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Visible light photocatalytic activity of MWCNT/TiO_2 using the degradation of methylene blue

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ABSTRACT

Multi-walled carbon nanotubes (MWCNT)-doped TiO_2 thin films were synthesized by the dip-coating method. The obtained products were characterized by SEM, EDX, XRD, and UV-vis absorption spectroscopy. The XRD patterns showed the presence of anatase phase. Absorption spectrum of MWCNT-doped TiO_2 revealed a red shift in the optical absorption edge due to carbon doping. The photocatalytic properties were investigated using methylene blue (MB) degradation under visible light (400-700 nm). MWCNT/TiO_2 thin films exhibited significantly higher photocatalytic activity as compared to undoped TiO_2 thin films due to reduction of the rate of electron-hole recombination by doping carbon. Photocatalytic activity studies with different light source (white light and blue light) indicated a significant enhancement in photocatalytic removal under white light irradiation.

1 Introduction

In recent decades, in connection with the rapid development of industry, humanity has faced a number of challenges regarding environmental problems. Therefore, to maintain survival, human needs to use new technologies to eliminate pollutions from the environment [1-5]. To meet the increasingly stringent standards of environmental regulations; catalytic techniques are being applied in the fields of environmental protection. Photocatalysis is one technique that has great potential to control contaminates.

Semiconductor photocatalysis (such as TiO_2, ZnO, WO_3, etc) are a well-established technique for pollutant degradation [6-10]. Among them, TiO_2 materials of different forms (powder, thin films, nanotube and nanorods) exhibit high efficiency in the photocatalytic activity due to low cost, non-toxicity, chemical stability, non-erosion & non-corrosion to light, and availability [11-14]. This semiconductor has a wide band gap (3.2 eV for anatase phase and 3 eV for rutile phase) that lays within the range of the UV spectrum, therefore only 4-5% of the solar light can be absorbed by TiO_2. Hence, developing new TiO_2-based compositions to absorb visible light irradiation is necessary [15-18]. Doping by nonmetal elements, such as nitrogen, sulfur and carbon is an appropriate method to improve photocatalytic properties of TiO_2 nanostructures in the visible region of the solar spectrum [19-23]. Recently, it has been reported that carbon modification of n-TiO_2 lowered its band gap energy; consequently enhanced photoresponse was

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observed [24]. Nanocomposites containing carbon nanotubes (CNTs) have attracted great attention due to their hollow structures, high surface areas, and high adsorption capacities [25-26]. In junction multiwall carbon nanotubes, (MWCNTs)/TiO_2 generated photoelectrons from TiO_2 particles under UV light illumination migrate to the surface of MWCNTs and get trapped. This process leads to hindering electron-hole pair recombination and improving the photocatalytic properties [27-28]. Sakthivel et al [29] in 2003 have reported a fivefold increase in photocatalytic activity of carbon-doped n-TiO_2 as compared to nitrogen-doped n-TiO_2. Xu et al. have published an article in 2006 [30] where they observed that the carbon-modified n-TiO_2 nanoparticles show a significantly enhanced photocatalytic activity as compared to the regular undoped. Most Studies dealing with CNTs/TiO_2 composites photocatalytic activity have been carried out under UV irradiation [31-33], but there are few reports on the photocatalytic activity of CNTs/TiO_2 composites under illumination of visible light. Dei et al. [34] in 2009 studied photocatalytic hydrogen generation using a TiO_2/CNTs nanocomposite under visible light irradiation. In 2010 Akhavan et al. studied visible light photo inactivation of Escherichia coli bacteria on surface of CNT-doped TiO_2 thin films with various CNT contents [35]. Their results showed that under visible light irradiation, the antibacterial activity of the CNT-doped TiO_2 thin films was highly improved.

In the present work, the visible light photocatalytic activity of MWCNT-doped TiO_2 thin film prepared by simple dip-coating method is investigated. The photocatalytic activity of MWCNT/TiO_2 thin film is evaluated by the photocatalytic discoloration of Methylene blue (MB) aqueous solution. Also, the effect of the film thickness and visible light source on photocatalytic degradation is studied.

2 Experiment

2.1 Preparation of the MWCNT/TiO_2 thin film

MWCNT/TiO_2 thin film was synthesized by dip-coating method. Briefly, 23 ml of ethanol (99%, Merck) is added to 2.3 ml Titanium (IV) n-butoxide (TB, 99%, Merck) and stirred for 30 min. Separately, 2 ml of nitric acid (65%, Merck) was mixed with 0.01 g of MWCNT, when the solution was added drop-drop to the first solution and was stirred for 2 h. The molar ratio of H_2O to ethanol was 0.046: 1. After leaving the solution for 24 hours, slide glass substrate was immersed in the solution for about 1 min before being pulled out at a speed of 1mm/s. After 24 h, the sample was kept in the oven at 100 ˚C for 1 hour. The sample was finally heated at 450˚C for 1 h. To investigate the effect of film thickness, in the other experiments without changing other parameters, just by increasing the number of times the immersion process takes place, two different thicknesses of 160 nm and 500 nm were obtained.

2.2 Characterization

The morphology and crystal structure of pure and MWCNT- doped TiO_2 thin films was studied by using scanning electron microscopy (FE-SEM: Co: TeScan, MIRAII LMU) and X-Ray diffraction (XRD: Rigaku Ultima iv) with Kα radiation (λ=1.54056 Å), respectively. The presence of MWCNT and its content in doped samples was determined by SEM with energy dispersive X- ray spectroscopy (EDX: SAMx). The optical properties were investigated by measuring UV-vis absorption spectrum (Ocean Optics HR, 4000 GG) in a wavelength region of 300-700 nm.

2.3 Photocatalytic activity

Photocatalytic degradation of Methylene blue aqueous solution was carried out under 10 LED lamps (400-700 nm) illumination with intensity 4.5-5.5 W/m^2 as the visible light source by placing the MWCNT/TiO_2 thin film (14 cm^2) into 25 mL of MB solution (10 mg/L). Before irradiation, the suspension was allowed to reach an adsorption-desorption equilibrium in the dark for 20 min. After visible irradiation, every 15 min, the solution was analyzed by measuring the MB concentration (at 661 nm). The absorption spectrum of the samples were measured by using a UV-vis spectrophotometer (Ocean Optics HR, 4000 GG).

To investigate the effect of visible light source, the same experiment was also carried out under 10 LED lamps (450 nm) illumination with intensity 1.5-2.5 W/m^2 as the blue light source.

3 Results and Discussion

3.1 Structural properties of the MWCNT/TiO_2 thin film

The morphology of multi–wall carbon nanotube (MWCNT) powders of 95% purity, undoped TiO_2 and MWCNT/TiO_2 thin films are investigated by SEM images as illustrated in Figure 1. According to Figure 1a the outer diameter of MWCNT was found to be 20–30 nm and length of 10-30 µm. The morphology of the undoped TiO_2 thin film (Figure 1b) shows a uniform and dense surface. The average particle size is approximately 11 nm which is in agreement with the values obtained from the XRD analysis. Figure 1c shows the surface morphology of the MWCNT/TiO_2 thin film prepared from MWCNT and titanium sources. As shown, the TiO_2 nanoparticle can be seen on the multi–wall carbon nanotube. In this case the outer diameter of MWCNT is approximately 60 nm that confirms the presence of TiO_2 nanoparticles on the carbon nanotube.

In order to show the presence of MWCNT and its content in TiO_2 thin films, samples were characterized by EDX. Table 1 indicates the content of the main element such as C, Ti, and O with their weight percentage and atomic percentage evaluated from EDX.

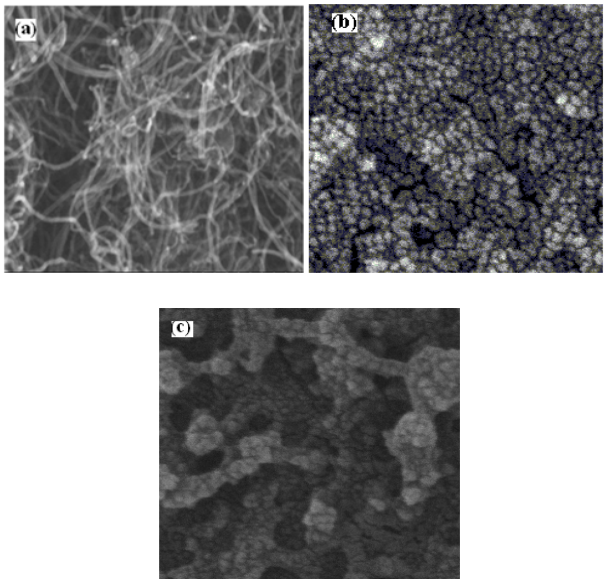

Figure 1. SEM images of (a) MWCNT, (b) undoped TiO_2 thin film, (c) the MWCNT/TiO_2 thin film. The scale bar indicates 500 nm.

Based on the MAUD analysis, Table 1 displays the real values and refined experimental values of ion positions, occupancy number, and quantity of the ions in a unit cell of the synthesized samples.

Table 1. Ti, O, and C element content of the MWCNT/TiO_2 thin film according to EDX analysis.

Element	W%	A%	Element
Ti	15.22	5.52	Ti
O	78.17	84.91	O
C	6.61	9.57	C

Figure 2 shows the XRD patterns of MWCNT-doped TiO_2 thin films. As seen, all of the peaks can be indexed on anatase phase according to JCPDS 9015929. The concentration of MWCNT used in the solution did not show significant effect on the crystal structure of the films.

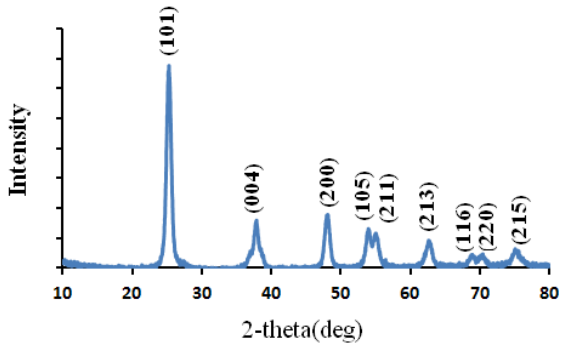

Figure 2. XRD patterns of the MWCNT/TiO_2 thin film.

3.2 Optical properties of the MWCNT/TiO_2 thin film

Figure 3 shows the optical absorption spectrum of pure and MWCNT-doped TiO_2 thin films with 500 nm thickness. Our measurements indicate an absorption edge around 387 nm for undoped TiO_2 thin films. However, MWCNT-doped TiO_2 thin films show red shift (400-500 nm) and better absorption in the visible region. This is due to the band gap narrowing, resulting in chemical bonding between TiO_2 and carbon. Also, the absorption spectrum of MWCNT-doped TiO_2 thin films has a higher intensity compared to undoped TiO_2. This could be attributed to MWCNT/TiO_2 junction band structural modification that leads to

reduction of the band gap energy for MWCNT-doped TiO_2 thin films. The band gap energy (E_g) of thin films is estimated by using the following equation [36]:

$$(\alpha h\nu)^m = C(h\nu - E_g)$$
$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right) \quad , \qquad (1)$$

Where α, t, and T are the absorption coefficient, thickness, and transmittance of the film, respectively. In semiconductor physics, the intersection between the linear fit of $(\alpha hv)^m$ and the photon energy axis gives the value of E_g. When m=2, the semiconductor has a direct band gap while when m=1/2, the semiconductor has an indirect band gap. Due to appearance of anatase phase with indirect band gap, here, we showed $(\alpha hv)^{1/2}$ versus hv in Figure 4. It can be seen that the band gap is almost 3.2 eV for pure TiO_2 thin films. Nevertheless, a red shift is found in the band gap MWCNT-doped TiO_2 thin films (2.87 eV).

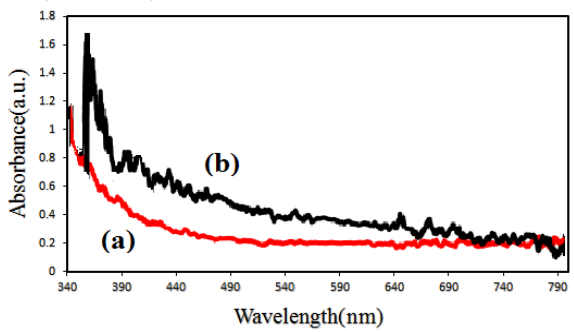

Figure 3. The absorption spectra. (a) Undoped TiO_2 thin films. (b) MWCNT-doped TiO_2 thin films.

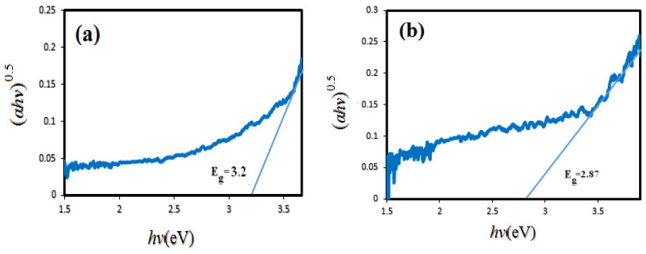

Figure 4. The band gap energy estimation. (a) Undoped TiO_2 thin film, (b) MWCNT-doped TiO_2 thin films.

3.3 Photocatalytic activity

3.3.1 The effect of doping MWCNT

Methylene blue (MB) is selected to evaluate the photocatalytic degradation. Figure 5(a) shows degradation of MB in aqueous solution by pure and MWCNT-doped TiO_2 thin films with thickness 500 nm under visible light irradiation (450-700 nm). It can be seen that the pure sample shows a little photocatalytic activity under visible light illumination (13% decreased of MB after 2h). In contrast, the MWCNT/ TiO_2 thin film significantly indicates photocatalytic activity (100% decreased of MB after 2h). Figure 5(b) indicates the color change of methylene blue by MWCNT/TiO_2 thin films. As seen, the initial blue color of MB solution became colorless after 2h. MWCNT could act as an electron donor in the composite photocatalyst to accept a photo-induced electron (e−) into the conduction band of TiO_2 particles under visible irradiation, thereby increased the number of electrons as well as the rate of electron-induced redox reactions [37]. Figure 6 indicates a schematic about photocatalytic mechanism. With using MWCNT in TiO_2 thin films, electrons can be transferred from the conduction band of MWCNT to the conduction band of TiO_2, followed by electrons moving from the valance band of TiO_2 to the valance band of MWCNT due to generated holes in the valance band of MWCNT. The mentioned processes can increase the charge carrier lifetime and reduce electron-hole recombination, resulting in improved photocatalytic activity.

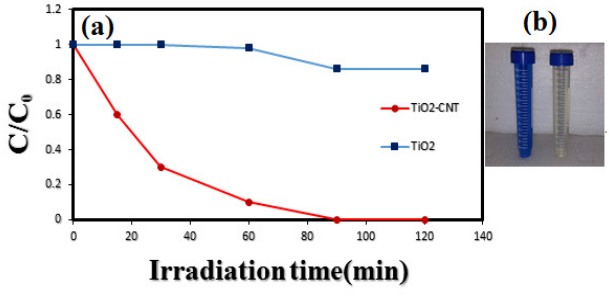

Figure 5. (a) Concentration of MB as a function of time with pure and MWCNT/TiO_2 thin films. (b) Colour change of methylene blue by MWCNT/TiO_2 thin films.

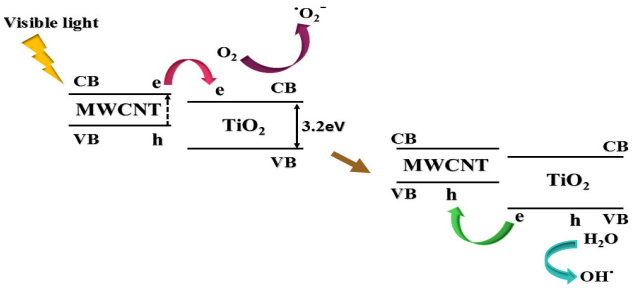

Figure 6. The mechanism of the photocatalytic activity of MWCNT/TiO_2 under visible light.

3.3.2 The effect of light source

To evaluate the effect of light source on photocatalytic activity MWCNT/TiO_2 thin films, two LED lamps with different wavelengths were selected. Spectra of two light sources, blue light (450 nm) and white light (450-700nm), is shown in Figure 7. Figure 8 shows MB degradation by MWCNT-doped TiO_2 thin films with different light source. A significant enhancement in photocatalytic activity is seen under irradiation of white light than blue light illumination (100% degradation of MB after 2h for white light and after 23h for blue light). Whereas the optical power of white light is higher than blue light which is due to the effect of optical power on improving photocatalytic activity. Thus, under white light irradiation, photocatalytic activity increases. Another reason can be described as follows: as previously mentioned, it is known that carbon nanomaterials are electron donors while semiconducting TiO_2 materials are electron acceptors under visible radiation. Due to the energy gap of carbon (2.8 eV), the levels which the electrons are separated from them are energized in the red range.

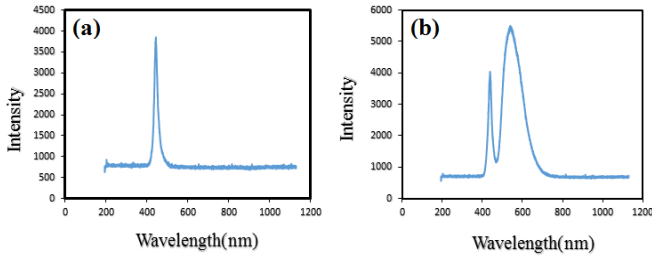

Figure 7. Spectra of two light sources. (a) Blue light (450 nm), (b) White light (450-700nm).

Since the white light has a wider width in this region compared to the blue region, photocatalytic activity is better under white light illumination.

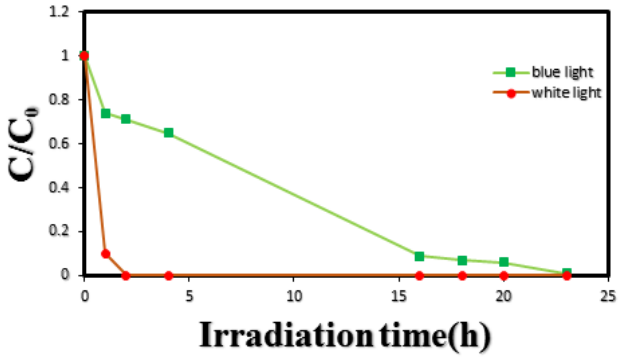

Figure 8. Investigation of the effect of light source on the photocatalytic activity of MWCNT/TiO_2 thin films.

3.3.3 The effect of thin film thickness

Figure 9 shows the relationship between the percent of degradation of MB and thickness of MWCNT/TiO_2 thin films under blue light irradiation (450 nm). With increasing thickness (from 160 nm to 500 nm), the percent of degradation increased. Higher thickness can have the highest photocatalytic activity, because as the thickness increases, light absorption is increased which leads to a higher increase in the e/h pair production on the photocatalyst surface. Also by increasing the layers number, surface roughness increases. Since the by porous surface increases active sites on the surface, photocatalytic activity improves [38-40].

In order to investigate the relationship between the MWCNT/TiO_2 thin films thickness and penetration depth, the penetration depth was calculated according to beer-lambert law:

$$I = I_0 e^{-\alpha d} \text{ and } \quad \alpha = 1/\delta \; and \; \alpha = \frac{2.3 * A}{d} \quad \text{[41-43].}$$

Therefore, we can calculate the penetration depth by $\delta = d/2.3 * A$' where d is the thickness, A is the absorption, and δ is the penetration depth. Our calculation showed that the average penetration depth under 300-700 nm illumination is 524.78 nm and 350.94 nm for films with thickness 500 nm and 160 nm respectively. By comparing the penetration depth and thickness, it is understood that for the film

with thickness of 500 nm, light completely penetrates in the film. However in the film with thickness 160 nm the penetration depth is more than the thickness (δ=350.94 nm). The result was that part of the light passed through the film leading to a decreasing light absorbance which followed by a decreasing photocatalytic activity.

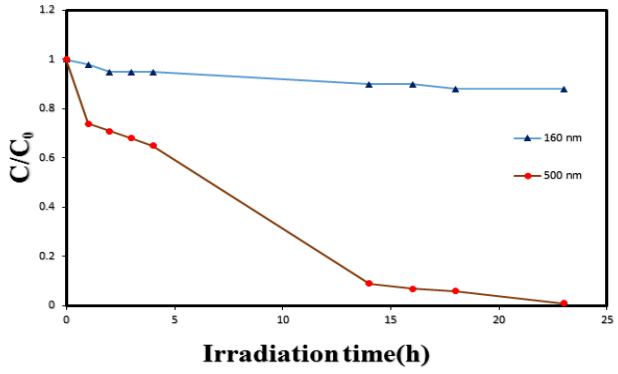

Figure 9. Photocatalytic MB degradation by MWCNT/TiO_2 thin films with different thicknesses equal to 160 nm and 500 nm.

4 Conclusions

MWCNT/TiO_2 thin films were prepared by the dip-coating method. In this work, methylene blue was destroyed by photocatalyst MWCNT/TiO_2 under visible light in a 2 hour period. Also, the effective parameters in the photocatalytic degradation of MB such as: thickness, energy gap, light source were investigated. During the photocatalytic process, MWCNT/TiO_2 thin films improve photocatalytic properties by decreasing the electron hole recombination by use of visible light instead of UV.

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