

# Solar Light Harvesting N-Graphene Quantum Dots Decorated TiO<sub>2</sub> for Enhanced Photocatalytic Activity

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**Abstract.** N co-doped graphene quantum dots (N-GQDs) incorporated with nanocubic likes titanium dioxide (TiO<sub>2</sub>) are synthesized via facile hydrothermal method. The morphology features of the synthesized N-GQDs/TiO<sub>2</sub> nanocomposites are seen to exhibited in cubic shape. The average lateral size of the synthesized nanocomposites is found to be ~5.1 nm. UV-Vis absorption spectra show vastly improvement in the visible light range when N-GQDs is introduced to TiO<sub>2</sub>. The photocatalytic activity clearly demonstrated its solar light harvesting capability of prepared nanocomposites by photodegrading 4-chlorophenol (4-CP) under sunlight irradiation.

## 1 Introduction

In the field of semiconductor photocatalysis, TiO<sub>2</sub> has always come in the limelight and being extensively studied for its environmental sustainable approach. TiO<sub>2</sub> is renowned for its chemical stability, oxidative power, nontoxicity, low cost and good efficiency in complex organic degradation [1]. Despite of all the advantages shown, one cannot deny the fact that TiO<sub>2</sub> has a wide energy band gap (3.2 eV) and only functions under UV irradiation (about 4% of solar spectrum). Therefore, the utilization of solar light has become an appealing challenge for photocatalyst development. Graphene quantum dots (GQDs), a new type of nanomaterial consists of few layer graphene with unique properties inherent from both graphene and quantum dots. GQDs have been reported by several researchers for its improvement in the light absorption and enhanced photocatalytic activity under visible light irradiation [2-3]. Herein we report the effect of synergistic combination of N-GQDs with nanocubic like TiO<sub>2</sub> on the structural, chemical functional group and optical properties. The

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study of 4-CP elimination using prepared nanocomposites with direct sunlight irradiation was also carried out.

## **2 Experimental methods**

### **2.1 Synthesis of N-GQDs, nanocubic like TiO<sub>2</sub> and N-GQDs co-doped TiO<sub>2</sub>**

An amount of 2.1 g of citric acid (R&M Chemicals, UK) and 1.8 g of urea (R&M chemicals, UK) was dissolved in 50 mL of deionized water. The as-prepared solution was transferred into a Teflon-line autoclave and hydrothermally heated at 160°C for 8 h. The as-obtained solution was denoted as N-GQDs. Meanwhile, 3.4 g of tetrabutyl titanate (Sigma Aldrich, USA) was mixed and stirred in 50 mL of ethanol for 120 min. White precipitate was observed and aged for 48 h at room temperature. The as-prepared solution was subjected to hydrothermal treatment at 100°C for 48 h. The solid product was then dried at 70°C and the as-obtained sample as denoted as nanocubic like TiO<sub>2</sub>. Subsequently, the TiO<sub>2</sub> and 20 mL of N-GQDs (1.5mmol/L) solution were mixed and stir continuously for 24 h. The resulting product was centrifuged and washed repeatedly with distilled water and dried overnight at 60°C. The sample obtained was denoted as N-GQDs/TiO<sub>2</sub>.

### **2.2 Characterization**

The morphology of the N-GQDs/TiO<sub>2</sub> was observed on field emission scanning electron microscopy (FESEM, Hitachi SU-8000). Particle sizes and lattice fringes were determined by high resolution transmission electron microscope (HRTEM, JEM-2100F, Jeol). Uv-vis diffuse reflectance spectra (UV-Vis DRS, Shimadzu UV-2600) was used to investigate the optical properties. Functional groups were verified using fourier transform infrared (FTIR, Perkin Elmer Spectrum 400) at range 450 – 4000cm<sup>-1</sup>.

### **2.3 Photodegradation of 4-chlorophenol**

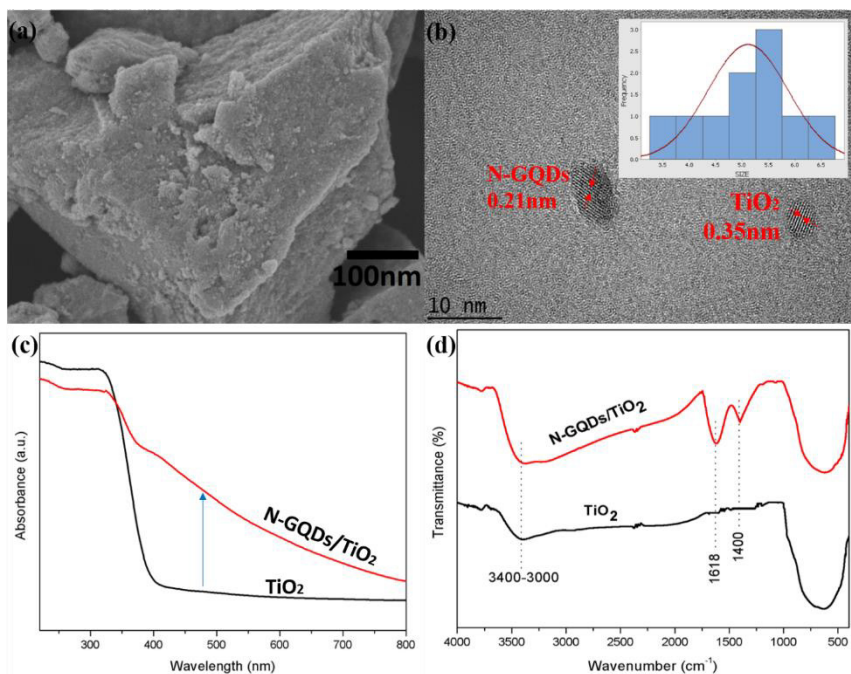
0.1 g of as-prepared nanocomposites were dispersed in a borosilicate glass beaker with 250 mL of 4-CP (5 mg L<sup>-1</sup>) solution. The mixture was carried out under dark condition for 3 h to establish adsorption-desorption equilibrium. Then the experiment was followed by 90 min of solar irradiation to determine the photocatalytic activity. Samples were collected at regular interval and analyzed through using high performance liquid chromatography (HPLC, Perkin Elmer N2980623) to measure the residual concentration of 4-CP with mobile phase of 60% ethanol to 40% water.

### **2.4 Reactive oxidation species**

1 mM of each benzoquinone (BQ), isopropyl alcohol (IPA) and ethylenediaminetetraacetic acid disodium salt (EDTA) were added into each glass beaker containing 250 mL 4-CP with 0.1 g of N-GQDs/TiO<sub>2</sub>. The photocatalytic procedure was repeated as above mentioned. The samples were collected and analyzed using HPLC.

### 3 Results and discussion

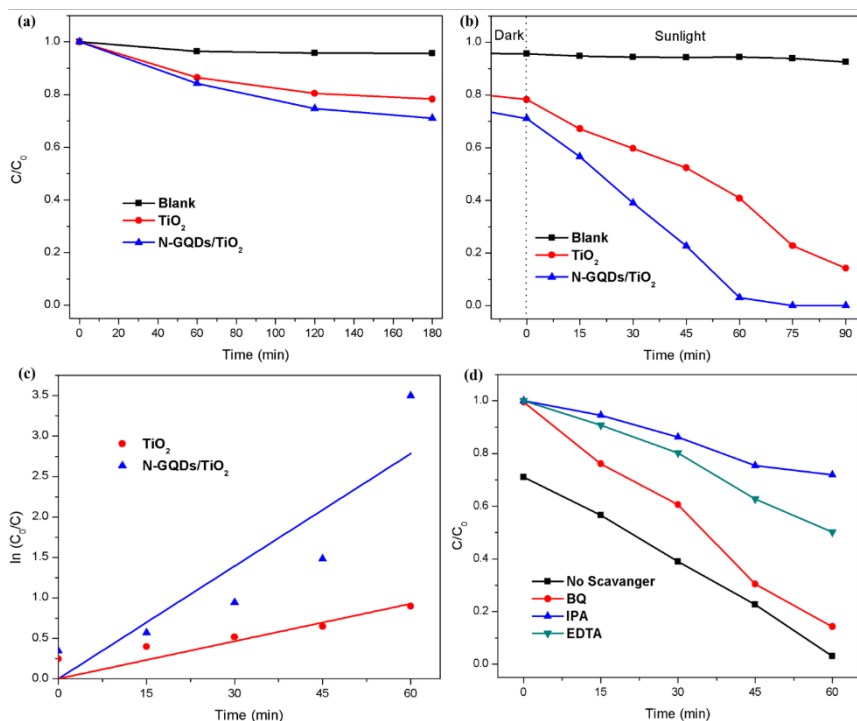
In figure 1(a), it can be clearly seen that TiO<sub>2</sub> nanoparticles were exhibited in cubic like morphology. The existence of N-GQDs in the nanocomposites would not have any effects on the morphology of TiO<sub>2</sub> [4]. The HRTEM image shown in figure 1(b) indicated the high crystallinity of N-GQDs/TiO<sub>2</sub> with lattice fringes of 0.21 nm and 0.35 nm for each N-GQDs and TiO<sub>2</sub> respectively. In addition, the nanocomposites size distribution (inset) showed an average size of ~5.1 nm. The absorption spectra of both as-prepared nanocomposites TiO<sub>2</sub> and N-GQDs/TiO<sub>2</sub> was displayed in figure 1(c). The incorporation of N-GQDs with TiO<sub>2</sub> demonstrated an observable increase in light absorption especially visible light range. Besides that, the band gap energies of nanocomposites can be calculated using the well-established Kubelka-Munk equation, which depicted the as-prepared nanocomposites band gap to be 3.0 eV. Furthermore, the presence of N-GQDs also introduced two functional groups to the nanocomposites. The strong intensity peak at 1618 cm<sup>-1</sup> is attributed to C=O stretching vibration in carboxylic acid while the weaker band at 1400 cm<sup>-1</sup> is ascribed to the stretching vibration of C-N in amine group [5-6].



**Fig. 1.** (a) FESEM, (b) HRTEM, (c) UV-DRS, and (d) FTIR spectrum of N-GQDs/TiO<sub>2</sub>.

The dark adsorption equilibrium was achieved in 3 h as shown in Figure 2(a). A control experiment (blank) where absence of photocatalyst was carried out to evidence that the 4-CP is a non-photosensitize pollutant. Figure 2(b) illustrated the solar irradiation photocatalytic activity of as-prepared nanocomposites. N-GQDs/TiO<sub>2</sub> depicted higher photodegradation which was complete degradation after 60 min as compared to nanocubic like TiO<sub>2</sub> which about 60% efficiency only. This signified the incorporation of N-GQDs could enhanced the photocatalytic activity by increasing the light absorption spectrum and narrowed the band gap energy. Besides that, N-GQDs could also act as an electron

reservoir to trap photogenerated electrons thus hinder electron-hole pair recombination whilst leaving more charge carriers to form active radicals ( $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$ ) which promote the degradation efficiency [1]. The degradation of 4-CP was fitted to pseudo-first order kinetics:  $\ln(C/C_0) = kt$ , where  $k$  is the apparent rate constant and  $t$  is the reaction time. The apparent rate constant of  $\text{TiO}_2$  and N-GQDs/ $\text{TiO}_2$  are  $0.01545 \text{ min}^{-1}$  and  $0.04641 \text{ min}^{-1}$ , respectively. This evidenced that the photocatalytic degradation rate of N-GQDs/ $\text{TiO}_2$  is 3 times higher than that over nanocubic like  $\text{TiO}_2$ . The reactive oxidation species was determined using scavenger test. Scavengers such as BQ, IPA and EDTA were used to scavenge superoxide radical ( $\cdot\text{O}_2^-$ ), hydroxyl radical ( $\cdot\text{OH}$ ) and photogenerated holes ( $h^+$ ), respectively. Figure 2(d) revealed that 4-CP is mainly oxidized by hydroxyl radicals, followed by holes and superoxide radicals, respectively.



**Fig. 2.** (a) Dark adsorption, (b) solar irradiation photocatalytic activity, (c) kinetic studies, and (d) scavenger test of N-GQDs/ $\text{TiO}_2$  on 4-CP.

## 4 Conclusion

In summary, this study demonstrated the successful synthesis of N-GQDs/ $\text{TiO}_2$  via hydrothermal method. The prepared nanocomposites performed better photocatalytic degradation than nanocubic like  $\text{TiO}_2$ . This is mainly due to the interaction of N-GQDs with  $\text{TiO}_2$  which extend the response to visible light. It also acts as electron acceptors and transporters, which then retard the recombination rate. Hence, it can be concluded that N-GQDs play an important role in improving the photocatalytic activity.

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