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NEW INSIGHTS INTO THE PHOTOCATALYTIC ENDOCRINE DISRUPTORS DIMETHYL PHATHALATE ESTERS DEGRADATION BY UV/MWCNTs-TiO$_2$ NANOCOMPOSITES

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Graphical abstract

Research Highlights

- 1-D MWCNTs/TiO$_2$ nanocomposites was successfully synthesized via one-pot sol-gel method
- The effect of different MWCNTs loading (3-15 wt %) on TiO$_2$ and photocatalytic performance of DMPEs nanocomposites was investigated
- A method based on high-performance liquid chromatography (HPLC) was developed to study the degraded DMPEs samples produced

Abstract

Dimethyl phthalate esters (DMPEs) are considered to be endocrine disruptors and environmentally hazardous materials in plastic industries wastewater because of its low solubility and accumulated persistent toxicity. In the present study, MWCNTs/TiO$_2$ nanocomposites were fabricated by modified sol-gel technique using titanium isopropoxide as titanium oxide sources and purified MWCNTs, to degrade DMPEs through photocatalysis using UV irradiation. The effect of MWCNTs loading (3-15 wt %) on TiO$_2$ and the photocatalytic performance of DMPEs in aqueous solution by UV/MWCNTs/TiO$_2$
nanocomposites were investigated. For experiments conducted with the same illumination time, the photodegradation of DMPEs was enhanced with increasing the MWCNTs contents from 3 to 10 wt % and then decreased with a further enhancement to 15 wt %. Basically, the presence of MWCNTs in the nanocomposites can lead to the decrease in the relative amount of TiO$_2$ in the photocatalyst and then to the decrease of the photogenerated carriers. This is because the same amount of photocatalyst was added for the photoreaction, and hence, the photodegradation of DMPEs decreases especially for the nanocomposites containing MWCNTs exceed than 10 wt %. The presence of functional group (-COOH) on the MWCNTs surface would help the achievement of direct chemical bonding between MWCNTs and the TiO$_2$ nanoparticles, resulting in the synergistic effect of MWCNTs and TiO$_2$ where the flow of photogenerated electrons in the space charge region to the MWCNTs surface. A method based on high-performance liquid chromatography (HPLC) was developed to study the degraded DMPEs samples produced after exposure to UV light.

**Keywords:** Photocatalysis, Dimethyl phthalate esters, MWCNTs/TiO$_2$, nanocomposites

1. Introduction

Nowadays, widespread concerns continue to be raised about the impacts of exposure to emerging persistent organic pollutants (POPs) with endocrine disrupting activities which mimicking endogenous hormones and disrupting hormone secretion or metabolism. These emerging POPs are globally concerned pollutants due to their widespread occurrence, long-term persistence, strong resistance, and potentially pose a great threat to human beings and ecosystems. Despite their low concentration present in the aquatic environment, PAEs have been listed as hazardous pollutants by both the USEPA and the European Union (EU) due to the fact that even a trace amount (parts per trillion) of them is found to be potentially harmful to human and the environment. The examples of PAEs that have been listed in the blacklist of water priority pollutants, by the USEPA, EU, China and other countries are summarized in Table 1. Generally, PAEs are relatively stable in the natural environment and the estimation for their hydrolysis half-life is to be about 20 years.

**Table 1:** Examples of blacklisted water priority pollutants, PAEs

<table>
<thead>
<tr>
<th>Blacklisted PAEs</th>
<th>Countries</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl phthalate (DMP)</td>
<td>China</td>
<td>[1]</td>
</tr>
<tr>
<td>Di-n-butyl phthalate (DnBP)</td>
<td></td>
<td>[2]</td>
</tr>
<tr>
<td>Di-n-octyl phthalate (DnOP)</td>
<td></td>
<td>[3]</td>
</tr>
<tr>
<td>Dibutyl phthalate (DBP)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Di(2-ethylhexyl) phthalate (DEHP)</td>
<td>Canada Taiwan, China</td>
<td>[6] [7]</td>
</tr>
</tbody>
</table>
A systematic search for reports in the past 20 years using keywords containing phthalates has been performed and the result indicating that the number of related reports on PAEs increased with each progressive year. Remarkably, the number of PAEs in 2014 is reported to be 12 times greater than in 1995 and this demonstrates the sharp increase of PAEs in the environment [8]. Since emerging POPs such as phthalate esters (PAEs) has become a class of concerning water pollutants, thus, there is a strong need to look for alternative and faster treatment processes for such pollutants. Particularly, dimethyl phthalate esters (DMPEs) are among the most frequently identified PAEs in the environment and a model compound of a series of common PAEs because of its common usage and its refractory biodegradability.

Methods of DMPEs wastewater treatment have received widespread attention of many scholars in recent years. Heterogeneous catalytic system, a kind of advanced oxidation process (AOPs), particularly semiconductor photocatalysis as one of the highly advanced promising technologies for the elimination of a wide range of recalcitrant organic pollutants. The pollutants from the complex molecules can be broken down into simple and non-toxic substances during the photocatalytic oxidation treatment, thus, no second treatment is involved for processing the sludge. Furthermore, the catalyst remains unchanged and can be reused which results in a significantly lower operating expense [9, 10]

Among all kinds of semiconductor photocatalysts (i.e. WO3, Fe2O3, CeO2, ZnO and ZnS), nanoscale anatase titania (TiO2) has received considerable attention because TiO2 is an inexpensive, thermal stability, non-toxicity, chemical inertness and easily attainable catalyst[11]. However, the photocatalytic efficiency of TiO2 is hindered by the wide band gap energy of TiO2 (3.2 eV for anatase phase and 3.0 eV for rutile phase), which may induce the fast recombination of electron-hole pairs. This extensively restricts the effectiveness of photo conversion by TiO2. Thus, to resolve the problems of the unmodified TiO2 listed above, continuous efforts have been conducted by coupling TiO2 nanoparticles with carbon nanomaterials. In this case, the combination of TiO2 nanoparticles with carbon nanomaterials must fulfill several basic requirements for better charge separation efficiency. For example, the carbon nanomaterials can act as effective electron transfer unit and can prompt electron transfer from the conduction band of the TiO2 nanoparticles towards the carbon surface due to their lower Fermi level [12-16].
In the present study, MWCNTs was selected as a suitable carbon nanomaterial to be coupled with TiO$_2$ nanoparticles. Indeed, the combination of MWCNTs with TiO$_2$ has attracted much attention, since MWCNTs take an important role in the way they link to TiO$_2$ nanoparticles and consequently, in the electronic and photocatalytic performance of the MWCNTs/TiO$_2$ composite. A good dispersion of TiO$_2$ nanoparticles in the MWCNTs/TiO$_2$ composite is attributed to the functionalization of MWCNTs with nitric acids leads to the creation of large amounts of carboxylic acid and phenol groups on the surface of the MWCNTs. Basically, the functional groups present on the surface of MWCNTs promote the anchoring of the TiO$_2$ nanoparticles as well as avoiding agglomeration and subsequently increasing the surface area of the resulting MWCNTs/TiO$_2$ composite. As a result, this strong interface interaction also favors electron transfer pathways, thus, the probability for electron/hole recombination is reduced. The formation of Ti-O-C bonds between the carboxylic acid groups of MWCNTs and the hydroxyl groups existent at the surface of TiO$_2$ during an esterification reactions, contribute to a synergetic effect due to the creation of an electronic interphase interaction between MWCNTs and TiO$_2$ phases. Herein, the MWCNTs coupled with TiO$_2$ nanoparticles was the ideal compound for DMPEs removal [17-19].

To the best of our knowledge, reports on the effect of MWCNTs loading on TiO$_2$ and its photocatalytic performance on DMPEs are still lacking. The first part of the present study aims to study the purification of MWCNTs in acid solutions for removing the carbonaceous impurities and metal catalyst particles on MWCNTs. The following part of the study was focused on determining the optimum loading of MWCNTs in order to achieve the desired MWCNTs/TiO$_2$ nanocomposites for the high efficient photocatalytic performance of DMPEs. This is because a detailed studies on physicochemical properties of MWCNTs/TiO$_2$ nanocomposites via modified sol-gel method for photodegradation of DMPEs are limited.

2. Experimentals

2.1 Materials

Multiwalled carbon nanotubes (MWCNTs, >95%, 10-20 nm in diameter were supplied by Bayer Material Science AG (Germany). Titanium isopropoxide (TTIP, 97%), concentrated nitric acid (65%), sodium dodecylbenzenesulfonate (SDS, 98%) and Dimethyl phthalate esters (>99%) with the molecular formula of C$_6$H$_4$-1, 2- (CO$_2$CH$_3$)$_2$ were purchased from Sigma-Aldrich, USA. Absolute ethanol, (>99.8%), glacial acetic acid and diluted ammonia solution
were obtained from Fisher Scientific, UK. All chemicals were used as received without further purification. Deionized water was used throughout this study.

2.2 Functionalization of MWCNTs

Purified MWCNTs were functionalized by concentrated nitric acid under reflux with vigorous magnetic stirring at 100 °C for 2 hours. In these conditions, the remaining iron particles will be removed and hydroxyl and carboxyl groups will be introduced onto the surface of the MWCNTs [17]. The solution was then cooled to room temperature, washed with distilled water and then oven dried at 100 °C.

2.3 Synthesis Procedures of MWCNTs-TiO$_2$ Nanocomposites

In a typical synthesis, MWCNTs/TiO$_2$ nanocomposites were prepared via a simple modified sol-gel method. An appropriate amount of functionalized MWCNTs was added with SDS in an aqueous solution with continually stirring for 24 hours. The prepared MWCNTs solution was then dispersed in ethanol and stirred for 30 minutes to achieve homogeneity [Solution A]. A mixture of titanium tetraisopropoxide, ethanol and acetic acid were stirred vigorously for 30 minutes to form a clear solution [Solution B]. Then, the solution B was added dropwise into the solution A under vigorous stirring at 28 °C for 2 hours. Diluted ammonia solution was then added dropwise into the mixture solution to hydrolyze and to form a well-uniform TiO$_2$ coated on the MWCNTs surface. The precipitate was centrifuged and rinsed with ethanol. The resulting sample was then oven-dried at 80 °C and then calcined at 450 °C in air for 2 hours.

2.4 Materials Characterization

X-ray diffraction (XRD) was used to study the crystal structure and the degree of crystallinity of MWCNTs/TiO$_2$. The XRD was performed at 40 kV and 30 mA at a scanning rate of 0.01°/s with a Cu Kα radiation (α = 1.5406 Å) on a Bruker axs D8 Advance diffractometer from 10° to 80°. The morphology and particle size was determined by using a Field Emission Scanning Electron microscope (FESEM) operating at 5.00 kV and high vacuum using a Quanta FEG 450. High-resolution transmission electron microscopy (HRTEM) was performed on a JEOL, JEM-2010 electron microscope with an accelerating voltage of 200 kV to study the morphology and lattice structures. Raman spectroscopy (Renishaw in Via) with a 514.5 nm Ar$^+$ laser as an excitation source was used to obtain graphitic structure of carbon bond and defects. DRS were recorded on Shimadzu UV-2700 UV-vis Spectrophotometer and DRS measurements were done in wavelength range of 200 to 800 nm using an integrating
sphere. Photoluminescence (PL) analysis (Renishaw in Via) was conducted to study the electron-hole pair recombination rate of MWCNTs/TiO$_2$ using Ar$^+$ laser with a wavelength of 325 nm. The FTIR analysis was carried out by FTIR Bruker Vertex 80/80v, the wavelength range from 4000 to 400 cm$^{-1}$. The XPS measurements were performed with a PHI Quantera II with Spherical Capacitor Analyzer (SCA) and a monochromatic Al Ka (1486.6 eV) source. The C 1s line of spurious carbon located at binding energy of 284.8 eV was used as the reference to correct the binding energies for the charge shift.

### 2.5 Photocatalytic Activity Test

Photocatalytic degradation of DMPEs was evaluated under irradiation of a 96 W UV lamp in a custom made photoreactor with five cylindrical quartz vessels (150 mL). In a typical reaction, 0.05 g of photocatalyst was added into a 100 mL of DMPEs solution (concentration: 1 mg/L). The suspension was stirred in darkness for 30 minutes to reach adsorption-desorption equilibrium before UV lamp was switched on to initialize the photodegradation of DMPEs. The suspensions were collected at certain time intervals and then filtered by a 0.22 µm membrane filter to remove the catalyst particles before being analyzed by using a UV-Vis spectrophotometer (Shidmadzu UV-2500). The concentration of DMPEs in the test solution was determined at $\lambda_{\text{max}}=227$ nm.

### 2.6 HPLC analysis and operating condition

The chromatographic analysis was performed on a HPLC system equipped with a series of 1100 Autosampler coupled with the UV detector model with diode array detector (DAD), while the separation was performed by an isocratic elution on C$_{18}$ (250 x 4.6 mm, 10 µm) from Agilent Technologies, (Palo Alto, CA,USA). Accordingly, the mobile phase used was a mixture of acetronitrile and water (60:40, v/v) with a flow rate of 0.5 mL/min; the injection volume was 20 µL and the UV detection was set at 227nm.

### 2.7 Ultra High Performance Liquid Chromatography Coupled With High Resolution Orbitrap Mass Spectrometry (UHPLC/ Orbitrap/MS)

LC/MS analysis is performed with the liquid chromatography equipment connect to Thermo Scientific Orbitrap Fusion which enhance the separation of unknown compounds and enable high-throughput workflows. The unique Orbitrap mass analyzers equipped with a quadrupole
mass filter, linear ion trap and Orbitrap mass analyzers from Thermo Fisher Scientific, San Jose, CA, U.S.A. provide the high-resolution, accurate-mass performance and identify the compounds more quickly. In this study, the separation was performed by an isocratic elution on RRHD SB-C18 (150 x 2.6 mm, 1.8 µm). A mixture of acetonitrile and water (20:80, v/v) was used as the mobile phase with a flow rate of 0.3 ml/min. An injection volume of 10 µL was used and the UV detection at 227 nm. The working principle of Orbitrap mass analyzer is based on trapping of ions in electrostatic field. When an ions around a central spindle electrode are trapped after they are ejected from the C-Trap (a curved quadrupole ion trap between the linear trap quadrupole and orbitrap that injects ions into the orbitrap), the Mass/charge (m/z) value can be derived from the harmonic oscillation frequencies of the trapped ions as they move across the trap spindle.

3. Results and Discussion

3.1 Surface Morphology and Elemental Analysis

The possible MWCNTs fragmentation occurred during oxidation treatment and the possible morphological changes on MWCNTs were examined using FESEM analysis (Figure 1). Figure 1(a) shows that the pristine MWCNTs formed large agglomerates with a high degree of entanglement, varying from 100 µm to several hundreds of micrometers, respectively. It was basically due to their high aspect ratio and van der Waals forces. In addition, straight tubes were hardly observed and the ends of the pristine nanotubes appeared to be carbon protective caps. Basically, the commercial pristine MWCNTs synthesized by chemical vapour deposition (CVD) containing carbonaceous impurities and metal catalyst particles [20, 21]. In CVD processing, a substrate was prepared and processed using a layer of metal catalyst particles (i.e. cobalt, and manganese) in combination with a catalyst support such as MgO or Al2O3 to develop the surface area for the higher by-product of the catalytic reaction of pure carbon. Depending on the adhesion and attachment between the substrate and the catalyst particle, the catalyst can remain at the nanotube base during growth and expansion. Thus, after the treatment with concentrated HNO3, the tube length of MWCNTs considerably became shorter and the functional groups of carboxyl groups were formed along the sidewalls (Figure 2) [22]. The treatment of MWCNTs with strong acid causes severe etching of the graphitic surface of the material, leading to tubes in shorter length with a large population of disordered sites.
From Figure 1(b), it can be observed that the purified MWCNTs were intertwined with each other and an individual of MWCNTs showed a tubular-like structure with an average diameter of 20 nm [23-25]. As shown in Figure 1(c), the chemical modification leads to the removal of catalyst from the carbon nanotubes and the opening of the tube caps (red circle), followed by an oxidative etching along the walls with the concomitant release of carbon dioxide. The final products are nanotube fragments where the ends and sidewalls are decorated with an oxygen containing groups (mainly carboxyl groups) [23, 26, 27]. During the purification, the tips of MWCNTs are opened up, and followed by the producing of defects at the MWCNTs neck. Amorphous and metal particles (including those entrapped between MWCNTs layers) are dissolved by acid and leave defect on the MWCNTs sidewall. Those defects are then being oxidized and attached by carboxyl groups [28]. TEM analysis shows the purified MWCNTs exhibited long and straight tubular structure. It consists of two or more concentric cylindrical shells of graphene sheets coaxially arranged around a hollow core with van der Waals forces between the adjacent layers (Figure 1(d)).
Figure 1: FESEM images of (a) Pristine MWCNTs, Purified MWCNTs with (b) low magnification and (c) high magnification, and (d) TEM image of Purified MWCNTs.

Figure 2: Pre-treatment oxidation of MWCNTs at 100 °C for 2h [28]

The quantitative elemental analysis of pristine MWCNTs and purified MWCNTs was carried out by FESEM-EDX. The presence of C, O, Mg, Al, Mn and Co elements in pristine MWCNTs are because of the MWCNTs were synthesized through a catalytic (CVD) method where a layer of metal catalyst particles (i.e. nickel, cobalt, and manganese) in combination with a catalyst support such as MgO or Al₂O₃ for producing higher by-product of the catalytic reaction of pure carbon [26]. It is necessary to remove these impurities as these residual metal-oxide particles will significantly decrease their adsorption efficiency. The critical drawbacks of CNTs in many applications are because of the poor dispersibility and bundling between CNTs as affected by the attractive van der Waals interactions among themselves. As displayed in Table 2, only C and O presented in purified MWCNTs and no other trace impurities were found. The weight percentage of each element was presented in Table 2.
Table 2: EDX elemental analysis (Weight %) of Pristine MWCNTs and Purified MWCNTs

<table>
<thead>
<tr>
<th>Element</th>
<th>Pristine MWCNTs (wt%)</th>
<th>Purified MWCNTs (wt%)</th>
<th>MWCNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>91.77</td>
<td>93.58</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>6.67</td>
<td>6.42</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>0.36</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.43</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.41</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.37</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

3.2 Raman analysis

The Raman spectra of the pristine and purified MWCNTs are shown in Figure 3. The changes in the surface chemistry of the MWCNTs before and after the acid treatment can also be examined from the Raman shifts. Both sample spectra exhibit two characteristic bands: D-band ~1338 cm⁻¹ (sp² carbon consists of impurities or other symmetry-breaking defects) and G-band ~1580 cm⁻¹ (high degree of ordering and well-structured carbon based structures), respectively [29, 30]. From the results presented in Figure 3 (b), one can observe that intensity of the D band in the acid treated MWCNTs increased due to the purification leads to a high density of defects on the tube walls. The purification of MWCNTs typically involves oxidation using acids, causing carboxyl groups to functionalize the defects at the end of the MWCNTs. Those defects are oxidized and carboxyl groups are attached on MWCNTs. Additionally, the left shift of the Raman response of the purified MWCNTs can be ascribed to the electron transfer from the MWCNTs to the covalently attached functional groups on the CNTs surface. It is also revealed that upshifting of the G-band occurs during the acid treatment step when the electrons are transferred from the MWCNTs to the covalent bonded (-COOH) groups on the MWCNTs surface. The purification of MWCNTs can be divided into two categories based on the type of bonds, namely non-covalent or covalent bonding between the CNTs and the functional groups. The covalent bonding depends on the chemical reaction between the carbon atoms of CNTs and conjugation of hydrophilic organic molecules on the surface of CNTs. The chemical treatment of pristine MWCNTs with most widely used strong oxidative agents (concentrated HNO₃) generates the oxygenated groups such as carboxylic at “end and defects”
sites and side walls of CNTs. An indication of the quality of CNTs and the chemical modification of MWCNTs or degree of “graphitization” can be depicted by the D and G mode intensity ratio ($I_D/I_G$) [31]. In addition, the extents of defects and impurities in the CNTs can also be indicated by the ratio of intensities of the characteristic peaks ($I_D/I_G$). The $I_D/I_G$ ratio decreases in the case of the purified samples which are mainly attributed to the removal of amorphous carbon from pristine MWCNTs and these results demonstrate the amount of defects and other carbonaceous phases are reduced. The treatment with nitric acid, while producing functional carboxylic groups, the amorphous carbon are being generated by shortening the MWCNTs and, causing increase in both the defects sites [29, 30, 32].

![Figure 3: Raman spectra for the (a) Pristine MWCNTs and (b) Purified MWCNTs](image)

3.3 Surface Morphology and Elemental Analysis

The mass ratio of MWCNTs and TiO$_2$ plays an important role in the combination of MWCNTs with TiO$_2$ in the way they link to TiO$_2$ nanoparticles and consequently, in the electronic and photocatalytic performance of the MWCNTs/TiO$_2$ composite. Figure 4 (a-d) shows the FESEM images of MWCNTs/TiO$_2$ nanocomposites with different weight percentage (3 wt to 15 wt %) of MWCNTs to TiO$_2$. All samples displayed that the incorporation of TiO$_2$ nanoparticles onto the surface of MWCNTs.

Generally, the synthesis method involving three main steps: i) The oxidation treatment of MWCNTs with concentrated HNO$_3$ introduced negative charged functionality –COOH onto the surface of MWCNTs; (ii) The hydrolysis of titanium isopropoxide produce titanium ions
that adsorb on the surface of MWCNTs. The formation of Ti-O-C bonds between the carboxylic acid groups of MWCNTs and the hydroxyl groups existent at the surface of TiO2 during an esterification reactions, contribute to a synergistic effect due to the creation of an electronic interphase interaction between MWCNTs and TiO2 phases and iii) The formation of anatase TiO2 nanoparticles on the surface of MWCNTs after the heat treatment. The heat treatment process is used to convert the amorphous structure of TiO2 nanoparticles to crystalline anatase phase [33-36].

As mentioned previously, the TiO2 nanoparticles may undergo aggregation due to the instability of the nanosized particle. From Figure 4(a), it can be observed that large agglomeration of TiO2 nanoparticles was formed on the surface of MWCNTs indicated that TiO2 nanoparticles do not have close contact with the surface of MWCNTs. With the increasing amount of MWCNTs up to 10 wt-%, the smaller sizes of TiO2 nanoparticles were attached on the surface of MWCNTs without agglomeration. The uniformity of the TiO2 varies according to the preparation method and the surface reactions of CNTs with TiO2 nanoparticles. 10 wt-% of MWCNTs/TiO2 nanocomposites showed a complete coverage of the MWCNTs by TiO2 nanoparticles. In this manner, the role of MWCNTs acts as a “dispersing template or support” for photocatalytically active materials to form MWCNTs/TiO2 composite photocatalyst. Basically, the functional groups present on the surface of MWCNTs promote the anchoring of the TiO2 nanoparticles as well as avoiding agglomeration and subsequently increasing the surface area of the resulting MWCNTs/TiO2 composite. However, non-uniform and large agglomerations of clumpy TiO2 structure were spotted with 15 wt-% of MWCNTs/TiO2 nanocomposites. This was probably due to the excessive loading of MWCNTs during the synthesis process [13, 35, 36].
TEM images of (3-15 wt-%) of MWCNTs/TiO$_2$ nanocomposites was displayed in Figure 5. It was observed that the formation of non-uniform and bigger agglomeration of TiO$_2$ clusters was formed with 3 wt-% and 5 wt-% MWCNTs/TiO$_2$ nanocomposites, respectively. On the
other hand, 10 wt-% MWCNTs/TiO$_2$ nanocomposites unveiled the relatively uniform TiO$_2$ nanoparticles wrapping the entire surface of MWCNTs, indicating the intimate interaction between the MWCNTs and TiO$_2$. A good dispersion of TiO$_2$ nanoparticles in the MWCNTs/TiO$_2$ composite attributed to the functionalization of MWCNTs with nitric acids leads to the creation of large amounts of carboxylic acid and phenol groups at the surface of the MWCNTs. However, the agglomeration of the bulk TiO$_2$ nanoparticles on the surface of MWCNTs was found in 15 wt-% of MWCNTs/TiO$_2$ nanocomposites due to an excessive amount of MWCNTs. Figure 5(e) is a high magnification of the 10 wt % of MWCNTs/TiO$_2$ which shows the obtained composites comprise of small spherical TiO$_2$ nanoparticles with less apparent aggregation of MWCNTs. The crystallographic morphology and crystal structure of the composites can be investigated through the measurement of the lattice fringe by HRTEM analysis in Figure 5(f). The good contact between MWCNTs and TiO$_2$ nanoparticles can be confirmed by HRTEM image. The anatase (101) phase of TiO$_2$ nanoparticles in MWCNTs/TiO$_2$ nanocomposites is confirmed with the lattice spacing of 0.35 nm while the (002) graphitic plane of the MWCNTs is assigned with the lattice spacing of 0.33 nm, revealing the heterojunction between MWCNTs-TiO$_2$ [37-41].
Figure 5: HRTEM images of (a) 3 wt%, (b) 5 wt%, (c) 10 wt % and (d) 15 wt % of MWCNT/TiO$_2$ nanocomposites, (e) high resolution of 10 wt % of MWCNT/TiO$_2$ and (f) lattice fringe of MWCNT/TiO$_2$ nanocomposites

The elemental composition of MWCNTs/TiO$_2$ nanocomposites prepared with different MWCNTs loadings were determined. The weight percent of Ti, C and O are tabulated in Table 3. From the table, all of the MWCNTs/TiO$_2$ nanocomposites showed the presence of Ti, C and O elements. The EDX data confirm that the carbon weight percentage in the samples increased and the amount of Ti decreased with an increasing loading of MWCNTs in the MWCNTs/TiO$_2$ nanocomposites.

Table 3: Elemental composition of (a) 3 wt %, (b) 5 wt %, (c) 10 wt % and (d) 15 wt % of MWCNTs/ TiO$_2$ nanocomposites
### 3.4 Phase Structure and Crystalinity

In this part of the experiment, XRD analysis was used to investigate the effect of MWCNTs loading on the crystallization and phase transition of MWCNTs/TiO$_2$ nanocomposites. The result clearly shows that the crystal structure of MWCNTs/TiO$_2$ nanocomposites is dependent on the MWCNTs loading. The XRD diffraction profiles exhibit identical patterns for all of the samples and only anatase phase of TiO$_2$ can be observed in the MWCNTs/TiO$_2$ nanocomposites. The formation of anatase phase can be obtained via the calcination process. The diffraction peaks at $2\theta = 25.9$ and $43.2$ corresponding with the (002) and (100) diffractions of the hexagonal graphite structure for MWCNTs samples. However, the peak at $2\theta = 25.9$ cannot be seen for MWCNTs/TiO$_2$ nanocomposites due to the peak was overlapped by the strong anatase TiO$_2$ peak at $2\theta = 25.2^\circ$. The MWCNTs is shielded by the peaks of anatase TiO$_2$ where the peak intensity of TiO$_2$ showing higher crystallinity than MWCNTs. The characteristic peaks in the pattern at 25.2 (101), 37.9 (004), 48.3 (200), 53.9 (105), 55.0 (211), 62.7 (204), 68.9 (116), 70.1 (220) and 75.5 (215) corresponded to TiO$_2$ crystalline anatase phase, compatible with those shown in the JCPDS No. 21-1272. As shown in Figure 6, the diffraction peak intensity decreases and the peak width becomes broader with increasing concentration of MWCNTs. This was due to the increased of MWCNTs that give rise to the smaller grain sizes and the degree of crystallinity. The presence of MWCNTs in the composite restrict the direct contact of grains and induce the small grain of TiO$_2$ nanoparticles in the MWCNTs/TiO$_2$ nanocomposites [12, 13, 33, 35, 42].

<table>
<thead>
<tr>
<th>Element</th>
<th>3 wt %</th>
<th>5 wt %</th>
<th>10 wt %</th>
<th>15 wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>61.68</td>
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<tr>
<td>O</td>
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<td>36.35</td>
<td>35.08</td>
<td>34.52</td>
</tr>
<tr>
<td>C</td>
<td>2.97</td>
<td>5.27</td>
<td>10.05</td>
<td>15.96</td>
</tr>
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</table>
**Figure 6:** XRD spectra of (a) TiO$_2$ nanoparticles, (b) 3 wt%, (c) 5 wt%, (d) 10 wt% and (e) 15 wt% of MWCNTs/TiO$_2$ nanocomposites

Table 4 presents the crystallite size, BET surface area and band gap energy of TiO$_2$ nanoparticles and MWCNTs/TiO$_2$ nanocomposites with various MWCNTs content. There was a correlation between crystallite size and surface area which revealed that the smaller the crystallize size, the larger the surface area. The crystallite size of the samples was calculated by the well-known Scherer’s equation [20]. For MWCNTs/TiO$_2$ nanocomposites, the crystallite size was found to decrease with increasing MWCNTs content. Typically, the full width at half maximum (FWHM) of the anatase peaks for MWCNTs/TiO$_2$ nanocomposites are slightly broadened with an increasing amount of MWCNTs, indicating a decrease in the size of anatase crystallite. This result suggests that the presence of the MWCNTs in the MWCNTs/TiO$_2$ nanocomposites hinders the anatase crystallite growth. Moreover, the crystallinity of TiO$_2$ in the MWCNTs/TiO$_2$ nanocomposites is impaired by loading MWCNTs, especially with higher content [33].

The BET results based on nitrogen sorption measurement showed the surface area of TiO$_2$ nanoparticles and MWCNTs/TiO$_2$ nanocomposites. As shown in Table 4, the combination of MWCNTs with TiO$_2$ showed an increase in the $S_{BET}$ as compared to the pure TiO$_2$ nanoparticles which may lead to an increase of the capability for adsorbing pollutants. The adsorption capacity of CNTs is very fast, which is mainly due to the highly accessible adsorption sites and the short intraparticle diffusion distance, which is related to their large specific surface area.
As a result, MWCNTs acts as supporting roles and strong adsorbent for enhancing the photocatalytic performance with the increasing of surface properties. The oxygen functional groups such as hydroxyl and carboxyl are introduced onto the CNT’s surface during the synthesis and purification process. These functional groups can influence the maximum adsorption capacity of CNTs and make them more hydrophilic and suitable for the adsorption [13, 43, 44]. The surface area of the MWCNTs/TiO$_2$ nanocomposites increased with the MWCNTs content. This phenomenon may be caused by the separation of TiO$_2$ crystalline particles due to the introduction of MWCNTs, and the consequently formation of a structure of high porosity. Moreover, the significant change of the TiO$_2$ crystallite size may also explain the increase in the specific area of the nanocomposites. Smaller particles or crystalline sizes will result in large surface area of the materials and thereby increasing the photocatalytic activity of the material. Also, as the crystalline size decreases, the number of active surface sites may increase.

The optical band gap of TiO$_2$ and MWCNTs/TiO$_2$ nanocomposites with various MWCNTs content was determined using the Kubelka-Munk expression and the estimated band gap is shown in Table 4. There is a correlation between the MWCNTs loading and absorption changes in the UV-Vis spectra. The increase amounts of MWCNTs obviously enhance the light absorption, owing to its good dispersion between TiO$_2$ and MWCNTs. The further elaboration on the effect of MWCNTs content on band gap energy of MWCNTs/TiO$_2$ nanocomposites will be discussed in Section 3.6.

Table 4: Effect of various MWCNTs content on crystallite size, BET surface area and band gap energy of MWCNTs/TiO$_2$ nanocomposites

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Crystallite size, nm</th>
<th>BET surface area (m$^2$/g)</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>12.9</td>
<td>75</td>
<td>3.23</td>
</tr>
<tr>
<td>3 wt%</td>
<td>10.8</td>
<td>80</td>
<td>3.10</td>
</tr>
<tr>
<td>5 wt%</td>
<td>9.1</td>
<td>96</td>
<td>3.06</td>
</tr>
<tr>
<td>10 wt%</td>
<td>8.9</td>
<td>108</td>
<td>2.48</td>
</tr>
<tr>
<td>15 wt%</td>
<td>7.5</td>
<td>163</td>
<td>2.34</td>
</tr>
</tbody>
</table>
3.5 Raman Analysis

In this study, Raman analysis was used to determine and understand the structural changes of MWCNTs/TiO$_2$ nanocomposites. Figure 7 shows the Raman spectra of the pure TiO$_2$ and MWCNTs/TiO$_2$ nanocomposites (3-15 wt %) which confirmed the presence of MWCNTs, even at the low concentrations. Five obvious Raman modes are present at 143 cm$^{-1}$, 198 cm$^{-1}$, 395 cm$^{-1}$, 517 cm$^{-1}$ and 639 cm$^{-1}$, which are belong to the E$_g$ anatase vibration mode, E$_g$ mode, B$_{1g}$ mode, B$_{1g}$ + A$_{1g}$ mode and weak E$_g$ mode, respectively. This result clear to show that anatase phase is predominantly in both TiO$_2$ and MWCNTs/TiO$_2$ nanocomposites. The intensity of the anatase peaks in MWCNTs/TiO$_2$ nanocomposites is lower than that of TiO$_2$, which revealed the decrease of crystallinity and the energy of lattice vibration. In MWCNTs/TiO$_2$ samples, the peak at 1315 cm$^{-1}$ was assigned to the structural disorder of the wall of the nanotubes (D-band) while the peak at 1594 cm$^{-1}$ was associated with the tangential vibrational mode (G-band). The intensity of the D and G-band increased with increasing MWCNTs concentrations, showing an interaction between TiO$_2$ and MWCNTs due to the creation of an electronic interphase interaction between MWCNTs and TiO$_2$ phases which enhanced the charge transfer from TiO$_2$ to the MWCNTs. On the contrary, the intensity of E$_g$ anatase mode decrease and the peak width becomes broadened with higher amount of MWCNTs, which is attributed to the abrupt reduction in TiO$_2$ percentage [12, 13, 33, 35, 36]. The E$_g$ anatase mode of TiO$_2$ in the nanocomposites was blue-shifted to a higher wavenumber as compared with the pure TiO$_2$ anatase, indicating different compressive stresses on the atoms of TiO$_2$ nanoparticles. It is basically due to the strength of the bonding between TiO$_2$ and the MWCNTs (Ti-O-C bond) and thus, different vibrational wavenumbers were produced. The quality of MWCNTs or degree of “graphitization”, originated from defects associated with the amount of sp$^3$ hybridization after purification of the MWCNTs. It was indicated by the intensity ratio of D band to G band (I$_D$/I$_G$) as shown in Table 5. The I$_D$/I$_G$ ratio of the MWCNTs/TiO$_2$ nanocomposites was increased with increasing amount of MWCNTs (Figure 8). An increased of the I$_D$/I$_G$ ratio was due to the nucleation of TiO$_2$ on the surface of MWCNTs and also attributed to the transfer of electrons from TiO$_2$ to MWCNTs. CNTs have an excellent electron transfer ability with a high electrical conductivity during photoexcitation, and transfer the electron away from the TiO$_2$ particles after photoexcitation. Additionally, it is noted that the D-band is red-shifting indicated a close interaction between MWCNTs with TiO$_2$ and the formation of C-O-Ti bonds stretches the in-plane covalent bonds. However, it is renowned that excessive amount of MWCNTs created more defects and increased the disorder of MWCNTs caused by Ti-C bonds in the interface. The formation of Ti-C bonds shows a determinant role.
in charge transfer enhancement. Substantially, XRD and Raman analysis confirmed the presence of anatase phase in the samples [13].

**Figure 7**: Raman spectra of (a) TiO$_2$, (b) 3 wt%, (c) 5 wt%, (d) 10 wt% and (e) 15 wt% of MWCNTs/TiO$_2$ nanocomposites

**Figure 8**: Raman shifts of the D band and G band of (a) 3 wt%, (b) 5 wt%, (c) 10 wt% and (d) 15 wt% of MWCNTs/TiO$_2$ nanocomposites
Table 5: I_D/I_G ratio of (3-15) wt% of MWCNTs/TiO_2 nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>I_D/I_G ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 wt% MWCNTs/TiO_2</td>
<td>0.75</td>
</tr>
<tr>
<td>5 wt% MWCNTs/TiO_2</td>
<td>0.94</td>
</tr>
<tr>
<td>10 wt% MWCNTs/TiO_2</td>
<td>1.10</td>
</tr>
<tr>
<td>15 wt% MWCNTs/TiO_2</td>
<td>1.33</td>
</tr>
</tbody>
</table>

3.6 FTIR and XPS analysis of MWCNTs/TiO_2 nanocomposites

The chemical bonding and functional groups of the MWCNTs/TiO_2 nanocomposites was investigated by Fourier Transform Infrared Spectroscopy (FTIR) and (XPS) analysis, respectively. The oxidation of MWCNTs with nitric acid has introduced many functional groups, such as hydroxyl, carboxyl, and carbonyl groups on the surface of purified MWCNTs. The appearance of absorption peak at 3430 cm\(^{-1}\) is attributed to the stretching vibration of –OH groups of the adsorbed water molecules as shown in Figure 9 (a). In addition, the peak at 2921 cm\(^{-1}\) was attributed to the H-C stretch modes of H-C=O in the carboxyl group. Meanwhile, the peak at 2371 cm\(^{-1}\) was assigned to hydrogen bonding due to the COOH groups present. The addition of HNO_3 leads to the formation of a carboxyl group (1720 cm\(^{-1}\)) in the purified MWCNTs due to the oxidation of some carbon atoms on the surfaces of the MWCNTs. The band at 1575 cm\(^{-1}\) was corresponded to the stretching vibrations of C=C on the nanotubes. The peaks at 1160 cm\(^{-1}\) demonstrates the formation of carbonyl groups in the purified MWCNTs. The FTIR spectrum of nanocomposites shows the characteristic peaks of Ti-O bond in the low wavenumbers at around 570 cm\(^{-1}\) [45-47].

In order to study the formation of the chemical bonds between Ti-O-C and Ti-C after loading TiO_2 with MWCNTs, the interaction between TiO_2 with MWCNTs was further investigated by the analysis of XPS results. Figure 9(b) displays the C 1s spectra of the MWCNTs/TiO_2 sample. Five peaks were observed in the C 1s spectra after peak fitting. The main peak located at 284.7 eV was associated with graphitic carbon and C–C bonds from MWCNTs. The second peak at 286.1 eV was attributed to C–O bonds, and the broad peaks located at 287.4 eV and 289.1 eV represented the C=O and COOH bonds, respectively [36, 48]. The presence of new peak at about 283.7 eV further supported the formation of titanium-carbide bond. It is thereby
concluded that the Ti–O and C–O bonds that present in the C 1s and O 1s XPS spectra after the peak fitting led to the anticipation of intimate connection between MWCNTs and TiO₂ through Ti–O–C bonds. [44, 49, 50].

Figure 9: (a) FTIR and (b) XPS spectra of MWCNTs/TiO₂ nanocomposites

3.6 Light absorption and photoluminescence (PL) properties

The optical properties of the as-prepared MWCNTs/TiO₂ nanocomposites with various MWCNTs content together with pure TiO₂ nanoparticles have been measured by UV-vis diffuse reflectance spectra in the range of 200-800 nm. As displayed in Figure 10, the absorption spectra of MWCNTs/TiO₂ nanocomposites was shifted towards longer wavelength (red shift) as compared to that of pure TiO₂ nanoparticles. MWCNTs/TiO₂ nanocomposites exhibited an increase in light absorption with increasing MWCNTs content which is in agreement with the colour changing from white to dark grey. These results revealed that MWCNTs enhance the light absorption of the entire UV-vis range because MWCNTs are good light absorptive materials. MWCNTs can also act as a metal to accept a photogenerated electron and reduce the charge recombination rate. As a result, the reduction in the band gap energies of TiO₂ nanoparticles will enhance the photocatalytic activity of MWCNTs/TiO₂. Basically, the band gap energies E₉ value was determined using the Kubelka-Munk function of optical absorption for allowing indirect transitions as shown in Table 4. The indirect band gap energy for 3 wt % MWCNTs/TiO₂, 5 wt % MWCNTs/TiO₂, 10 wt % MWCNTs/TiO₂ and 15 wt % MWCNTs/TiO₂ were 3.1, 3.06, 2.48 and 2.34 eV, respectively, this enhancement of absorption
increases with the enhancement of the MWCNTs contents. It can be attributed to the enhancement of the surface electric charge of the TiO$_2$ in the nanocomposites because of the introduction of MWCNTs, which leads to the possible electronic transitions between the orbital of TiO$_2$ and MWCNTs. The great improvement in the light absorption and the reduced energy band gap can influence on the fundamental process of the photogenerated carrier formation and separation in the photocatalytic process [12, 13, 33, 35, 36].

![Figure 10: UV spectra of (a)TiO$_2$ nanoparticles, (b) 3 wt%, (c)5 wt%, (d)10 wt% and (e)15 wt% of MWCNTs/ TiO$_2$ nanocomposites]

The PL spectroscopy has been widely used to provide information such as charge carrier trapping, immigration, and charge transfer. One of the factors limiting the photocatalytic performance of the TiO$_2$ photocatalyst is the fastest recombination of the photogenerated electron holes pairs besides the wide band gap phenomenon. During the photocatalysis process, the emission of photons prompts to PL in virtue of electron hole/pairs recombination. This is attributed to the reverse radiative deactivation from the excited-state of the Ti species. The PL spectra of the TiO$_2$ and MWCNTs/TiO$_2$ nanocomposites were presented in Figure 11. As
anticipated, TiO$_2$ nanoparticles display a broad PL emission band and higher PL intensity, indicating highest charge recombination rate. Obviously, the MWCNTs/TiO$_2$ nanocomposites show diminished PL intensity as compared to the pure anatase TiO$_2$ nanoparticles. This indicates that the electron-hole recombination rate of self-trapped excitation in TiO$_2$ is reduced by the introduction of MWCNTs. Figure 11 indicates the effect of the MWCNTs content on the recombination rate of the electron holes/pairs. Basically, MWCNTs have a variety of electronic properties, it may also possess metallic conductivity as one of the many possible electronic structures. MWCNTs have a large electron-storage capacity which acts as an electron reservoir for trapping electrons, particularly generated from the photoexcitation of TiO$_2$ nanoparticles. The recombination time for the photogenerated electron-hole pairs has the order of $10^{-9}$ s while the time scale for the chemical interaction with adsorbed pollutant species was in the ranges of $10^{-8}$ to $10^{-3}$ s [51]. The intensity of PL decreased with increasing in MWCNTs loading. This implies a suppression of charge recombination in the presence of MWCNTs [12, 33]. Several studies have proved that MWCNTs would act as scavengers of the photogenerated electrons arisen from the immobilization TiO$_2$ nanoparticles and thus, the fast electron transfer at the interface between the carbon and the TiO$_2$ layers are improved. The mixing of the delocalized p state of the carbon with O 2p orbital in the valence band of TiO$_2$, which in turn shift the valence band edge of TiO$_2$ upwards to narrow down the band-gap of TiO$_2$ significantly.

![Figure 11: PL spectra of (a) TiO$_2$, (b) 3 wt%, (c) 5 wt%, (d) 10 wt% and (e)15 wt% of MWCNTs/ TiO$_2$ nanocomposites](image)

The photocatalytic efficiency of MWCNTs/ TiO$_2$ nanocomposites (97 %) is higher than TiO$_2$ (71 %) due to the MWCNTs acting as electron sinks and thereby hinders the
recombination rate of the electron-hole pairs. The photogenerated holes are captured by MWCNTs/TiO$_2$ nanocomposites and transform to hydroxyl radicals, which are the main reactive species involved in decomposition of organic pollutants. There are more hydroxyl radicals being produced by MWCNTs/TiO$_2$ nanocomposites, which greatly improve the photocatalytic degradation rate [13, 35]. The photocatalytic degradation studies of DMPEs were carried out for (3 wt % - 15 wt %) of MWCNTs/TiO$_2$ to further investigate their photocatalytic performance (Figure 12). It can be seen that only small changes in concentration were observed when the experiment was performed with a photocatalyst in the darkness, indicating the stability of the DMPEs. This result confirms that degradation of the DMPEs in the presence of photocatalyst, but without light irradiation is insignificant. The reason is that no electron-hole pair could be generated in the semiconducting material without the assistance of light irradiation. The photodegradation of DMPEs during the 3 h photoreactions increase upon enhancing the MWCNTs contents from 3 to 10 wt % and then decrease with a further enhancement to 15 wt %. The reason is that MWCNTs can act as electron acceptors and transfer channels and improve the charge separation efficiency. Once the amount of MWCNTs exceed than 10 wt %, especially for 15 wt % of MWCNTs/TiO$_2$ nanocomposites, the photodegradation of DMPEs decreases. It can be seen that 10 wt % of MWCNTs exhibited an optimal photocatalytic activity among the samples, although the absorbance is continuously increased with the enhancement of the MWCNTs loadings. When the amount of MWCNTs increases, photon absorption would also increase, but increased adsorption capacity could not counteract the influence of fewer active sites. Basically, the presence of MWCNTs in the nanocomposites can lead to the decrease in the relative amount of TiO$_2$ in the photocatalyst and then to the decrease of the photogenerated carriers. This is because the same amount of photocatalyst was added for the photoreaction, and hence, the photodegradation of DMPEs decreases especially for the nanocomposites containing MWCNTs larger than 10 wt %. In addition, an apparent enhancement of visible light absorption was observed for MWCNTs/TiO$_2$ nanocomposites, this was mainly attributed to the introduction of more MWCNTs and does not necessarily mean an improved photoactivity of TiO$_2$ [33, 36]. Thereby, it has been shown that an optimal amount of MWCNTs to incorporate in the composite is needed to obtain good improvement in the catalyst efficiency. Furthermore, several authors have made similar observation that little TiO$_2$ or excessive CNTs addition shielded the TiO$_2$ and reduced the UV intensity, due to photon scattering by the nanotubes. However, a high TiO$_2$ content was found to be ineffective in suppressing exciton recombination due to the large distance between the titania and the nanotubes. Based on this study, it is clear that the MWCNTs/TiO$_2$ composite provides high
surface area which is beneficial for photocatalytic activity, as it provides high concentration of target organic substances around sites activated by UV irradiation [33, 52].

![Figure 12: Photocatalytic activity of a) TiO$_2$, b) dark adsorption with MWCNTs/TiO$_2$ and c-f) 3, 5, 10, 15 wt% of MWCNTs / TiO$_2$ to degrade DMPEs](image)

3.7 The identification of photoproducts by HPLC analysis

The formation of intermediate products was studied in two experiments, in which DMPEs in aqueous solution was degraded in the MWCNTs/TiO$_2$ and TiO$_2$ systems, respectively. The applicability of the proposed method for the determination of DMPEs and its degradation products was demonstrated by analysing 7 aliquots of MWCNTs/TiO$_2$ and TiO$_2$. HPLC analysis was run just after sample preparation (t=0) and at the following times: 15, 30, 45, 60, 120 and 180 min. The HPLC data show that DMPEs is sensitive to photodegradation under the conditions used in this study. During irradiation of DMPEs three photoproducts were detected, as can be seen in the chromatogram (Figure 13). In both reactions, all photoproducts with shorter retention times than that of DMPEs (8.99 min) correspond to compound of greater polarity than the parent compound based upon retention times on the analytical column and mobile phase composition. Degradation of DMPEs increased with increasing exposure time and reached 97% and 71% for MWCNTs/TiO$_2$ nanocomposites and TiO$_2$ nanoparticles after 3 h; also an increase in the number and concentration and photodegradation products were observed. The results have shown that a large decrease in the concentration of DMPEs for MWCNTs/TiO$_2$ after exposure to UV light was observed and detected in HPLC assay. This
decrease is an important source of concern and suggests further studies about its photodegradation mechanism.
Figure 13: HPLC chromatogram of (a) TiO$_2$ nanoparticles and (b) MWCNTs/TiO$_2$ nanocomposites on photodegradation of DMPEs over time

3.8 Photocatalytic degradation pathway of Dimethyl phthalate pollutant

The reaction network for the photo degradation of dimethyl phthalate was analysed using the reaction intermediates by UHLPC/Orbitrap/MS analyzer. Table 6 reports the identified dimethyl phthalate (DMPEs) degradation intermediates and relative mass (m/z) value observed using MWCNTs/TiO$_2$ nanocomposites. Based on LCMS/MS/MS peaks, the major reaction attack occurred involving the hydroxylation of the aromatic ring which enables the plotting of potential degradation pathway. The obtained m/z at 194.02172 shows presence of DMPEs after 180 min of photocatalytic reaction and indicates an incomplete removal of DMPEs. The degradation pathway involves the attack of the •OH radicals on the pollutant, where they were commonly reported according to their decrease molecular weight. The photoproduct underwent an addition of •OH radicals on the aromatic rings to form hydroxyl-DMP at m/z 211.19134. The attack of the OH radicals led to the formation of 4-hydroxyl-DMP photoproducts on the aromatic ring, followed by the loss of a hydrogen atom at m/z 210.18340. Next, dimethyl hydroxyphthalate underwent the subsequent removal of two methoxy group forming the stable intermediate, 4-hydroxyl-1, 2-dibenzoic acid which contained two aldehyde functional group at m/z 150.13140.

<table>
<thead>
<tr>
<th>Compound name</th>
<th>Structure formula</th>
<th>Molecular formula</th>
<th>Mass (m/z)$^a$</th>
<th>Mass spectrum</th>
</tr>
</thead>
<tbody>
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<td>Dimethyl phthalate</td>
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<td>211.19134</td>
<td></td>
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<tr>
<td>4-hydroxyl-DMPEs</td>
<td>C$<em>{10}$H$</em>{10}$O$_5$</td>
<td></td>
<td>210.1834</td>
<td></td>
</tr>
</tbody>
</table>

Table 6: Dimethyl phthalate degradation intermediates UHLPC/Orbitrap/MS using MWCNTs/TiO$_2$ nanocomposites
4-hydroxyl-1,2-dibenoic acid

\[ \text{C}_8\text{H}_6\text{O}_3 \]

\[ 150.1314 \]

\(^a\) MS analysis in +ve ion mode

4. Conclusions

A series of MWCNTs/TiO\(_2\) nanocomposites with different MWCNTs contents were successfully synthesized via incorporation of TiO\(_2\) nanoparticles on the purified MWCNTs surface by a modified sol-gel method. For the effect of MWCNTs loading (3 wt% to 15 wt%), the results showed that the surface area of MWCNTs/TiO\(_2\) nanocomposites has increased when the MWCNTs loading was increased up to 15 wt%. In addition, the PL results divulged that the 15 wt% of MWCNTs/TiO\(_2\) showed the highest electron charge efficiency with the lowest electron recombination rates. The suitable loading of MWCNTs appeared to be highly dependent on the morphology of the MWCNTs/TiO\(_2\). The apparently contradictory findings could be partially explained because of TiO\(_2\) is the photoactive phase while MWCNTs is acting as an electron sink, it is beneficial to incorporate higher percentages of TiO\(_2\) to promote exposed TiO\(_2\) surface area. The higher loadings of MWCNTs (>10 wt%) has caused the blockage of TiO\(_2\) active sites, and thus, lower the photocatalytic activity of MWCNTs/TiO\(_2\) nanocomposites. Besides, excess MWCNTs have caused aggregation of TiO\(_2\) nanoparticles (as observed in the FESEM result), leading to a decreased in amount of DMPEs being adsorbed on the surface of MWCNTs/TiO\(_2\) nanocomposites. Nevertheless, 10 wt% MWCNTs/TiO\(_2\) nanocomposites was found to be the optimum loading as it has showed the highest photocatalytic efficiency among the samples.

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References


