

Physical Mixing Of N-Doped Graphene Quantum Dots Functionalized TiO₂ For Sustainable Degradation Of Methylene Blue

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Abstract. An in-situ physical assisted mixing was applied for uniform incorporation of N-doped graphene quantum dots (N-GQDs) with TiO₂ nanoparticles to construct N-GDQs/TiO₂. The unique characteristics of N-doped graphene quantum dots enable it to act as a rich optical light harvesting. The strong absorption under the UV-Vis spectroscopy shows the efficacy in absorbing visible and Near Infrared (NIR) photon. The photocatalysis of the synthesized composite was evaluated through the efficiency of photodegradation of Methylene Blue in aqueous solution under direct sunlight irradiation. A complete degradation was achieved within 150 mins for 1.5% N-GQDs/TiO₂ composite as compare to pure. The vast improvement of this photocatalysis efficiency is much attributed to the strong light absorbance in the entire solar spectrum. Hence, the formation of N-GQDs/TiO₂ could be broadly used as future sustainable photocatalyst for treating various organic pollutants in the field of aquatic environmental remediation.

1. Introduction

With the rapid industrialization increases the water pollution where various toxic matters enter the water bodies. This directly influences the quality of water in our water bodies. One of the main pollutants that happen in Malaysia is dyes. These pollutants are manufactured from many sources such as textile, plastics, paper industries and many others. Methylene Blue (MB) is the most common industrial dye which causes severe environmental issues due to its high toxicity and accumulation in the environment. Therefore, it is important to address this issue effectively and photocatalysis nanotechnology could be a vital solution.

Semiconductor mediated photocatalyst has attracted enormous attention worldwide as it has proven its ability in eliminating environmental pollutants and generating energy. In the context of efficiently harness abundant sunlight for sustainable environmental remediation, the visible and near infrared light sensitive photocatalyst is necessary to be developed. This makes them an appropriate tool to address the alarming environmental issues such as dyes and organic pollutant in the near future by utilizing the entire solar spectrum. To date, titania (TiO₂) is considered a well-known and promising photocatalyst due to its several unique characteristics such as chemically stable, environmentally



friendly product, cheap and etc [1,2]. Regrettably, it retarded its ability in extending the light absorption to longer than 390 nm due to its relatively wide band gap energy of 3.2 eV [3].

Massive modifications have been studied to extend to higher wavelength such as doping with metal and non-metal elements [4], depositing with noble metal [5,6], sensitizing with organic dyes [7,8] and so on. However, recently N-doped graphene quantum dots have turned out to be a new candidate in harvesting visible and near-infrared light [9]. N-doped graphene quantum dots, a zero dimensional allotrope of graphitic carbon have gradually become a promising photocatalysts due to its tunable band gap, stable photoluminescence and good biocompatibility [10]. It has been used in various applications such as biosensors, drug carriers, nuclear targeted drug delivery and other energy conversion [11-13]. Herein, we incorporate TiO_2 with N-doped graphene quantum dots through a facile physical mixing route to enhance its utilization of the entire solar spectrum for photodegradation of Methylene Blue.

2. Experimental

2.1. Materials

Titanium (IV) Oxide (Anatase TiO_2 , >99%, Sigma Aldrich), urea powder and citric acid were purchased from Sigma Aldrich and ethanol was purchased from R&M Chemical. All chemicals were analytical grade and used as received without any further purification.

2.2. Synthesis of N-GQDs & N-GQDs/ TiO_2

N-GQDs were synthesized by mixing 1 mmol of citric acid and 3 mmol of urea and dissolve into 5 ml of distilled water. Solution was then stirred gently until clear solution was formed. Then transfer it to an 80 ml Teflon-lined-stainless-steel autoclave and heated at 160°C for 8 hours in an oven. The obtained N-GQDs resulted in a green luminescence solution. Different percentage amount of obtained N-GQDs (0.5% and 1.5%) are physically mixed with 0.4 g TiO_2 under 2500 rpm for an hour. The resulted solution was then washed with ethanol and distilled water repeatedly. The samples were dried at 80°C overnight.

2.3. Characterization

The morphology of the composite was investigated by field emission scanning electron microscope (FESEM, Hitachi SU-8000) equipped with an energy dispersive X-ray spectroscopy (EDS, Zeiss Auriga). The images were recorded at an accelerating voltage of 20 kV. High resolution transmission electron microscope (HRTEM, JEM-2100F, Jeol) images were obtained at 200 kV. UV-Vis diffuse reflectance spectra (UV-DRS) were performed through Shimadzu UV-2600 spectrophotometer equipped with an integrating sphere attachment to characterize the optical properties. The absorption spectra were obtained with BaSO_4 as a reference.

2.4. Photocatalysis Experiment

The photocatalytic performance of the developed composites was studied by degrading Methylene Blue (MB). All the photocatalysis experiments were performed in a simple 500 ml borosilicate beaker with a working volume of 250 ml. The initial concentration of the dye was set to 20 mg/L with 1 g of photocatalyst under continuous stirring conditions. One hour dark reaction was performed to achieve the absorption and desorption equilibrium. Then, the experiment is continue under bright sunlight for a duration of 180 mins. Control experiment was carried out with the absent of photocatalysts. The residual concentrations of MB in the samples were estimated through UV-Vis spectrometer.

3. Results And Discussion

The morphology of the synthesized composites is illustrated in Fig. 1. As shown, it is clearly indicate the homogenous nature and well dispersed of TiO_2 with N-GQDs as captured by FESEM analysis. From the HRTEM image (Fig. 1b), the N-GQDs/ TiO_2 photocatalysts are nearly spherical in shape with lattice spacing of 0.21 nm, which corresponds well to the graphitic carbon (100) plane [14]. This

correlate well with the formation of sp^2 hybridized carbon nanostructures. Moreover, it proves that the simple physical mixing is capable in incorporating both TiO_2 and N-GQDs.

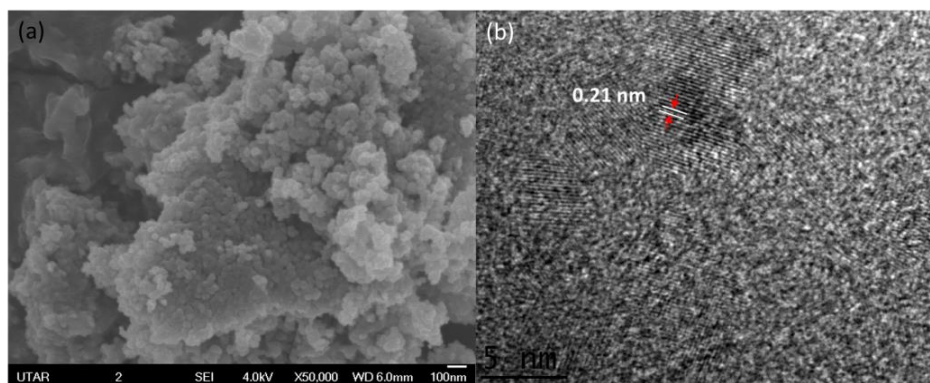


Figure 1. (a) FESEM and (b) HRTEM image of 1.5% N-GQDs/ TiO_2 .

Fig. 2 shows the obtained optical absorbance spectra of the synthesized composites. As shown in Fig. 2, pure TiO_2 exhibits low absorption in the region of 390 – 800 nm due to its wide band gap energy of 3.2 eV. This limiting the capability of TiO_2 in harvesting of UV light only. However, the composites show obvious enhancement in light absorption especially in the visible and NIR light region after incorporating with N-GQDs. This enhancement is contributed to the unique characteristics of N-GQDs that promoted red shift towards higher wavelength. This is attributed to the $n-\pi^*$ transition of graphene quantum dots [15]. Moreover, the absorption intensity of N-GQDs/ TiO_2 increases with increasing amount of N-GQDs.

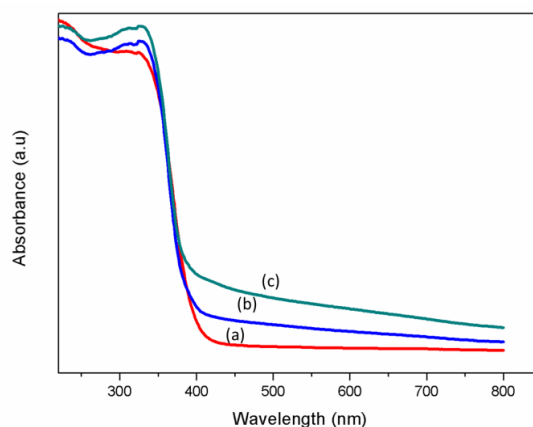


Figure 2. UV-Vis absorption spectra of (a) TiO_2 , (b) 0.5% N-GQDs/ TiO_2 and (c) 1.5% N-GQDs/ TiO_2 .

The photoluminescence of the synthesized composites was performed under the excitation wavelength of 315 nm and it is shown in Fig. 3. Pure TiO_2 exhibited a high and strong emission peaks at about 540-550 nm indicating its drawback of having high recombination rate of electron and hole pairs. However, this was eradicated with the incorporation of N-GQDs. The presence of N-GQDs has drastically separated the electron and hole pairs from recombine to generate heat. This enhanced separation had resulted to a low PL counts that was achieved by the composite (0.5% and 1.0% N-GQDs/ TiO_2) and it is clearly shown in Fig. 3. The higher percentage of N-GQDs give rise to a better electron and hole pairs separation. Hence, its prolonged the lifetime of these charge carriers. The separated electrons and holes will then undergo redox reactions and formed excess of active radicals. These active radicals are responsible for the photodegradation of MB and will result to an enhanced photocatalytic activity.

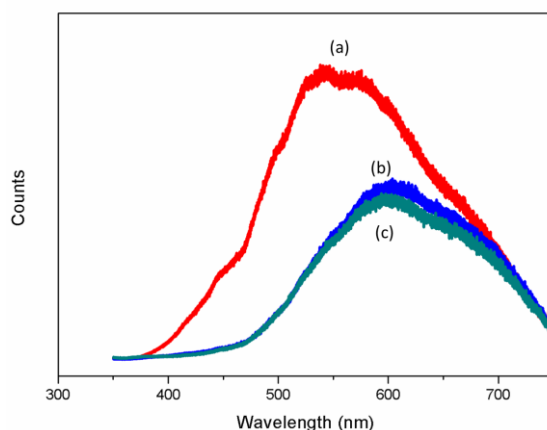


Figure 3. Photoluminescence spectra of (a) TiO_2 , (b) 0.5% N-GQDs/ TiO_2 and (c) 1.5% N-GQDs/ TiO_2 .

Fig. 4 portrays the photodegradation profile of MB with the presence of synthesized composite photocatalysts. The N-GQDs/ TiO_2 shows great photocatalysis enhancement as compare to pure TiO_2 . Result revealed that, 1.5% N-GQDs/ TiO_2 only required 150 mins for a complete removal of MB under bright sunlight as compare to pure TiO_2 (180 mins). The superiority degradation efficacy of 1.5% N-GQDs/ TiO_2 is due to the presence of N-GQDs that extended the light absorption range of pure TiO_2 to visible and near-infrared region as shown in the above UV-vis spectra analysis. With the strong light absorption capacity has increase the massive generation of electron and holes pairs in the synthesized photocatalysts. The free generated electrons will then formed the superoxide anion radicals ($\bullet\text{O}_2^-$) and followed by protonation that yields $\bullet\text{HO}_2$ radicals. These instable radicals will further form H_2O_2 and lead to the formation of hydroxyl radicals $\bullet\text{OH}$. Hence, this active radical are the key species in eliminating MB. However, 0.5% N-GQDs/ TiO_2 could not achieve a complete degradation under the same duration is due to the weak absorption of visible and NIR light. This leads to a lower generation of free electrons in the photocatalysts. The low generation of free electron will resulted to minimum formation of active radicals to eliminate methylene blue dyes.

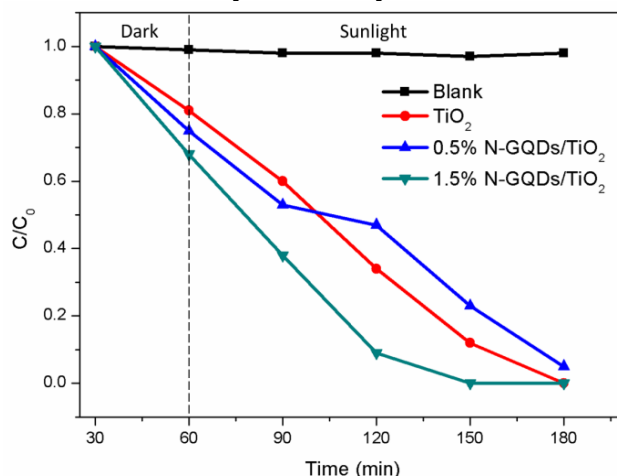


Figure 4. Photodegradation of Methylene Blue under dark and sunlight irradiation.

4. Conclusions

The present study shows the successful synthesized of N-GQDs functionalized TiO_2 through a simple physical mixing route to extend light absorption towards visible and near infrared light. Various characterizations proved the homogenous incorporation of N-GQDs with TiO_2 . A complete removal of

Methylene Blue was achieved in 150 mins by 1.5% N-GQDs/TiO₂ under sunlight irradiation. The improved photocatalysis was contributed by the red shift toward higher wavelength that enhanced the light absorption capacity of TiO₂ after incorporation with N-GQDs. This resulted to the massive generation of active radicals that responsible for photodegradation of MB. The absorption over the full solar spectrum laid a sustainable pathway for future practical applications. Hence, the synthesized composite will play a dynamic role as a sunlight sensitive photocatalyst in promoting sustainable environmental remediation in the near future.

Acknowledgment

This research work was supported by Universiti Tunku Abdul Rahman Research Fund, UTARRF (IPSR/RMC/UTARRF/2016-C2/L05)

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