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Carbon modified anatase TiO₂ for the rapid photo degradation of methylene blue: A comparative study

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Abstract
Activated carbon (AC) and carbon nanotubes (CNTs) doped anatase titania were prepared using cetyl trimethylammonium bromide (CTAB) as a dispersant and anchoring agent. The XRD and Raman spectroscopy revealed that the carbon doped titania retained its anatase structure, even upon calcination at 500 °C. The SEM/TEM images showed that the TiO₂ particles were well dispersed with the carbon source. N₂ adsorption-desorption analysis indicates a distinct change in the surface area of the AC doped TiO₂ in which the presence of micropores is clearly evident. The photoluminescence analyses showed that doping the titania with carbon enhanced the separation of the charge carriers (e⁻/h+), resulting in a lower recombination rate, thus increasing the longevity of the photocatalysts. The XPS peaks at ~285 eV showed the presence of carbon. Both AC and CNT doped titania exhibited excellent photocatalytic ability for the degradation of MB under UV irradiation. The carbon doped titania samples also showed high stability under prolonged UV irradiation and could be used up to four cycles without significant loss of catalytic efficiency.

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1. Introduction
Water borne pollutants such as pesticides and dyes are a serious threat to the environment. These pollutants are mostly non-biodegradable, carcinogenic and in some cases highly poisonous towards aquatic and human life. The continuous discharge of these pollutants has caused detrimental effects towards the environment. Therefore, several steps were taken to combat this problem by removing the pollutants from the water system before discharging it into main water bodies. Advanced oxidation processes (AOPs), biodegradation using microbial organisms and adsorption are some of the methods currently employed for the removal of hazardous organic pollutants [1–4].

Among these methods, AOP is considered by far the most efficient and environmentally friendly way of pollutant removal and it is widely studied by scholars. AOP utilizes the hydroxyl radical (·OH) and several other reactive oxygen species (ROS) to oxidize the molecules of pollutants (usually organic) into smaller fragments and eventually into carbon dioxide and water. Titanium dioxide powder is able to produce the hydroxyl radicals once it is excited by photons (UV light), enabling it to be utilized as a photocatalyst and therefore, is widely used to decontaminate polluted water systems.

Honda and Fujishima discovered the potential of using titanium dioxide as a photocatalyst after witnessing its capability to split water molecules into hydrogen and oxygen atoms [5]. Ever since, titanium dioxide has been synonymous for water treatment studies around the globe. Anatase titania is known for its excellent photocatalytic capabilities. Therefore, many studies have been reported on the photo degradation of organic pollutants, usually dyes [6–8] and herbicides using titanium dioxide powder [9,10]. However, the large band gap energy (3.2 eV) and high electron-hole recombination rate inhibit its potential as an efficient photocatalyst [11]. Furthermore, the relatively low surface area of unmodified anatase powder limits its adsorption capacity towards the pollutant molecules [12]. In addition, the nano-sized titanium dioxide powder is extremely miscible in aqueous solutions and readily forms a milky white solution in water which requires expensive and tedious filtration methods [13]. This limits its recoverability and reusability.

These shortcomings have spiralled into a range of studies on the modification of titania using a wide range of materials such as silica, carbon nanotubes (CNTs), activated carbon (AC), transition metals and lanthanides [14–18]. These modifications are mainly aimed at improving the photocatalytic performance of anatase ti-
tania. Doping of carbon onto the titania matrices has been increasingly reported in recent years. It is generally known that tubular carbonaceous materials such as CNT doped titanium dioxide could exhibit hetero junction properties [15]. This in turn would enhance the separation of the photo-induced charge carriers and therefore, exhibit enhanced photocatalytic activity of the carbon-TiO$_2$ composite due to the lower electron-hole recombination rate [15]. Furthermore, carbon doping would also increase the adsorption capabilities of titanium dioxide and thus, attract more organic molecules to be photo-catalysed in any given time [16]. In particular, AC and CNTs have garnered some attention in recent photocatalytic studies. AC is reputed for its large surface area, porosity and amorphous nature [19], while CNTs are known for their crystalline and ordered structure [20]. These allotropes of carbon have contrasting intrinsic properties and are likely to exhibit interesting effects when doped onto the titanium dioxide particles.

The focal point of the present study is to investigate the effects of doping AC and CNTs respectively onto the matrices of titanium dioxide particles. AC and CNTs were doped onto the anatase titania particles with the aid of cetyl trimethylammonium bromide (CTAB) as a dispersant and anchoring agent. The use of CTAB as an anchoring agent for anatase has not been reported in the literature. Photocatalytic studies were carried out with these two composites via the degradation of methylene blue (MB) as a model pollutant under UV irradiation.

2. Experimental

2.1. Materials

Titanium dioxide (99% anatase, Sigma) was used as the source of metal oxide in the study. In addition, other chemicals such as CTAB (Riedel-de Haen, 98%), sodium hydroxide pellets (Qrec, 99%), potassium hydroxide pellets (Qrec, 99%), nitric acid (Qrec, 69%), ethanol (Qrec, 98%), terephthalic acid (Aldrich, 98%) and methylene blue (MB, Sigma, $\lambda_{max} = 661$ nm) were also used. The rice husk (RH) was obtained from a rice mill in Penang, Malaysia. All chemicals were of analytical grade and used without further purification.

2.2. Preparation of activated carbon (AC) from rice husk

Activated carbon was prepared from RH according to the method reported in Muniandy et al. [19]. The RH was burnt at 400 °C in a muffle furnace after the removal of silica via alkali leaching to obtain the rice husk charcoal (RHC). The RHC was mixed with KOH (40% w/w solution) in the ratio of 1:5 (RHC: KOH) and activated at 850 °C for 60 min under nitrogen aeration. The AC was later washed with 3 M HNO$_3$ until neutrality (pH ~6.8-7.2) and dried at 100 °C for 24 h.

2.3. Preparation of carbon nanotubes (CNT) via chemical vapor deposition of methane

The carbon nanotubes were prepared via CVD method from methane gas as reported elsewhere [21]. About 0.05 g of the mixed metal oxide catalysts (Co-Mo/MgO, with a composition ratio of 10:20:70) was weighed onto a quartz boat which was then placed at the center of the tubular furnace. The furnace was heated from room temperature to 800 °C under nitrogen aeration at 150 mL min$^{-1}$. The temperature was maintained at 800 °C for 30 min as methane was introduced into the furnace for the formation of CNTs. After the given time, the temperature of the furnace was allowed to cool down under nitrogen flow. The CNTs collected was washed with 150 mL of 3.0 M HNO$_3$ for 1 h to remove the metal oxide catalyst. The CNTs were later filtered and rinsed until the pH of the filtrate reached 6.8-7.2.

2.4. Preparation of AC and CNT modified anatase

The required mass of the AC (or CNT) was first weighed and added to 100 mL of ethanol. A specified mass of CTAB (AC: CTAB = 1:1, ratio by mass) was added as a dispersing and anchoring agent into the mixture and it was left to sonicate for 1 h in a separate preparation, about 10 g of anatase titania was weighed and stirred in 100 mL of ethanol for 30 min followed by sonication for another 30 min. The mixture of CTAB and AC was added dropwise into the ethanolic anatase solution while stirring. The carbon-anatase mixture was later sonicated for 2 h followed by rapid stirring for another 1 h. The mixture was then allowed to age for 24 h under room conditions. After aging, the mixture was dried at 105 °C for 24 h. The dried modified anatase solid was then ground to powder and calcined under N$_2$ aeration at 500 °C for 1 h. The resulting catalyst was labelled as xAC-TiO$_2$ (x = 2.5, 5, 7, 9 percent AC). A similar method was adopted for preparing the CNT modified anatase based on the optimised AC loading. This sample was labelled as 7CNT-TiO$_2$.

2.5. Characterizations

The prepared samples were characterized using FT-IR spectroscopy (Perkin Elmer System 2000 FT-IR Spectrophotometer) with pellets prepared using KBr, FT- Raman spectra (Renishaw in Via Raman with HeNe laser, $\lambda_{max} = 633$ nm, 2 mW) $\mathrm{N}_2$ adsorption-desorption analysis (Micromeritics ASAP 2020 porosimeter), powder x-ray diffraction (Siemens Diffractometer D5000 Kristalloflex, equipped with Cu $\mathrm{K\alpha}$ radiation, $\lambda = 0.154$ nm, voltage = 40 kV, current = 30 mA) from 10° to 90° and thermal gravimetric analysis (TGA/SDTA 851e Mettler Toledo) under oxygen flow with a heating rate of 20 °C min$^{-1}$ from 30 °C to 900 °C. The surface/topography of the modified titania samples were studied via scanning electron microscopy (SEM Leica Cambridge). The morphology of the prepared samples was investigated using transmission electron microscopy (TEM Phillips CM12). In addition, further characterizations such as photoluminescence (PL) (MicroRaman Renishaw, helium cadmium laser, $\lambda_{max} = 325$ nm with CCD detector) and XPS analysis (AXIS Ultra DLD, Kratos, equipped with an Al $\mathrm{K\alpha}$ X-ray source −1486.6 eV at 10 mA, 15 kV to analyze a $300 \mu m \times 700 \mu m$ area under 7.6 × 10$^{-9}$ Torr - ultra vacuum environment in the sample analyzing chamber) were also carried out.

2.6. Photocatalysis studies

About 400 mL of 50 mg L$^{-1}$ MB solution was prepared from 1000 mg L$^{-1}$ stock solution. The MB solution was then added to 0.25 g of the required photocatalyst and stirred in the dark for 1 h before it was irradiated with UV light (UV-RS-1 equipped with a medium pressure mercury lamp, $\lambda_{max} = 375$ nm), with air being pumped through the UV reactor using an aquarium pump as the aeration source at a steady rate of 200 mL min$^{-1}$ (MOUSE Air Pump M101) as shown in Scheme 1. The concentration of the MB solution was monitored periodically at selected time intervals using a UV/Vis spectrophotometer (UNICO 2100 Spectrophotometer) at the wavelength of 661 nm corresponding to the $\lambda_{max}$ of MB. The percentage of MB remaining and rate constants of the photocatalytic reactions were calculated from the following equations;

\[
\text{MB remaining} = \frac{C_t}{C_0} \times 100 \% \\
\ln \left( \frac{C_t}{C_0} \right) = kt, \ k = \text{rate constant} \left( \text{min}^{-1} \right)
\]

Where $C_t$ and $C_0$ are the concentration of MB at time t and zero respectively.
2.7. Detection of hydroxyl radicals with spectrofluorometer

Terephthalic acid (TA) solution was employed for the detection of hydroxyl radicals using a spectrofluorometer. The TA solution was prepared by following the method reported by Xiao et al. [22]. Firstly, the desired amount of TA powder was dissolved in $2 \times 10^{-3}$ M solution of NaOH producing TA solution with a fixed concentration of $5 \times 10^{-4}$ M. The TA solutions were irradiated under UV light in the presence of the catalysts. Samples were withdrawn every 15 min interval to determine the intensity of the fluorescence spectra (with an excitation wavelength of 315 nm using Perkin Elmer LS 55 Fluorescence Spectrophotometer) which indirectly corresponds to the amount of hydroxyl radicals generated.

2.8. Reusability studies of the AC and CNT modified anatase

The reusability studies were carried out using two different methods of regeneration of the catalyst: (a) the catalyst was
filtered and dried at 105 °C for 72 h after each successive run before being tested again under the same conditions to determine its photocatalytic activity. (b) the catalyst was filtered and dried for 24 h at 105 °C. Then it was collected and stirred in 250 mL of distilled water for 6 h before being filtered and rinsed with acetone/water mixture several times. The catalysts were then subjected for thermal activation at 105 °C for 72 h, before reused in the catalysis reaction.

2.9. Mineralization studies

Total organic carbon (TOC) was carried out to determine the degree of mineralization of the MB under UV irradiation. The
Fig. 5. The general XPS scans for the AC and CNT doped TiO$_2$ samples.

Fig. 6. The XPS narrow scans. (a and b) For C 1s, (c and d) for Ti 2p and (e and f) for O 1s in 7AC-TiO$_2$ and 7CNT-TiO$_2$ respectively.

Fig. 7. The effect of various AC loadings onto anatase TiO$_2$ for the degradation of MB under UV irradiation (400 mL of 50 mg L$^{-1}$ MB, 0.625 g L$^{-1}$ catalyst dosage, under aeration ~200 mL min$^{-1}$).
MB solution was withdrawn at selected time intervals, filtered with 0.45 μm syringe filter and analyzed using TOC-L Shimadzu analyzer.

Ion chromatography (IC) analysis was conducted using an IC equipment (Metrohm 792 Basic IC) for anion detection with column specifications; METROSEP ASUPP 5–150, (size: 150 mm × 4.00 mm, particle size: 5.00μm) equipped with conductivity detector and ICNet 2.3 computer software. The mobile phases used were 1.00 mmol L⁻¹ sodium carbonate with 3.20 mmol L⁻¹ sodium bicarbonate as the first eluent and 100 mmol L⁻¹ of sulfuric acid as the second eluent. The flow rate of the column and injection volume was maintained at 0.70 mL min⁻¹ and 1.00 mL respectively.

3. Results and discussion

3.1. Characterizations of the prepared catalysts

Fig. 1a shows the TGA-DTG plots (under oxygen aeration) showing the carbon content of the modified anatase. There are two distinct stages of weight loss for both 7AC-TiO₂ and 7CNT-TiO₂. The first stage of weight loss occurred around 30–100 °C. This was attributed to the evaporation of water molecules trapped on the surface and within the pores of the sample [19]. The weight loss calculated was 0.70 and 1.51 wt. % for 7CNT-TiO₂ and 7AC-TiO₂ respectively. The 7AC-TiO₂ exhibited higher weight loss due to its larger surface area which enabled it to adsorb more moisture compared to 7CNT-TiO₂ [19]. The second stage of weight loss took place between 465 and 900 °C for both samples. The weight loss at this stage was attributed to the degradation of the AC and the CNT which were doped into the anatase matrix [23]. The weight loss observed was 5.93 and 5.77 wt. % for 7CNT-TiO₂ and 7AC-TiO₂ respectively. In comparison, the pure anatase TiO₂ sample did not exhibit any significant weight loss (< 1 wt. %) from the TGA analysis as shown in Fig. 1a.

The powder XRD spectra in Fig. 1b shows that the crystallinity of the samples were similar to that of pure anatase. The peaks at 25.3°, 37.8°, 48.1°, 54.1°, 55.1°, 62.8°, 68.9°, 70.1°, 75.2° and 82.9° correspond to the (101), (004), (200), (105), (211), (204), (115), (220), (215) and (224) planes of anatase titania [24]. The XRD spectra for 7AC-TiO₂ and 7CNT-TiO₂ did not exhibit any phase transformations even after being calcined at 500 °C. In addition, the Raman spectrum in Fig. 1c also shows the similarity between 7AC-TiO₂, 7CNT-TiO₂ and the unmodified TiO₂. The peaks (Fig. 1c) at 142 (E₂g), 195 (B₁g), 395 (B₂g), 515 (A₁g + B₂g - doublet) and 636 (E₁g) cm⁻¹ [24] are signals typical for anatase TiO₂. Rutile peaks (at 439.6 (E₆g), 612 (A₁g), and at 834 (B₂g) cm⁻¹ [25]) were, however, not detected in the prepared samples. Thus carbon doping could lead to the suppression of phase transformation from anatase to rutile, thereby stabilizing the anatase samples under prolonged heat treatment [26].

In addition, the magnified region of the FT-Raman spectra in Fig. 1d shows the appearance of the D and G bands which prove the presence of graphitic carbon for both AC and CNT doped titania samples respectively [27]. The D band (1340 cm⁻¹) refers to the degree of disorderness of a carbonaceous sample, whereas the G band (1590 cm⁻¹) refers to the presence of the graphitic structure [27,28]. From Fig. 1d, it was observed that the intensity of the D band (1340 cm⁻¹) was higher in 7AC-TiO₂ compared to that of 7CNT-TiO₂. This shows that AC was amorphous, hence the lack of ordered structure compared to the crystalline and ordered CNTs in 7CN-TiO₂.

The elemental analysis in Table 1 was obtained from the EDX analysis. The presence of Br (due to CTAB) in both 7AC-TiO₂ and 7CNT-TiO₂ was shown to be present in significant amount, which proves the presence of CTAB in the samples. Thus the CTAB has indeed been incorporated into 7AC-TiO₂ and 7CNT-TiO₂.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Elements</th>
<th>Ti</th>
<th>C</th>
<th>O</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>7AC-TiO₂</td>
<td></td>
<td>31.74</td>
<td>12.62</td>
<td>54.84</td>
<td>0.80 (0.96)</td>
</tr>
<tr>
<td>7CNT-TiO₂</td>
<td></td>
<td>31.55</td>
<td>12.87</td>
<td>53.36</td>
<td>0.32 (1.83)</td>
</tr>
<tr>
<td>Anatase TiO₂</td>
<td></td>
<td>59.95</td>
<td>-</td>
<td>40.05</td>
<td>-</td>
</tr>
</tbody>
</table>

*Results in parentheses are obtained from XRF analysis.

Table 1 The elemental analysis for the photocatalysts used in the present study.
0.054 cm³ g⁻¹. In addition 7AC-TiO₂ showed an additional mesopore volume of 0.018 cm³ g⁻¹.

The isotherm plots in Fig. 2 indicate that the anatase TiO₂ and 7CNT-TiO₂ samples exhibit type III isotherm, which is common for materials that have weak solid-gas interaction. The 7AC-TiO₂ sample showed type III isotherm as well, but with a high knee (0 - 0.2 P/PO) which is a distinctive feature of microporous materials [19]. The pore width (D₃₄₅) of 7AC-TiO₂ (11.2 nm) is smaller than that of anatase TiO₂ (20.6 nm) and 7CNT-TiO₂ (22.5 nm). As expected the smaller pore 7AC-TiO₂ resulted in a large surface area. However, 7AC-TiO₂ also showed the presence of micropores as shown in Table 2 and also from the pore distribution curve in Fig. 2 (inset).

Fig. 3 shows the SEM and TEM images of 7CNT-TiO₂ and 7AC-TiO₂. CTAB (anionic surfactant) which was used as a dispersant has both hydrophilic and hydrophobic ends. The carbon materials (dopant) would anchor/arrange itself at the hydrophobic tail of the CTAB while the titanium dioxide would arrange itself at the hydrophilic head. This results in a successful incorporation of the carbon materials onto titanium dioxide. Takenaka et al. [29] reported the use of urea as linker for the deposition of TiO₂ on CNFs via sol gel synthesis. They postulated that the free amine group from the urea would react with the CNFs and result in the formation of a uniform coverage of the CNFs with TiO₂ nanoparticles.

Photoluminescence (PL) analyses were carried out to study the effect of the electron-hole (e⁻/h⁺) recombination rate for the different types of catalysts used in the present study. It is known that the emission peak for anatase TiO₂ appears at 520 nm. All samples showed the presence this peak as seen in Fig. 4a [30]. Carbon based materials are well known electron traps/scavengers [31,32] which is crucial in enhancing the efficiency of the photocatalyst. PL signals are basically well known electron traps/scavengers [31,32] which is crucial in enhancing the efficiency of the photocatalyst. PL signals are basically well known electron traps/scavengers which are needed to reduce the recombination of the photogenerated e⁻/h⁺ pair [33]. Therefore, the intensity of the signals generated could be correlated directly to the rate of the recombination of the e⁻/h⁺ pair. 7CNT-TiO₂ exhibited the lowest PL intensity followed by 7AC-TiO₂ and finally the anatase TiO₂.

CNTs are 1D nanostructures which have been reported to conduct electricity at room temperature without any resistance. This could be attributed to the fact that the electrons in CNTs are able to move freely [34] due to its unique sp² hybridized graphitic structure. Therefore, the highly feasible transportation of electrons within the CNTs during photoexcitation would enhance the electron’s separation efficiency and thus, would reduce the recombination rate of the e⁻/h⁺ pair [34]. Therefore, it could be assumed that the CNT doped sample would have the lowest e⁻/h⁺ recombination process taking place during a photocatalysis reaction as shown in Fig. 4a. The band gap energies for the photocatalysts shown in Table 1 were estimated from the Kubelka-Munk plot in Fig. 4b. The band gap energy of anatase TiO₂, 7AC-TiO₂ and 7CNT-TiO₂ was found to be 3.09, 3.18 eV and 3.14 eV respectively. It can be observed that carbon doping, did not result in a significant change in the band gap values. This is in line with the results obtained by Nawi et al. [26].

Fig. 5 shows the XPS analyses which were carried out on the modified titania samples. Both samples exhibited three peaks at ~530 eV, 459 eV and 285 eV, which correspond to the oxygen (O 1s), titanium (Ti 2p) and carbon (C 1s) moieties [35].

Fig. 6a and b indicates the presence of several carbon functional groups. Both samples have an intense peak at 285.5 eV and 285.9 eV respectively, which are attributed to the presence of elemental carbon (sp² hybridized) carbon, which actually has the same binding energy to that of intercalated graphite compounds [36]. The peaks appearing at ~284.5 eV for both samples were found to be the result of interference of carbon signals due to the carbon tape used during sample preparation for the XPS analyses [35]. Both 7CNT-TiO₂ and 7AC-TiO₂ samples have a peak at ~289 eV, which is possibly attributed to the presence of the C–O bond corresponding to a carbonate moiety [37]. In 7CNT-TiO₂ however, a signal at 282.7 eV (1.80%, Fig. 6b) was detected due to the substitution of Ti–O bond with Ti–C bond (anionic substitution) [38]. On the other hand, no such peak at ~282 eV was found for 7AC-TiO₂.

Fig. 6c and d, exhibit the narrow scans for Ti 1s core levels of 7AC-TiO₂ and 7CNT-TiO₂. Both samples projected strong signals at ~459 eV and 465 eV, which are due to the Ti 2p₃/₂ and Ti 2p₁/₂ peaks respectively, which are higher than the binding energy of pure anatase titania powder (458.4 eV/464.2 eV) [39].

This is most probably because of the oxygen vacancy defects which took place during the synthesis of the catalysts. It has been reported that high temperature annealing could contribute to the replacement of the oxygen atom in the TiO₂ lattice structure with that of carbon (Ti–O to Ti–C) as clearly proven by the peak at 282.7 eV for 7CNT-TiO₂. This would contribute to the enhancement of the electrical conductivity of the titania-carbon composite eventually increasing the photocatalytic activity of the catalyst [40].

Liu et al. had also reported similar observations in which the authors indicated that higher binding energy for the Ti 2p₃/₂ and Ti 2p₁/₂ peaks would be more feasible for the formation of Ti³⁺ ions. In fact, Ti³⁺ ions could also act as an electron trap thus, preventing the recombination of the charge carriers [41]. In addition, the deconvolution of the XPS Ti 2p of 7CNT-TiO₂ spectra also exhibited a peak at 461.1 eV, which is due to the formation of the Ti-C bond [42]. The narrow XPS scans of O 1 s core levels for the 7AC-TiO₂ and 7CNT-TiO₂ modified titania are shown in Fig. 6e and f respectively. Both samples exhibited strong peaks at ~530 eV, which is the result of Ti–O bonds. In addition, both samples have also projected peaks at ~532 eV, which was attributed to the presence of hydroxyl groups (OH) due to adsorbed moisture [43].

3.2. Photocatalytic studies of the prepared catalysts using MB as a model pollutant

3.2.1. Optimization of AC loading on anatase TiO₂

Varying the amount of carbon loading on TiO₂ was expected to result in changes in the photocatalytic activity of the modified titania catalysts. This was demonstrated as shown in Fig. 7 and Table 3. It can be observed that the photocatalytic degradation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sₘₜₜ (m² g⁻¹)</th>
<th>Vₚₜ (cm³ g⁻¹)</th>
<th>Dₘₜₜ (nm)</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>106</td>
<td>0.546</td>
<td>0.003</td>
<td>18.4</td>
</tr>
<tr>
<td>AC [19]</td>
<td>2696</td>
<td>1.496</td>
<td>0.274</td>
<td>2.63</td>
</tr>
<tr>
<td>Anatase TiO₂</td>
<td>11.1</td>
<td>0.040</td>
<td>20.6</td>
<td>3.09</td>
</tr>
<tr>
<td>7CNT-TiO₂</td>
<td>16.5</td>
<td>0.086</td>
<td>22.5</td>
<td>3.14</td>
</tr>
<tr>
<td>7AC-TiO₂</td>
<td>77.2</td>
<td>0.054</td>
<td>11.2</td>
<td>3.18</td>
</tr>
</tbody>
</table>
rate of the MB solution for AC doped catalysts increased steadily from 0.0928 to 0.1410 min\(^{-1}\) as the carbon content was increased from 2.5 wt. % to 7 wt. %. This was expected because increasing the amount of AC would enhance its surface area and therefore would increase the adsorption of the dye molecules. This brings the adsorbed dye molecules closer to the titania surface to be photodegraded.

The presence of AC functions as a bridge, which links the dye molecules to the titania surface and thereby increasing the photodegradation rate of MB. In addition to the synergistic adsorption effect, doping with carbon particles had also reduced the e\(^{-}\) and h\(^{+}\) recombination effect of the TiO\(_{2}\) nanoparticles as shown from the PL analysis (Fig. 4). This, in turn, would increase the photocatalytic rate of MB.

However, upon increasing the carbon content to 9 wt. %, the photodegradation rate of the modified titania showed a decrease in its activity. This was due to the excessive amount of AC which clouded the TiO\(_{2}\) particles from the UV illumination, thereby reducing the amount of UV light reaching the surface of the anatase TiO\(_{2}\). This would contribute to the reduction in the photocatalytic rate of MB [44]. A similar conclusion was made by Nawi et al. [26] in which the authors justified that the thickness of the carbon layer is vital for the photocatalytic activity. The thickness of the carbon coating would affect the intensity of the light reaching the TiO\(_{2}\) surface. The photocatalytic activity of the prepared AC loaded TiO\(_{2}\) catalysts conform to the following trend: 2.5AC-TiO\(_{2}\) < 5AC-TiO\(_{2}\) < 9AC-TiO\(_{2}\) < 7AC-TiO\(_{2}\). From these observations, 7 wt. % AC loading was the optimum amount required for the enhancement of the TiO\(_{2}\) anatase.

### 3.2.2. Photocatalytic activity of anatase TiO\(_{2}\), 7AC-TiO\(_{2}\) and 7CNT-TiO\(_{2}\) on the degradation of MB

From Fig. 8, it can be clearly observed that 7AC-TiO\(_{2}\) exhibited better photocatalytic activity compared to pure TiO\(_{2}\) and 7CNT-TiO\(_{2}\). The photocatalytic activity of the samples conformed to the trend as follows: TiO\(_{2}\) anatase < 7CNT-TiO\(_{2}\) < 7AC-TiO\(_{2}\), 7AC-TiO\(_{2}\) and 7CNT-TiO\(_{2}\) performed 2.7 and 1.5 times faster in the decolourisation of MB (with aeration) respectively compared to pure anatase TiO\(_{2}\). 7AC-TiO\(_{2}\) performed better than 7CNT-TiO\(_{2}\) in the degradation of MB due to its higher specific surface area (77.2 m\(^2\) g\(^{-1}\)). AC is amorphous and hence possesses a larger surface area as reported by Munianty et al. [19] compared to the crystalline CNTs.

Having a large surface area is beneficial as this would contribute to having more active sites on which more MB molecules can adsorb resulting in faster degradation. Hence, the synergistic effect of having a high surface area and low recombination of e\(^{-}\)/h\(^{+}\) had therefore attributed to 7AC-TiO\(_{2}\) having better photocatalytic activity compared to anatase TiO\(_{2}\) and 7CNT-TiO\(_{2}\) in the degradation of MB.

Gao et al. [16] carried out a similar study by doping AC onto TiO\(_{2}\) using titanium isoproxide as the precursor and found that the AC particles enabled the dye molecules to congregate on the TiO\(_{2}\) surface for rapid photo-oxidation by the -OH radicals. The AC enhanced the dispersion of the TiO\(_{2}\) nanoparticles thereby reducing the agglomeration of the photocatalyst [16]. However, for 7CNT-TiO\(_{2}\), the crystalline nature of the CNTs did not contribute much to the enhancement in the surface area (16.5 m\(^2\) g\(^{-1}\)) even though it had resulted in the lowering of the e\(^{-}\)/h\(^{+}\) recombination process as demonstrated in the PL analysis.

It should be noted that the C 1 s XPS results for 7CNT-TiO\(_{2}\) indicated the formation of the Ti-C bond based on the de-convoluted peak at 282.7 eV The presence of this Ti-C bond is crucial for the enhanced photocatalytic capability of 7CNT-TiO\(_{2}\). It was reported that chemically bonded CNTs with TiO\(_{2}\) interface has a profound impact on the photocatalytic activity of the composite [45]. Yu et al., had reported that composites of TiO\(_{2}\) and CNTs synthesized via mechanical mixing would not exhibit an enhancement in its photocatalytic activity and in fact, had shown poor results in comparison with pure TiO\(_{2}\) in the photo-degradation of acetone [45]. It has been hypothesized that the physical mixing of CNTs with TiO\(_{2}\) would not facilitate the effective separation of the charge carriers (e\(^{-}\)/h\(^{+}\)) and also the electron transfers [45]. However, this was not the case in the present study.

For the present study, however, it is believed that the electrons which were excited from the conduction band would be trapped in the carbon (AC or CNTs) upon recombination (Eq. (1)) and hence these electrons would be stored for further reactions with oxygen molecules (Eq. (3)) to generate other reactive oxygen species (ROS). Therefore, the trapings of these electrons would facilitate the rapid photocatalytic activity [45].

\[
\begin{align*}
C-TiO_2 + h\nu &\rightarrow C(e^-) + TiO_2 (h^+) \\
TiO_2 (h^+) + OH^- &\rightarrow TiO_2 + OH \\
C(e^-) + O_2 &\rightarrow C + O_2^-
\end{align*}
\]
indicating a higher concentration of hydroxyl radicals being produced. This could be attributed to the effect of carbon doping whereby the carbon would enhance the separation of the charge carriers and lower the recombination effect of the $e^-/h^+$. The reduction in the recombination of the charge carriers would induce the generation of higher concentration of hydroxyl radicals, consistent with the results shown in Fig. 10. However, 7AC-TiO$_2$ in particular exhibited higher intensity in the fluorescence spectral analysis compared to 7CNT-TiO$_2$ which could be due to the former having larger surface area than the latter. Large surface area could increase the amount of TA uptake via adsorption and hence increase the chances of reaction between the TA molecules with the hydroxyl radicals forming HTA.

### 3.2.4. Reusability studies of the photocatalysts

The reusability studies for 7AC-TiO$_2$ and 7CNT-TiO$_2$ were carried out to determine the versatility under repeated cycles. Two possible methods of regenerating the catalysts were studied: the first process involved washing the used catalyst with water/acetone mixture, and the second process was to reuse the catalyst without washing. These separate processes were carried out to determine the most economical way to regenerate the catalyst before reuse.

As observed in Fig. 11, the most efficient way to regenerate the catalyst was to wash the used catalyst repeatedly with water and acetone. This is probably because washing the catalysts after each successive run would clean the active site by removing the adsorbed degradation products. Fig. 11 shows that the catalyst could be reused four times without loss of catalytic activity by regenerating the catalyst by washing with water and acetone. Catalyst reused without washing showed decrease in efficiency during the third and fourth cycle.

It must be noted that with the washed regeneration method, the first order rate constant for 7AC-TiO$_2$ shows a slight decrease as the reuse cycle is increased. On the other hand, for 7CNT-TiO$_2$ the first order rate constant stays almost constant throughout the four cycles. For both samples, the unwashed reuse of the catalyst results in a drastic drop in the first order rate constant. This shows that washing the catalysts maintains the efficiency of the catalysts. The cleansing process is more efficient for the 7CNT-TiO$_2$ than 7AC-TiO$_2$. This is because the surface porosity of 7AC-TiO$_2$ may prevent access of the washing solvent into the micro pores thus decreasing its efficiency.

The FT-IR analysis for 7CNT-TiO$_2$ (Fig. 12) after the photocatalytic reaction showed a sharp band at around 1380 cm$^{-1}$. This band is due to the nitrate (NO$_3^-$) ions [46,47] which is one of the degradation products obtained following the photocatalytic of MB. In addition, another band was observed at around 1125 cm$^{-1}$ which was attributed to the presence of the sulphate ions (SO$_4^{2-}$). It has been reported that the presence of nitrate, chloride and nitrate species on the catalysts would suppress the photocatalytic reaction in the degradation of MB [48].

However, the FT-IR spectra of 7CNT-TiO$_2$ after the washing procedure did not exhibit any of these bands (top most spectra in Fig. 12). This shows that the washing procedure was able to remove these ionic species from the active sites on the surface of the catalysts.

### 3.3. Mineralization studies on the degradation of MB

Total organic carbon (TOC) analysis was carried out to determine the degree of mineralization of the MB solution (initial concentration = 50 mg L$^{-1}$) after 120 min of irradiation. The results in Fig. 13 show that 90.1% and 84.9% of mineralization had been achieved for 7AC-TiO$_2$ and 7CNT-TiO$_2$ respectively. Furthermore,
ion chromatography (IC) analysis (Fig. 14) was used to identify the products after the photocatalysis reactions. The main ionic moieties identified were chloride (Cl\(^{-}\)), nitrate (NO\(_3\)\(^{-}\)) and sulphate (SO\(_4^{2-}\)) as shown in Eq. (6) [49];

\[
C_{16}H_{18}N_3SCl + 25.5O_2 \rightarrow 16CO_2 + 3NO_3^- + SO_4^{2-} + 6H^+ + 6H_2O
\]  

(6)

The samples were collected at 30 min intervals up to 120 min. The concentration of sulphate anion is a very important indicator as it signifies the degree of mineralization of MB (initial concentration = 50 mg L\(^{-1}\)). The sulphate concentration observed were 9.79 and 9.02 mg L\(^{-1}\) for 7AC-TiO\(_2\) and 7CNT-TiO\(_2\) respectively, after 120 min of UV irradiation. Higher concentration of SO\(_4^{2-}\) ions from the photocatalytic degradation of MB using 7AC-TiO\(_2\) indicates the effectiveness of the synergistic adsorptive/photocatalytic process on the active sites of the catalysts.

It must be noted that the chloride ion concentration remains constant as this is a free ion from the MB molecule. As the degradation proceed, the concentration of the other ions increases, showing a progressive degradation taking place.

4. Conclusions

In conclusion, the doping of carbon (AC or CNT) onto anatase titania had resulted in an accelerated performance on the photocatalytic degradation of MB under UV irradiation. This increase in catalytic activity of the carbon modified titania catalysts was mainly attributed to two important factors which are the inhibition of the recombination process of the charge carriers (e\(^{-}\)/h\(^{+}\)) and also the increase in the catalyst's total surface area. AC is amorphous and hence contributed to the enhancement of the surface area of 7AC-TiO\(_2\) in addition to reducing the recombination of the e\(^{-}\)/h\(^{+}\) during photo catalysis. Thereby, enhancing it to perform 2.7 times faster compared to the conventional anatase TiO\(_2\). CNTs on the other hand, are crystalline with very low surface area. However, 7CNT-TiO\(_2\) generated the lowest PL signal indicating better charge separation efficiency. Furthermore, it was also deduced that the substitution of Ti-O bond with Ti-C had taken place in 7CNT-TiO\(_2\). These modifications improved the catalytic activity by 1.5 fold over anatase TiO\(_2\). Therefore, this study shows that doping TiO\(_2\) with AC leads to accelerated degradation of MB under UV irradiation.

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