

## Diamond Thin Film as a Photocatalyst for Photodegradation of Dyes

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Diamond is known as the hardest material with excellent properties including high thermal conductivity at ambient temperature. The ability of diamond to withstand high temperature allows the synthesis of doped diamond by introducing dopants into its structure. The introduced dopants are boron and nitrogen which act as either *p*-type or *n*-type, respectively. The doped diamond can act as a photocatalyst for the purpose of water treatment. In this study, different types of dopants introduced into the diamond lattice contributed to different photocatalytic activities. The characterization of Diamond Thin Film (DTF) was done using Scanning Electron Microscopy (SEM) and laser Raman spectrophotometer. Photocatalytic activities of DTF were investigated by degradation of methylene blue and methyl orange as models for the organic pollutants. The concentration of the organic pollutants degraded was analyzed using UV-Vis Spectrophotometer. As a result, *n*-type doped diamond showed better photocatalytic activities compared to *p*-type doped diamond with 725 mg/cm<sup>2</sup> of methylene blue degraded over the period of 150 minutes.

**Key words:** Diamond Thin Film; dopant; photocatalyst; water treatment; organic pollutants

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Textile industry has applied a large amount of dyes on textile fiber for coloration process compared to cosmetics, food, leather, paper, plastic, printing, and pharmaceutical industries [1]. The combination of dye molecules onto fiber molecules can be done through dyeing process. However, it becomes a huge risk towards the environment when textile waste effluents containing non-biodegradable pollutants such as remaining dyes, organic compounds, and surfactants are released into rivers, lakes, and oceans.

These pollutants are hardly to be degraded through chemical or biological techniques. Therefore, various methods have been studied by previous researchers to ensure the polluted substances are removed before discharge into natural streams and water bodies [2]. Photocatalytic degradation is the most potential technique because of increasing strict standards of controlling environmental pollution prior to discharging into the environment [3].

Photocatalyst is generally defined as any substance that can break down or decompose other materials with the assistance of light [4]. Generally, when sunlight or a light source (photon) hits the surface of a photocatalyst, this produces positive hole (h<sup>+</sup>) and negative electron (e<sup>-</sup>) pairings.

The formation of h<sup>+</sup> and e<sup>-</sup> pairs occurs when electrons are excited to the conduction band from the valence band and leave empty spots which are called holes. In order to promote an excited electron, the absorbed energy by photon (light) must be greater or equivalent to the band gap. Then, these photo-generated charges are transferred to the photocatalyst surface to initiate the degradation process. This cycle continues with respect to the availability of photon [5].

According to previous studies, photocatalysis that uses semiconductors as photocatalysts such as titanium dioxide (TiO<sub>2</sub>), zinc oxide (ZnO), and tin dioxide (SnO<sub>2</sub>) have gained considerable attention because the photocatalysts are safe, easy to produce, and affordable. However, the ability of diamond to be doped and behaves as a semiconductor shows an excellent property that has the potential to be used in industry. Diamond is an allotrope of carbon with arrangement in tetrahedral framework. Each carbon atom in diamond is surrounded by other four carbon atoms and the atoms are connected to each other by covalent bonds.

This structural arrangement gives diamond the strongest chemical linkage [6]. Diamond is recognized as the hardest material and naturally occurs rarer than gold [7]. Moreover, its ability to be doped and forms

*p*-type and *n*-type semiconductors establish the versatility of diamond as electrode in photocatalytic application.

There's a report on boron-doped diamond electrode that showed an enhancement in water treatment and thus produced water suitable for drinking which may be useful during disasters. The method was the combination of electrolysis on BDD electrodes and photocatalysis by TiO<sub>2</sub>. However, this system required large amounts of electric power during electrolysis and photocatalysis under solar energy showed low efficiency if only TiO<sub>2</sub> was used [8]. Apart from that, the system took longer time to purify wastewater by taking 3 hours of electrolysis and another 5 hours for photocatalysis.

Another study reported that BDD electrode was favored both in color (95%) and organic load (87%) removal processes due to its chemical structure rupture in different parts of dye. But, BDD film must be deposited on a substrate material to improve the conductivity of electrode. On the other hand, the rough and porous structure resulted in deterioration of the film adhesion and electrode's stability [9].

Semiconductor materials with heterostructure help in enhancing photocatalytic activities due to effective electron-hole pair separation through interfacial junction. For example, TiO<sub>2</sub> NRs/ZnO/BDD heterojunction allowed 60% and 70% of photodegradation at 160°C and 200°C, respectively. Though after calculating the band gap energy, it was shown that the band gap energy of heterostructure fabricated at 160°C and 200°C, which were 3.25 and 3.19 eV, respectively, were still higher than bulk TiO<sub>2</sub> (3.0 eV) due to the size quantization of TiO<sub>2</sub> nanorods on BDD film. For a better photocatalytic activity, the photocatalyst should be efficient not only in UV light region but also in visible light region [10].

Besides all the above problems, most of the photocatalysts used today are in the powder form due to the large surface area that undergoes photodegradation efficiently [11]. Unfortunately, the photocatalysts need to undergo filtration process to separate the photocatalysts from the effluent which leads to increases in the production costs in industries. In addition, there are limited researches related to diamond film as photocatalyst apart from combining it with other materials to form heterojunction structures.

## EXPERIMENTAL SECTION

### Materials and Methods

DTF used in this study were Nitrogen Doped Diamond (NDD) and Boron Doped Diamond (BDD). Both doped diamonds were purchased from Element Six Ltd. The

model pollutants used were methylene blue and methyl orange bought from Sigma-Aldrich. Distilled water was used throughout the experiment as solvent.

### Preparation of Methylene Blue and Methyl Orange Solutions

In this study, methylene blue (MB) and methyl orange (MO) were used as organic pollutant models. Firstly, a standard solution of 10 ppm for each MB and MO was prepared from 1000 ppm stock solutions. From 10 ppm of both organic pollutants, further dilution was performed to prepare 2 ppm, 4 ppm, 6 ppm, and 8 ppm solutions. The dilution was prepared in 10 mL volumetric flasks in order to generate a standard calibration curve using a UV-Vis spectrophotometer. The standard calibration curve was essential to determine the concentration of MB after introducing photocatalyst into the solution in later part of the research.

### Photocatalytic Activity of BDD and NDD

The photocatalytic activity of NDD and BDD was investigated on MB and MO. The process was performed at two different concentrations, which were 5 ppm and 10 ppm. Firstly, 50 mL of 10 ppm MB was poured into a beaker. Then, DTF was introduced into the MB solution and it was important to ensure the location of DTF in the MB was near to the surface of the solution where the distance from the UV lamp to the center of the beaker was measured at 20 cm for proper irradiation of light onto DTF. After that, the solution was stirred using a magnetic stirrer for 15 minutes in an isolated box to ensure adsorption equilibrium.

Next, the solution with DTF was illuminated under a 6-watt UV lamp at the wavelength of 302 nm for three hours with continuous stirring. During the illumination, 4 mL of MB was collected for each 30 minutes interval and stored in dark bottles immediately to avoid any further self-degradation when exposed to the surrounding before underwent further analysis with the UV-Vis spectrophotometer. The same steps were repeated for 5 ppm MB concentration and when MB was substituted with MO. For each concentration, the experiment was investigated on different conditions as represented in Table 1 to establish control experiments on adsorption and self-degradation of dyes.

The absence and presence of DTF in this experiment acted as the controls of the experiment. This was important to determine the degradation of organic pollution underwent photocatalysis reaction or other mechanism. By the absence of DTF either with or without the assistance of the UV light lamp (Trial 3 and Trial 4) indicated self-degradation of the organic pollutants. Meanwhile, in the presence of DTF without

**Table 1.** Experimental conditions

Organic pollutant	Trial	UV lamp	DTF (NDD, BDD)
	1	/	/
Methylene Blue/ Methyl Orange	2	X	/
	3 (control)	/	X
	4 (control)	X	X

illumination from UV light lamp (Trial 2), the reduction of the concentration of the organic pollutants occurred due to adsorption-desorption mechanism.

### Characterization of Photocatalyst

DTF were characterized using Zeiss Evo MA10 LaB<sup>6</sup> for scanning electron microscopy (SEM) technique and Renishaw 2000 was used for laser Raman spectroscopy technique. SEM was used to investigate the surface morphology of DTF and the sample analyses were performed without prior coating with accelerating voltage of 10-12kV and working distance of 8 mm. Laser Raman spectroscopy was performed using He:Cd gas as excitation source for 325 nm wavelength to determine the existence of *sp*<sup>3</sup> and *sp*<sup>2</sup> carbon in the DTF samples. Then, the photocatalytic activities of DTF on MB and MO dyes were determined out using a UV-Vis spectrophotometer in the range of 380 nm to 800 nm.

## RESULTS AND DISCUSSION

### Photodegradation of Methylene Blue

The UV-Vis spectrophotometer was used to measure the MB degradation. At 5 ppm MB concentration, it was found that the highest absorbance occurred at the

wavelength between 661 nm to 666 nm. The MB photodegradation can be calculated by Equations 1 and 2:

$$\text{Degradation (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

$$= \frac{A_0 - A}{A_0} \times 100 \quad (2)$$

Where, *C*<sub>0</sub> = initial concentration of MB, *C* = final concentration of MB, *A*<sub>0</sub> = initial absorbance intensity of MB, and *A* = final absorbance intensity of MB.

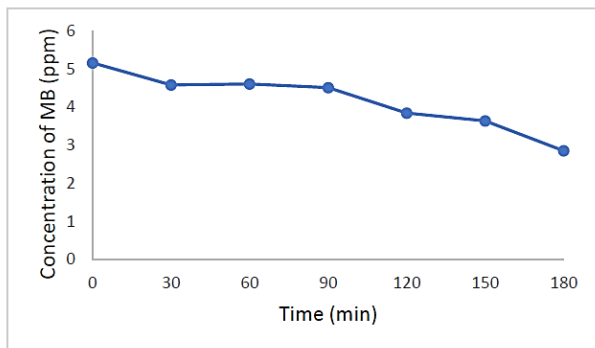
Figure 1(a) shows the concentration of MB after the photodegradation process occurred when BDD was used as a photocatalyst. The MB concentration decreased greatly after 90 minutes illumination under 302 nm UV light. However, the result was contradicted with theoretical prediction whereby 244 nm is needed to excite electron from the dopant energy level into the conduction band to initiate the photocatalytic reaction. This degradation of MB might due to the contribution of grain boundaries in between the grains in BDD samples that can be observed using laser Raman spectroscopy in Figure 5. The existence of grain boundaries consisting of *sp*<sup>2</sup> carbon improved the conduction of the sample due to the free electrons in the structure.

Meanwhile, Figure 1(b) shows the concentration of MB for photodegradation performed using NDD photocatalyst. The concentration of MB after photodegradation process indicated a huge reduction after 120 minutes illumination with 302 nm UV lamp.

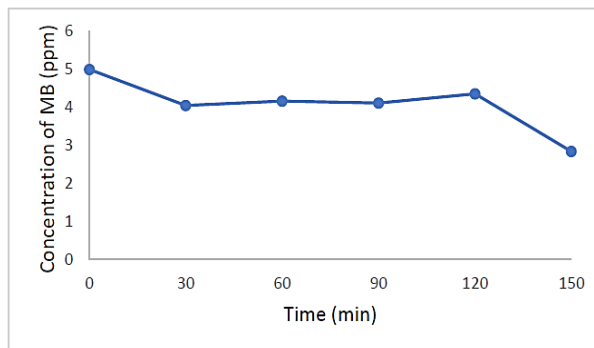
The percentage of MB degraded with assistance of DTF was determined using Equation 3:

$$\% \text{MB degraded} = \frac{x}{I_0} \times 100 \quad (3)$$

Where, *x* = photodegradation intensity of MB and *I*<sub>0</sub> = initial absorbance of MB.



(a)



(b)

**Figure 1.** Photodegradation of MB by (a) BDD and (b) NDD.

Figure 2 shows the percentage of MB photodegraded by BDD and NDD photocatalysts. For MB, the percentage increased from 0 to 11% after 30 minutes due to the absorption of MB onto BDD surface. While the percentage of MB did not show any significant changes between 30 to 90 minutes due to the activation time needed for photodegradation to occur. Then, photodegradation increased significantly over time with 29% and 39% at 120 minutes and 150 minutes, respectively. This trend indicated that if the photodegradation of MB with BDD photocatalyst was given a longer time, higher percentage of photodegradation can be achieved. However, it is not economically viable as industries prefer efficient catalysts that work in shorter time.

For NDD, for the first 30 minutes, the graph showed that the adsorption process onto NDD was similar to BDD. Activation period was also observed in NDD with no significant changes between minutes 30 to 90. Photodegradation escalated and increased to 49.5% at 150 minutes. This was because the photodegradation process of MB by NDD only began after 120 minutes illumination under UV light and the drop between minutes 90 and 120 was not accounted as the percentage difference was not exceeding 5%.

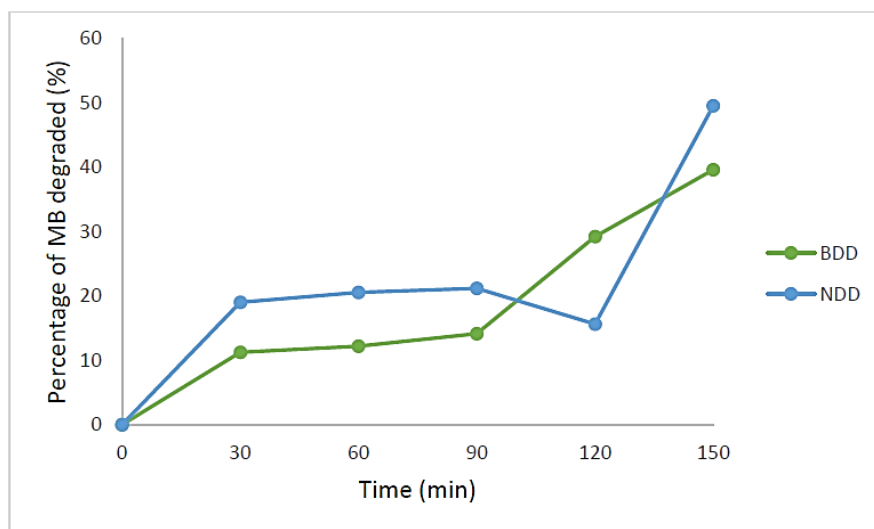
NDD showed higher percentage of photo-

degradation of MB compared to BDD in the first 90 minutes. The average percentage of MB degraded by NDD was 20.3% while the average percentage of MB degraded by BDD was 12.5%.

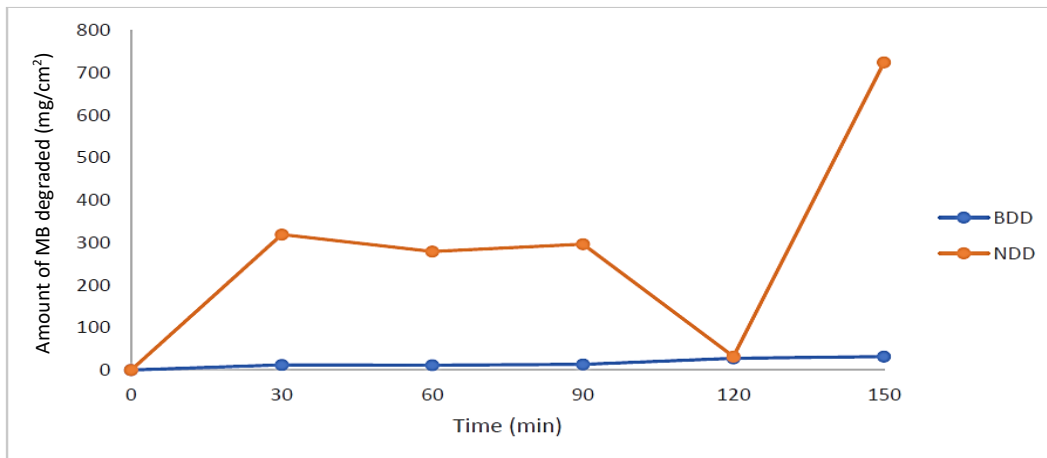
This indicated higher initial adsorption rate of NDD compared to BDD and not due to the photodegradation process of the DTFs. Degradation of MB in the presence of NDD was almost two times the degradation of MB by BDD. After 150 minutes of illumination, the percentage of MB degraded by BDD was 9.9% lower than the percentage of MB degraded by NDD. This was due to lower activation energy of NDD, as suggested in a previous study that the donor level of NDD only required 1.7 eV (729 nm) to be excited into the CB while the illumination provided to NDD was of a much higher energy (4.1 eV, 302 nm). Thus, the excited free electrons in NDD were easily promoted into the CB. Therefore, the results indicated that NDD has higher photocatalytic activity compared to BDD.

Further analysis was done to compare the performance of DTF based on the surface area of DTF used, as both DTF came in different sizes. Equation 4 was used to evaluate the amount of MB degraded per surface area used:

$$\text{Amount of MB degraded} = \frac{\text{mass of MB degraded (mg)}}{\text{surface area of DTF (cm}^2\text{)}} \quad (4)$$



**Figure 2.** Comparison of the percentage of MB photodegradation between BDD and NDD.



**Figure 3.** Amount of MB photodegraded per unit area performed by BDD and NDD.

Figure 3 displays the amount of MB degraded per unit area by BDD and NDD. Based on the graph, the surface area of BDD and NDD were  $2.4 \text{ cm}^2$  and  $0.1485 \text{ cm}^2$ , respectively. From the analysis, the mass of MB photodegraded per unit area of BDD against time was much lower compared to NDD. Therefore, n-type doped diamond (NDD) can be considered as a better photocatalyst for degradation of MB compared to BDD under illumination of 302 nm UV lamp with activity of  $725 \text{ mg/cm}^2$  BDD.

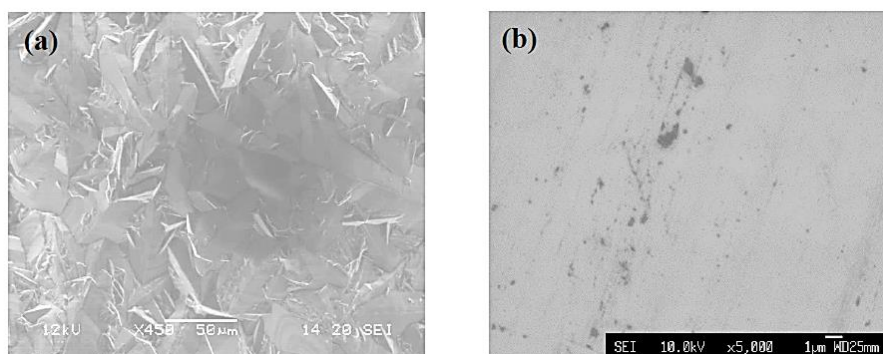
### Photodegradation of Methyl Orange

The photodegradation of MO solution by DTF underwent a series of experiments similar to MB solution and determined using a UV-Vis spectrophotometer. However, the data showed inconsistent results with the overall highest absorbance of MO was observed between 400-500 nm. Therefore, the attained results might be inconclusive due to the incompatibility of DTF to degrade MO. This was due to different molecule structure between MB and MO. Based on dyes classification, MB is a cationic dye

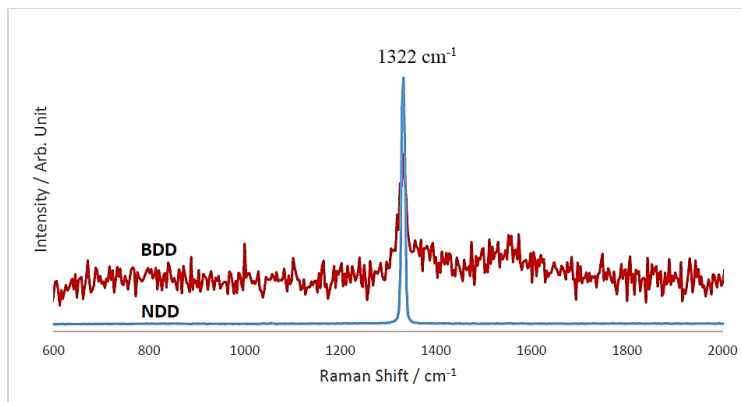
while MO is an anionic dye. Cationic dyes can be easily attracted to the surface of DTF, due to the oxygen species that bind to DTF forming oxygen-terminated surface after long exposure in air. While anionic dyes such as MO contain negatively charged oxygen that will be repelled by the surface oxygen which exists on DTF. Hence, it can be concluded that the DTF were only sensitive towards cationic dyes but not anionic dyes due to the oxygen-terminated surface on the DTF.

### Characterization of Diamond Thin Film

Figure 4 shows the surface morphology for BDD and NDD observed using SEM. The SEM micrograph of BDD showed a polycrystalline surface with triangle facets, while NDD exhibited a smooth, flat (100) diamond surface [12-16]. NDD used in this study was a single crystal that contained only one crystal facets compared to polycrystalline facets in BDD. Hence, the surface of NDD was much smoother compared to BDD.



**Figure 4.** Surface morphology results by SEM: (a) BDD and (b) NDD.



**Figure 5.** Raman spectra for BDD and NDD with wavelength of UV laser at 325 nm.

Figure 5 illustrates the Raman spectra of BDD and NDD films. It was shown that NDD only exhibited carbon  $sp^3$  at  $1322\text{ cm}^{-1}$  while BDD showed an additional peak at  $1580\text{ cm}^{-1}$ , which indicated the presence of  $sp^2$  carbon present in grain boundaries due to its polycrystalline nature. There was no significant difference when the Raman spectra were captured before and after photocatalytic activities, which suggested no structural damages after the photodegradation process occurred.

### CONCLUSIONS

MB was successfully photodegraded by n-type and p-type diamond thin films with 302 nm UV light source. Between these two types of DTF, n-type which was NDD showed a better photocatalytic activity compared to BDD as p-type. Furthermore, based on the mass of MB degraded per surface area of photocatalyst used, NDD showed better results than BDD, as MB underwent photodegradation at  $725\text{ mg/cm}^2$  of NDD used.

For the characterization using laser Raman spectra, both BDD and NDD exhibited  $sp^3$  peak, indicating the existence of diamond peak. In SEM analysis, BDD existed as polycrystalline diamond while NDD exhibited (100) single crystal facets. In addition, there were no significant structural damages detected for both BDD and NDD after the photodegradation process.

It was found that the DTF used in this study were only sensitive towards cationic dye (MB) and not anionic dye (MO).

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