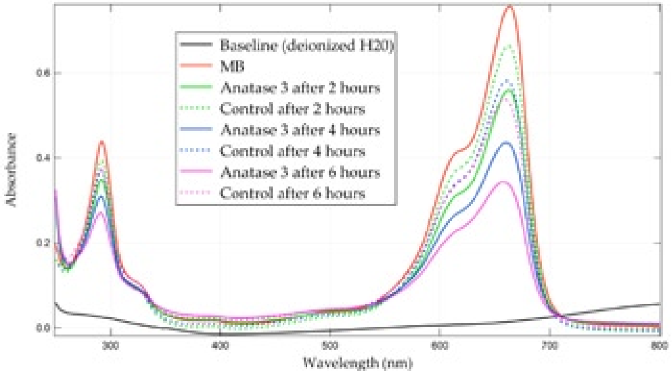

Figure 3. Optical absorbance of the MB solution exposed to the Anatase 3 and Control Anatase 3 films after various hours of UV exposure.

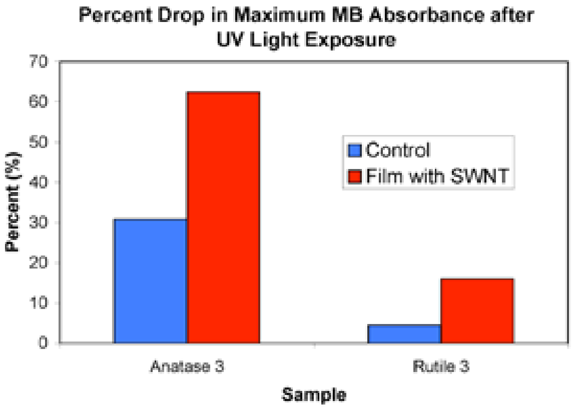

Figure 4. The drop in MB absorbance as a percentage of the initial value of MB of the Anatase 3, Rutile 3, and control films after UV exposure.

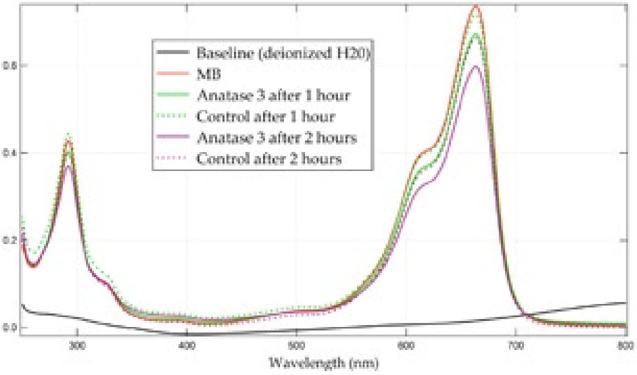

Figure 5. Optical absorbance of the MB solution exposed to the Anatase 3 and Control Anatase 3 films after two hours of exposure to the 514 nm laser.

Raman Spectroscopy

In addition, Raman spectroscopy was used to analyze the films. This study focused on the G-band in particular. Comparing the shapes and widths of the peaks at the G-band of the anatase films and SWNT film demonstrated the level of interaction between the nanotubes and the TiO_2. (For more information about Raman spectroscopy of SWNTs, please see Reference 5.)

Results

Conductance

Exposure to UV light had a significant effect on the films. When the films with TiO_2 were exposed to UV light, the current decreased while the resistance increased. Once the UV light was turned off, the current and resistance began to recover to their original values. The SWNT film, on the other hand, did not exhibit this drastic change and recovery when exposed to UV light (Figure 2). In fact, the SWNT film demonstrated a small overall drop in current that did not recover. This drop was caused by general electric changes within the film, rather than the UV exposure.

UV Exposure

The films were also exposed to 365 nm UV light for several hours in the presence of MB solution to observe their catalytic properties and ability to degrade the MB. As time progressed, the absorbance of the MB solutions decreased for all TiO_2. Also, the absorbance of the MB solutions exposed to films with SWNT and TiO_2 was consistently lower than the absorbance of those exposed to the respective control films with only TiO_2 (Figure 3). The Anatase 3 film produced a drop in MB absorbance that was approximately 2 times greater than that of its control film, while the Rutile 3 film produced a drop about 3.7 times greater than its control. However, the total drop in MB absorbance was greater for the films with anatase than the films with rutile (Figure 4). In fact, the films with rutile saturated after only a few hours.

Visible Light Exposure

In addition to UV exposure, the Anatase 3, Rutile 3, and their respective control films were exposed to visible light in the presence of MB solution. These films were illuminated with a laser with a wavelength of 514 nm. After exposure, all the films caused a decrease in MB absorbance. However, the films with SWNTs and TiO_2 produced a greater decrease in absorbance than the control films (Figure 5). Also, the film with rutile TiO_2 and SWNTs caused a greater drop in MB absorbance than the film with anatase TiO_2 and SWNTs (Figure 6). In fact, the

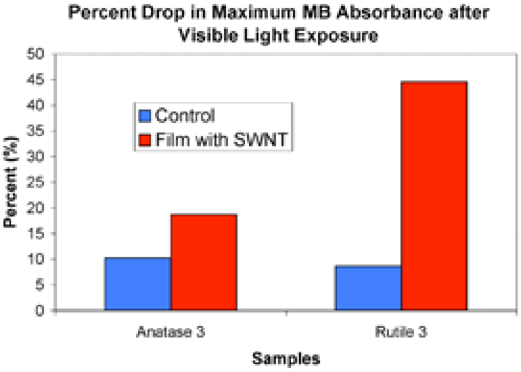

Figure 6. The drop in MB absorbance as a percentage of the initial value of MB of the Anatase 3, Rutile 3, and control films after visible light exposure.

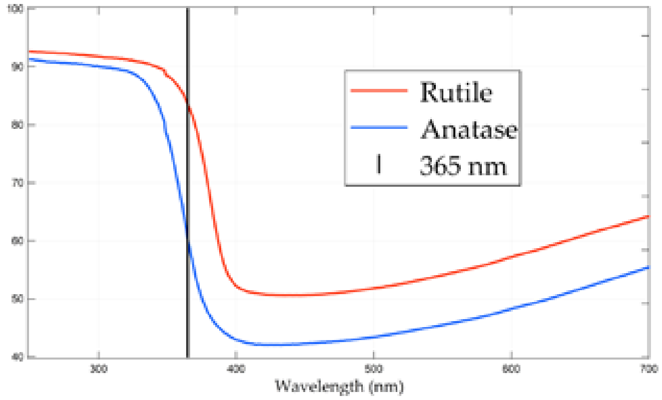

Figure 7. The percent absorbance of rutile and anatase TiO_2 when exposed to various wavelengths of light.

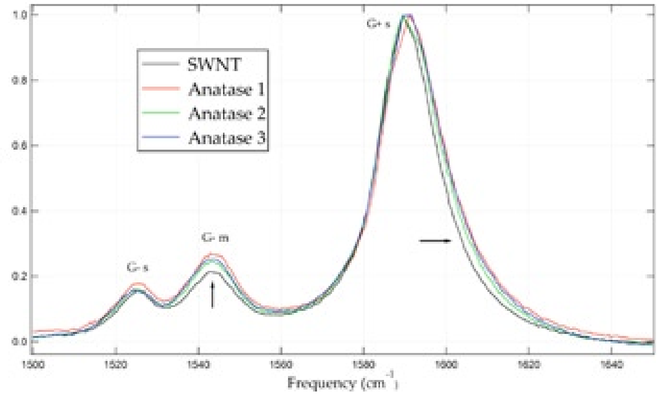

Figure 8. Raman spectra of various anatase TiO_2 and SWNT samples at the G-band. The changes in the peaks are emphasized by the arrows.

Anatase 3 and Rutile 3 films produced overall drops in MB absorbance that were approximately 1.8 and 5.1 times greater, respectively, than those produced by their control films.

Absorbance of TiO_2

The percent absorbance of the rutile and anatase TiO_2 was calculated at various wavelengths. At 365 nm, the wavelength of the UV light, the anatase and rutile showed different amounts of absorption (Figure 7). The rutile absorbed about 83% of the light, while anatase absorbed only about 60% of the light.

Raman Spectroscopy

Raman spectroscopy was also performed on the films with anatase and the SWNT control. Specifically, the G-bands were analyzed because they reflect the diameter of the nanotubes and how they vibrate. The films with anatase exhibited a slight broadening of the G-band peak in comparison to the film with only SWNTs (Figure 8).

Discussion

When the films with TiO_2 and SWNTs were exposed to UV light, they exhibited a change in current and resistance that was not observed with the SWNT film. This data suggest that electronic coupling is occurring between the TiO_2 particles and SWNTs. UV light exposure and visible light exposure were also performed in the presence of MB to examine the films' catalytic properties. When they were exposed to UV light, the films with TiO_2 and SWNTs caused a greater degradation of MB than the control films. This suggests that the presence of SWNTs and the electronic coupling enhanced the photocatalytic properties of TiO_2 under UV light.

Although both rutile and anatase exhibited this increase in MB degradation when combined with SWNTs, the anatase produced a greater change than rutile. This occurrence can be explained by the difference in absorbance of the anatase and rutile. When exposed to UV light (365 nm), the rutile absorbed a relatively high percentage of light and interacted with the nanotubes as it would throughout the UV spectrum. The anatase, on the other hand, absorbed a smaller percentage of light and interacted with the nanotubes as it would in the visible spectrum. This difference in interaction is probably what led to the difference in performance between the rutile and anatase.

Much like the UV exposure, the Anatase 3, Rutile 3, and their control films were exposed to a laser with a wavelength of 514 nm and MB solution. Once again, the films with TiO_2 and SWNTs produced a greater degradation of MB than the control films. This finding suggests that when combined with SWNTs, TiO_2 can act as a photocatalyst when exposed to visible light as well as UV light. Thus, the presence of SWNTs extended the catalytic properties and photoresponsiveness of TiO_2 into the visible spectrum. Additional research should be done to examine which wavelengths of visible light affect TiO_2 and to what extent.

Raman spectroscopy was also conducted to examine how the TiO_2 particles interact with the SWNTs. A broadening of the G-band peaks was observed for the films with anatase and SWNTs in comparison to the film with only SWNTs. This finding indicates that the presence of the TiO_2 affected the vibrations of the SWNTs. In other words, the TiO_2 and the SWNTs interacted electronically to some extent. It is this interaction that enhanced the catalytic properties of TiO_2 and extended its photoresponsiveness into the visible region of light. Although a change was observed and interaction did occur, the TiO_2 and SWNTs could probably be mixed more thoroughly and their interaction could be increased. Further research should be done to optimize the mixing process and create films with a maximum amount of interaction between the TiO_2 and the SWNTs.

Conclusion

This study examined the effects of SWNTs on the catalytic properties of TiO_2. Heterogeneous films were made with various amounts of anatase and rutile TiO_2 and analyzed. Conductivity tests demonstrated that electronic coupling occurred in these films between the TiO_2 and SWNTs. When combined with MB and exposed to 365 nm UV light and 514 nm visible light, the films with TiO_2 and SWNTs produced a greater degradation of MB than the control films without SWNTs. Thus, the electronic interaction between the TiO_2 and the SWNTs magnified the catalytic properties of TiO_2 and extended the photoresponsiveness into the visible light range. Raman spectroscopy of the G-band confirmed that the TiO_2 and SWNTs were interacting nanoscopically. However, future work should be done to increase the nanoscopic interaction between TiO_2 and SWNTs by optimizing the mixing process. Also, SWNTs should be mixed with other materials to investigate whether or not the presence of SWNTs enhances the catalytic properties of particles other than TiO_2.

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