



# Carbon modified anatase TiO<sub>2</sub> 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 TiO<sub>2</sub> particles were well dispersed with the carbon source. N<sub>2</sub> adsorption-desorption analysis indicates a distinct change in the surface area of the AC doped TiO<sub>2</sub> 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<sup>-</sup>/h<sup>+</sup>), 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 pho-

tocatalyst 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-

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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<sub>2</sub> 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<sub>3</sub> 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<sup>-1</sup>. 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<sub>3</sub> 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<sub>2</sub> aeration at 500 °C for 1 h. The resulting catalyst was labelled as xAC-TiO<sub>2</sub> (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<sub>2</sub>.

### 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 inVia Raman with HeNe laser,  $\lambda_{\max}$  = 633 nm, 2 mW) N<sub>2</sub> adsorption-desorption analysis (Micromeritics ASAP 2020 porosimeter), powder x-ray diffraction (Siemens Diffractometer D5000 Kristalloflex, equipped with Cu K $\alpha$  radiation,  $\lambda$  = 0.154 nm, voltage = 40 kV, current = 30 mA) from 10° to 90° and thermal gravimetric analysis (TGA/SDTA 851<sup>e</sup> Mettler Toledo) under oxygen flow with a heating rate of 20 °C min<sup>-1</sup> 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 microscope (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 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  $\times$  10<sup>-9</sup> Torr - ultra vacuum environment in the sample analyzing chamber) were also carried out.

### 2.6. Photocatalysis studies

About 400 mL of 50 mg L<sup>-1</sup> MB solution was prepared from 1000 mg L<sup>-1</sup> 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<sup>-1</sup> (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;

$$\text{MB remaining} = \frac{C_t}{C_0} \times 100 \% \quad (1)$$

$$\ln\left(\frac{C_t}{C_0}\right) = kt, \quad k = \text{rate constant (min}^{-1}\text{)} \quad (2)$$

Where C<sub>t</sub> and C<sub>0</sub> are the concentration of MB at time t and zero respectively.

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