Photocatalytic degradation of methylene blue under visible light using carbon dot/titanium dioxide nanohybrid

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Abstract. Due to the large band gap and the rapid recombination of electron-hole pairs of TiO₂, carbon quantum dots (CQDs) modified TiO₂ photocatalyst had been given intensive attention in visible light photodegradation. In this study, the oil palm frond-derived NCQDs/TiO₂ was adopted for the first time in the photodegradation of Methylene Blue (MB) under visible light irradiation. TiO₂ photocatalyst and NCQDs/TiO₂ nanocomposites with different NCQDs contents were successfully synthesised through a facile in-situ hydrothermal method. The surface morphology and crystalline structure of NCQDs-decorated semiconductor photocatalyst were characterized by high-resolution transmission electron microscope (HRTEM), field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD), respectively. Fourier transform infrared spectroscopy (FTIR) and energy dispersive X-ray (EDX) were utilized to prove the successful attachment and the uniform dispersion of NCQDs on TiO₂ surface, respectively. The best-performed photocatalyst with the optimum amount of NCQDs (NCQDs/TiO₂-1) displayed a degradation efficiency of 40.9% within 60 minutes, which is 2.6 times faster than that of pure TiO₂ (15.6%). The improved photocatalytic performance could be attributed to the better charge separation since NCQDs act as an electron reservoir which impeded the recombination of electron-hole pairs. The present work proposed a simple synthetic route for the preparation of NCQDs/TiO₂ nanocomposites and the use of biomass as a natural precursor which contributed to green and sustainable fabrication of photocatalyst in environmental application.

1. Introduction

Due to the new discoveries in science and technology, rapid industrial development involves tremendous water usage, hence resulted in severe water pollution where water scarcity remains a major challenge throughout the world. This alarming problem has attracted the awareness of all nations to search for environmental remediation and pollution control technologies. Owing to the inefficiency of the traditional method, intensive research had been directed towards new technologies like advanced oxidation processes (AOPs) to overcome the insufficient removal of organic pollutants through conventional wastewater treatment. Among all the AOP methods, photocatalysis is more commonly used to degrade pollutants in water since it only needs light source as stimulant, water as precursor and the presence of photocatalysts to produce free radicals.

Titanium dioxide (TiO₂) nanoparticle has emerged as one of the most potential semiconductors in photocatalysis owing to its unique properties including strong oxidizing power, chemical stability, nontoxicity and most importantly, economical affordable [1]. However, the photocatalytic performance
of TiO$_2$ under visible light irradiation was strictly restricted by the rapid recombination of photogenerated electron-hole pairs and short light absorption spectra which are associated with its wide bandgap nature [2]. Therefore, great efforts have been made to tune the band structure of TiO$_2$ by supporting it on various types of carbon materials.

In recent years, fluorescent CQDs has been widely adopted in various application fields such as bioimaging, chemical sensing, nanomedicine and photocatalysis owing to its tunable optoelectronic feature, outstanding optical property and high biocompatibility [3]. In the work of Kavitha et al., fluorescence carbon dots were fabricated using dated oil palm frond as renewable carbon precursors. Dated oil palm frond demonstrated huge potential in the synthesis of green CQDs which could inspire scientific attention in diverse applications [4]. Previous research showed that the modification of TiO$_2$ with coal tar pitch derived CQDs was able to degrade rhodamine B (RhB) completely within 6 h compared to pure TiO$_2$ in which the degradation of RhB was less than 10% [5]. The enhanced photocatalytic activity of composites over the pristine TiO$_2$ was mainly contributed by the beneficial roles of CQDs as electron acceptor and photon conversion center [6]. Recently, Martins et al. fabricated nitrogen-doped carbon quantum dots (NCQDs) to achieve surface functionalization and passivation of carbon dots [6]. The inclusion of nitrogen atoms would efficiently induce charge delocalization and lower work function of carbon, which was probably the main reason for the enhanced fluorescence emission of CQDs [7]. It is noteworthy that the synthesis route selected for the preparation of composite photocatalyst may greatly affect the work function of CQDs. In recent years hydrothermal method has gained immense attention due to its low cost, low energy consumption and facile preparation steps. Hydrothermal process eliminates the complex carbonization process needed and the use of harsh acid pretreatment during the extraction of CQDs [8]. Herein, a simple one-pot hydrothermal method is strongly proposed for the assembling of CQDs on the host catalyst by forming chemical bonds, especially –OH bonding between the interfacial surfaces of CQDs and TiO$_2$ [8].

Therefore, the idea of coupling of nitrogen-doped carbon quantum dots with pristine TiO$_2$ was provoked to counter the shortages associated with the intrinsic wide band gap of semiconductor photocatalyst. In this study, oil palm frond was selected as the green precursor for the preparation of CQDs and one-pot hydrothermal method was adopted for the subsequent TiO$_2$ formation and incorporation process. The photocatalytic activity of NCQDs/TiO$_2$ composites and the optimum NCQDs loading were evaluated through the degradation of methylene blue (MB) under visible light irradiation.

2. Experimental

2.1. Materials

In this study, isopropanol (IPA), ethylenediamine (EDA) and ethanol were purchased from Merck while Titanium (IV) isopropoxide (TTIP) was obtained from Sigma-Aldrich. All chemicals were used as received without further purification. The biomass precursor for NCQDs, dated oil palm frond was collected locally from an oil palm estate in Tanjung Tualang, Perak.

2.2. Synthesis of NCQDs/TiO$_2$ composites

Briefly, the waste oil palm frond powder collected was washed and grinded into powder. The oil palm frond powder was then added into a mixture of IPA, EDA and distilled water. The mixture was then transferred into an autoclave and heated at 180 °C for 12 h. After that, the brown dispersion was centrifuged at 10,000 rpm followed by vacuum filtration to remove large particles and the NCQDs solution was kept in dark before use. Next, the synthesis of NCQDs/TiO$_2$ composites was carried out through one-pot hydrothermal method by mixing 0.5 ml of NCQDs with 5 ml of TTIP precursor and a suitable amount of isopropanol aqueous solution. After stirred for 2 h, the resulting solution was transferred to autoclave and heated in an oven at 220 °C for 4 h. After it was cooled down, the NCQD/TiO$_2$ composite was washed and rinsed thoroughly with distilled water and ethanol followed by drying at 80 °C for 24 h. The above procedure was repeated by changing the volume of NCQDs to 1 ml
and 4 ml. Hereafter, the photocatalyst annotation was made as NCQDs/TiO$_2$-x where x represented the volume of NCQDs solution added, which were 0.5 ml, 1 ml and 4 ml.

2.3. Photocatalytic activity

Photocatalytic experiment was conducted to assess the photocatalytic performance of the prepared NCQDs/TiO$_2$ nanocomposites and bare TiO$_2$ through the degradation of MB under visible light irradiation. 0.05 g of the prepared photocatalyst was dispersed into 50 ml of 10 ppm MB solution (1g/L) and was monitored for 1 h to determine the rate of degradation. Prior to the photodegradation process, the suspension was stirred in dark condition for 1 h to establish adsorption-desorption equilibrium. After equilibrium, 4 ml of aliquot was withdrawn and taken as initial concentration ($C_0$). The solution was then illuminated by an 80W LED bulb. Every 15 min, MB solution was withdrawn and the collected aliquot was analysed using UV-vis spectrophotometer (PG Instruments T60) to determine the residual MB concentration at wavelength 663nm. Similar procedures were repeated for control set using blank MB solution for comparison purpose. The degradation efficiency of each photocatalyst was computed by equation (1) below:

$$\text{Degradation efficiency} = \frac{C_o - C_t}{C_o} \times 100\%$$

where $C_o$ and $C_t$ represent initial MB concentration and MB concentration at time $t$, respectively.

2.4. Characterisation

XRD (Shidmazu, XRD-6000) was employed to investigate the crystalline phase structure of various photocatalysts under Cu-K$_\alpha$ radiation with a 20 diffraction angle of 5°–80° at a scanning speed of 2°/min. HRTEM (Technai, G2F20) and EDX (Hitachi, S-3400N) were conducted to study the morphological structure and identify the elemental composition of the samples, respectively. FTIR (Nicolet IR10) analysis was used to identify the functional groups present on the prepared samples scanning from 400 to 4000 cm$^{-1}$.

3. Results and discussions

3.1. Characterisation of photocatalysts

TEM and HRTEM analysis was employed to investigate the morphology and structure of NCQDs and NCQDs/TiO$_2$ composites. Figure 1(a) demonstrates that NCQDs nanoparticles prepared by hydrothermal method exhibited relatively uniform and small spherical particles with dimensions around 6.3–8.7 nm. On the other hand, figure 1(b) shows the HRTEM image of NCQDs/TiO$_2$-1 composites. The modified nanocomposite shows clear lattice fringe spacing of 0.24 and 0.35 nm which correlated to the (100) facets of graphitic NCQDs and (101) plane of anatase TiO$_2$, respectively. This finding was similar to that obtained by Kumar et al. [9].

On the other hand, figure 1(c-d) show that pure TiO$_2$ exhibited small and discrete spherical particles while the NCQDs/TiO$_2$-1 nanocomposite has similar appearance as that of pure TiO$_2$. However, it was noticed that numerous particles formed larger aggregates after the attachment of NCQDs nanoparticles, which was similar to the observation by Kumar et al. [9].
EDX analysis was carried out to confirm the presence of elements including titanium (Ti), oxygen (O), carbon (C) and nitrogen (N) in NCQDs/TiO$_2$ composites. According to the elemental composition presented in Table 1, pure TiO$_2$ composed mostly of Ti and O atoms with a trace amount of C atoms whereas NCQDs/TiO$_2$-1 nanocomposite showed obvious Ti, O, C and N signals. The presence of C and N elements which originated from NCQDs proved the successful incorporation of carbon dots on the surface of TiO$_2$.

Table 1. EDX results for pure TiO$_2$ and NCQDs modified photocatalysts.

| Sample          | Weight percentage (%) | Atomic percentage (%) |
|-----------------|------------------------|-----------------------|
|                 | Ti          | O         | C         | N         | Ti          | O         | C         | N         |
| Pure TiO$_2$    | 55.24      | 42.97     | 1.79      | 0.00      | 28.92      | 67.35     | 3.73      | 0.00      |
| NCQDs/TiO$_2$-1| 51.02      | 39.67     | 3.09      | 6.23      | 25.09      | 58.39     | 6.05      | 10.47     |

Figure 2 shows the XRD patterns of bare TiO$_2$ and NCQDs/TiO$_2$-1 nanocomposite. The XRD pattern of bare TiO$_2$ shows peaks of 2θ value at 25.3°, 37.9°, 48.3°, 54.1°, 55.1°, 62.8°, 69.2°, 70.3° and 75.4°, which were assigned to the (101), (004), (200), (105), (211), (204), (116), (220) and (215) planes of anatase TiO$_2$, respectively [10]. The XRD patterns of NCQDs/TiO$_2$-1 nanocomposite show a similar phase structure of bare TiO$_2$ with no observable shift in peak, indicating the introduction of NCQDs had no significant impact on the crystalline structure of TiO$_2$. However, the characteristic peak of NCQDs was not detected in the modified composite due to the low NCQD content and poor crystallinity of NCQDs in the heterostructure of composite [5].
Figure 2. XRD pattern of pure TiO$_2$ and NCQDs/TiO$_2$-1 nanocomposite.

FT-IR analysis was performed to identify the various functional groups present on the surface of pure TiO$_2$, NCQDs and NCQDs/TiO$_2$-1 modified composite as shown in figure 3. It can be observed that the modified nanocomposite exhibited similar absorption peaks as TiO$_2$ around 1640 cm$^{-1}$ and a broad band over the range of 3100–3600 cm$^{-1}$ which were corresponded to O–H stretching and bending vibration of water molecules physically adsorbed on TiO$_2$, respectively [6]. Besides, the characteristic absorption peaks of NCQDs around 2920 cm$^{-1}$ and a shoulder peak at 1438 cm$^{-1}$ were ascribed to the stretching vibration of C–H and C=C groups, respectively [11]. In addition, the C=O peak at 1640 cm$^{-1}$ was also observed [7]. The presence of the C–H bond, C=O functional group and aromatic C=C stretch confirmed the strong coupling of NCQDs with TiO$_2$ in NCQDs/TiO$_2$ binary composites [10]. The broad band observed below 1000 cm$^{-1}$ was originated from the Ti–O–Ti bond, however when NCQDs were loaded, the band showed a gradual red-shift and became wider compared to pristine TiO$_2$, indicating the combination effect of Ti–O–Ti and Ti–O–C stretching vibration [10].

Figure 3. FT-IR spectra of pure TiO$_2$, NCQDs and NCQDs modified photocatalyst.
3.2. Photocatalysis

Figure 4 depicts the degradation rate of methylene blue performed by pure TiO\(_2\), NCQDs/TiO\(_2\)-0.5, NCQDs/TiO\(_2\)-1 and NCQDs/TiO\(_2\)-4. The degradation efficiency of various photocatalysts was found to be: NCQDs/TiO\(_2\)-1 > NCQDs/TiO\(_2\)-4 > NCQDs/TiO\(_2\)-0.5 > Pure TiO\(_2\), which recorded 40.93 %, 36.13 %, 28.44 % and 15.55 % of degradation rate, respectively. Obviously, the negligible decrease in MB concentration in the blank experiment proved the stable structure of MB did not undergo self-degradation through photolysis. These results demonstrated all NCQDs modified photocatalysts exhibited enhanced photocatalytic activity compared to that of pristine TiO\(_2\). Furthermore, NCQDs/TiO\(_2\)-1 nanocomposite shows a comparable performance to the CTP/TiO\(_2\) composite synthesised from waste coal tar pitch, which degraded 91.1% of RhB within 6 h of visible-light irradiation [5]. The significant improvement in degradation efficiency was mainly related to the role of NCQDs serving as an electron reservoir which retarded the recombination rate of photo-induced electron-hole pairs [7]. The strong interaction between the NCQDs/TiO\(_2\) heterostructure provided an electron transfer route that promoted efficient interfacial charge separation [5]. Hence, more free radicals could be generated and participated in the photodegradation process [6]. It is noteworthy that the NCQDs dosage played a significant role in the photocatalytic degradation of methylene blue. In this case, 1 ml of NCQDs was found to be the optimum amount added to TiO\(_2\) which achieved the highest degradation efficiency among all modified photocatalysts. The further increase in NCQDs dosage beyond 1 ml suppressed the photocatalytic activity of composites due to the agglomeration of NCQDs which block the penetration of light to reach TiO\(_2\) and reduced the surface contact between TiO\(_2\) and MB pollutants [5]. Therefore, an appropriate amount of NCQDs loaded is an important factor that should be taken into consideration to achieve a balance in light absorption and electron transfer.

![Figure 4](image-url)

**Figure 4.** Photocatalytic degradation of MB in the presence of pure TiO\(_2\) and NCQDs-TiO\(_2\) nanocomposites.

3.3. Possible mechanisms

During visible light irradiation, shorter wavelength light can be utilized by TiO\(_2\) to generate electron-hole pairs. The electrons are excited from valence band to conduction band of TiO\(_2\) while the holes remain at the valence band [10]. The electrons on the conduction band will migrate to the neighbour NCQDs surface, which plays an important role in electron storage and hinders the excited electrons from falling back to the ground state [6]. The trapped electrons on the NCQDs surface will then reduce the adsorbed oxygen molecules to produce superoxide radicals (•O\(_2^-\)). The highly reactive superoxide radicals will further react with H\(^+\) to generate hydroxyl radicals (•OH). On the other hand, the separated holes accumulated on the valence band directly react with water and hydroxide (•OH) molecules to yield •OH radicals [7]. Both superoxide and hydroxyl radicals are highly reactive species that can decompose...
the structure of methylene blue into non-harmful carbon dioxide and water [7]. The incorporation of NCQDs prolongs the lifetime of photo-induced charge carriers for the generation of free radicals which eventually enhance the photocatalytic degradation of MB [10].

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4. Conclusions
The NCQDs decorated TiO$_2$ was successfully fabricated via a facile and green one-pot hydrothermal method. The optimum NCQDs loading was the key factor in determining the degradation of methylene blue. In this study, NCQDs/TiO$_2$-1 was found to be the best-performed photocatalyst which achieved a remarkable degradation efficiency of 40.9\% under 1 h of visible light irradiation. In conclusion, NCQDs serving as an electron reservoir had efficiently retarded the recombination rate and prolong the lifetime of electron-hole pairs.

5. References
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