

# Bioinspired Synthesis of Carbon Dots/g-C<sub>3</sub>N<sub>4</sub> Nanocomposites for Photocatalytic Application

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**Abstract.** This study reports a fast and green preparative strategy to synthesize water soluble and fluorescent carbon quantum dots (CQDs) through hydrothermal method by using low cost organic waste of human fingernails as the carbon precursor for the first time. The coupling of CQD with pure carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) was further explored to enhance the latter's performance in photocatalysis of 2,4-dichlorophenol (2,4-DCP), a toxic and recalcitrant compound mostly released from industrial effluent. Such coupling overcame the weakness of pure g-C<sub>3</sub>N<sub>4</sub> in photocatalysis process by broadening its visible light absorption and promoting the charge separation. As a result, the removal rate of CQD/ g-C<sub>3</sub>N<sub>4</sub>(10) was up to 71.53%, which was approximately 1.5 times higher than that of pure g-C<sub>3</sub>N<sub>4</sub> under sunlight irradiation. The morphological structure, optical properties and chemical compositions of CQDs/g-C<sub>3</sub>N<sub>4</sub> composites were characterized using various spectroscopic techniques including field emission scanning electron microscopy (FESEM), Energy Dispersive X-Ray (EDX) and Ultraviolet-visible diffuse reflectance spectra (UV-DRS).

## 1 Introduction

Endocrine disrupting chemicals (EDCs) are chemical compound which might disrupt the endocrine system, eventually causing harmful effects in an intact organism [1]. Among all EDCs, 2,4-dichlorophenol (2,4-DCP) is regarded as one of the main pollutants in varied industrial effluents owing to its wide usage in pesticides, herbicides, insecticide, and antiseptic manufacturing process [2]. 2,4-DCP is very recalcitrant and difficult to remove especially in contaminated groundwater. The health problems that might brought by 2,4-DCP included faint, itch, and disruption of the human phospholipid bilayer.

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Advanced oxidation processes (AOPs) have been regarded as a promising solution for treating EDC compound [3]. Heterogeneous photocatalysis, as one of the AOPs, degrades complex pollutants into simple and non-hazardous substances without leaving significant secondary pollutants after the process. Carbon nitride ( $g\text{-C}_3\text{N}_4$ ) which is widely employed as photocatalyst possesses outstanding properties including economical viability, environment friendly, thermal stability and suitable band structures [4]. However, short light absorption spectra and rapid recombination of photogenerated electron-hole pairs hinder the efficiency of  $g\text{-C}_3\text{N}_4$  in photocatalytic application [5].

The carbon quantum dot (CQD) is a newly discovered nanomaterial of carbon family with size of below 10nm. CQD demonstrates unique and excellent optical properties such as excitation wavelength dependent fluorescence and excellent photostability [6]. The photoluminescence CQD is highly soluble in water, inert to chemical and negligible toxicity, plus its role as electron acceptors or donors in redox reaction make it suitable for photocatalytic applications when combining with  $g\text{-C}_3\text{N}_4$ . Development of CQD/  $g\text{-C}_3\text{N}_4$  nanocomposite shown improved performance compared to commercial photocatalyst in term of photocapability. A study reported that the composite of  $\text{C}_{60}$  monomer and  $g\text{-C}_3\text{N}_4$  matrix was able to degrade Methylene blue dye solution within 3 h [7]. Another successful attempt on CQD-modified  $g\text{-C}_3\text{N}_4$  hybrid shown 3 fold higher photodegradation rate compared to that of pure  $g\text{-C}_3\text{N}_4$  [8].

Hence, to counter the problem of short light absorption spectra and rapid recombination of photogenerated electron-hole pairs of pure  $g\text{-C}_3\text{N}_4$ , carbon quantum dot was coupled with pure  $g\text{-C}_3\text{N}_4$  to modify as well as improving the latter's weaknesses. In this research, human fingernail was used as the green precursor for synthesizing the CQD compound. The photoactivity of fingernail derived carbon dots/ $g\text{-C}_3\text{N}_4$  nanocomposites was evaluated by degradation of 2,4-DCP solution under sunlight irradiation.

## 2 Experimental sections

### 2.1 Materials

All the chemical reagents used in the project were of analytical grade and purity. The green precursor for the synthesis of CQDs were human fingernails whereas the initial material for  $g\text{-C}_3\text{N}_4$  was urea. Distilled water was used in the whole project. 2,4-dichlorophenol (2,4-DCP) (Uni-Chem, 98.5%) served as the EDCs pollutant sample for photocatalysis.

### 2.2 Synthesis of CQD/ $g\text{-C}_3\text{N}_4$ composites

Fingernails (1g) was added into distilled water (15 mL). The mixture was then transferred into an autoclave and heated in an oven at 200 °C for 3 h. Next, the CQDs were centrifuged at 12 000 rpm for 10 min to remove the large dots and dried in a vacuum oven for 48 h. Then,  $g\text{-C}_3\text{N}_4$  was prepared through heating of urea at 550 °C for 2h. 0.05g of CQD was mixed with 1g of  $g\text{-C}_3\text{N}_4$  to achieve 5wt% of CQD in the composite. The mixture was stirred for 24 h, transferred to autoclave and heated at 100 °C for 2 h. The CQD/ $g\text{-C}_3\text{N}_4$  composite residue were collected by removing excess CQD solution through centrifugation and dried at 60 °C. The experiment was repeated by changing weight percentage of CQD to 10wt% and 15wt%.



**Fig. 1.** Image of (A) human fingernail, (B) solid CQDs, (C) pure g-C<sub>3</sub>N<sub>4</sub> and (D) CQD/g-C<sub>3</sub>N<sub>4</sub>.

### 2.3 Characterization

Field emission scanning electron microscopy (FESEM) was used to determine the topographical and elemental information of the samples. Energy Dispersive X-Ray (EDX) was used to provide elemental identification and quantitative compositional information. Ultraviolet-visible diffuse reflectance spectra (UV-DRS) were used to determine the light absorption spectra of the samples.

### 2.4 Photocatalysis

Photodegradation test was carried out to assess the photocatalytic performance of CQD/g-C<sub>3</sub>N<sub>4</sub> samples under sunlight irradiation. The rate of degradation of the 2,4-DCP solution aided by various photocatalyst samples was monitored for 2 h. 0.1g of CQD/g-C<sub>3</sub>N<sub>4</sub> was added with 250 mL aqueous solutions for 2,4-DCP in a beaker. Before starting photodegradation process, the mixture solutions were stirred without exposing to light for 1 h to achieve adsorption-desorption equilibrium. Then the solution was brought to outdoor to run for degradation under sunlight. The experimental setup of MG and photocatalyst was illustrated in Fig. 2. For every 15 min interval, dye samples were analyzed for residual 2,4-DCP concentration with high-performance liquid chromatography (HPLC) in a period of 2 h. The experiment was conducted simultaneously by using the prepared photocatalysts namely: blank, pure g-C<sub>3</sub>N<sub>4</sub>, CQD/g-C<sub>3</sub>N<sub>4</sub>(5), CQD/g-C<sub>3</sub>N<sub>4</sub>(10) and CQD/g-C<sub>3</sub>N<sub>4</sub>(15). The degradation rate of each photocatalyst was computed by equation:

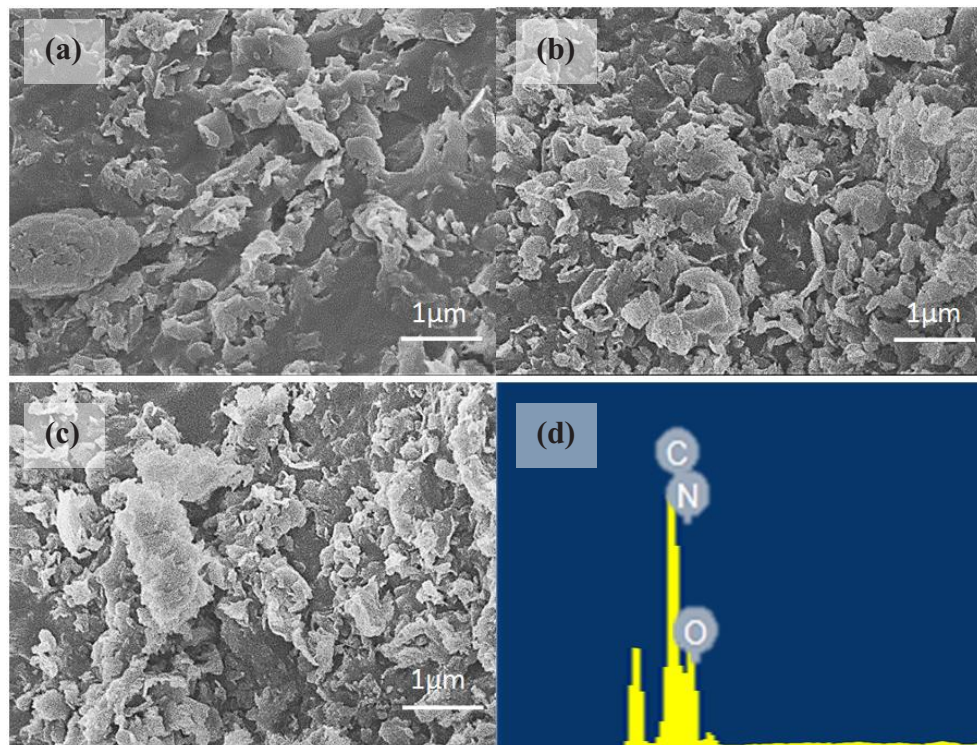
$$\text{Degradation Rate} = \frac{\text{Initial Concentration, } C_o - \text{Final Concentration, } C}{\text{Final Concentration, } C} \quad (1)$$

## 3 Result and discussion

### 3.1 Morphology and structure properties

FESEM analysis was conducted to determine the morphology and structure of CQD/g-C<sub>3</sub>N<sub>4</sub> composites. In Figure 2(a-c), it clearly shows that wrinkled structure of g-C<sub>3</sub>N<sub>4</sub> provided a better support for the attachment of C-dots at different concentration where higher concentration CQD/g-C<sub>3</sub>N<sub>4</sub> composite exhibited a more packed and aggregated morphological structure.

In order to identify the elemental composition of CQD/g-C<sub>3</sub>N<sub>4</sub> composites, EDX was carried out to confirm the presence of carbon (C), nitrogen (N) and oxygen (O) in CQD/g-C<sub>3</sub>N<sub>4</sub>(15) composite. Through Figure 2(d), the weight percentage of C, N and O were found to be 37.13, 57.45 and 5.42 %. The C and N elements originate from g-C<sub>3</sub>N<sub>4</sub> while O element was contributed by the reaction between urea and oxygen during the preparation of g-C<sub>3</sub>N<sub>4</sub>.



**Fig. 2.** FESEM Images of (a) CQD/g-C<sub>3</sub>N<sub>4</sub>(5) ; (b) CQD/g-C<sub>3</sub>N<sub>4</sub>(10) ; (c) CQD/g-C<sub>3</sub>N<sub>4</sub>(15); and (d) EDX of CQD/g-C<sub>3</sub>N<sub>4</sub>(15).

### 3.2 Optical properties

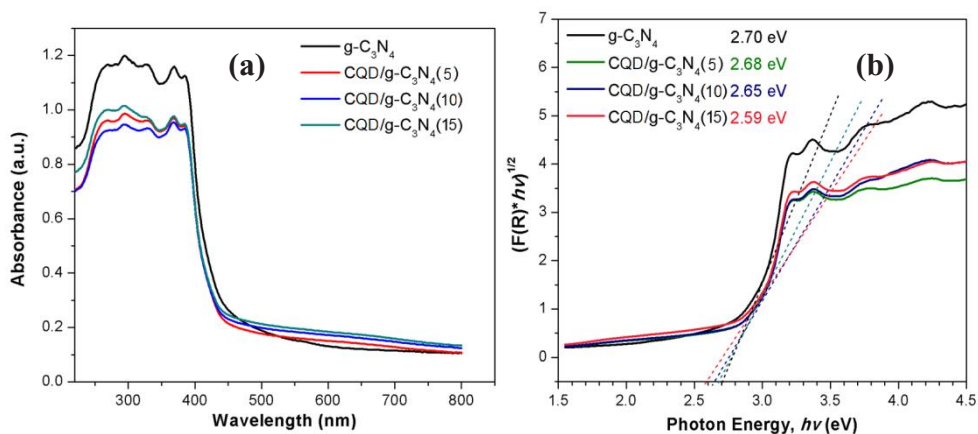
The study of ultraviolet-visible diffuse reflectance spectroscopy (UV-DRS) is demonstrated in Figure 3(a). The absorption spectra for all CQD/g-C<sub>3</sub>N<sub>4</sub> composites is blue-shifted towards UV region before the cut-off wavelength at 450 nm but the absorption spectra start to red-shift towards visible region after 450 nm. The band gap of photocatalyst can be determined using Tauc plot where  $(F(R) \cdot hv)^{1/2}$  was plotted against photon energy,  $hv$  as shown in Figure 3(b). Kubelka-Munck function,  $F(R)$  is defined by the following equation:

$$F(R) = (1 - R/100)^2 / 2R \quad (2)$$

where  $R$  is the diffuse reflectance. Meanwhile,  $hv$  or band gap energy was calculated using the recorded wavelength,  $\lambda$  was calculated using equation 3.

$$hv = 1240/\lambda \quad (3)$$

The band gap of each photocatalysts was obtained from x-intercept by drawing a tangent line of each curve. The band gap for  $g-C_3N_4$  is 2.70 eV whereas the band gap recorded for  $g-C_3N_4$ , CQD/ $g-C_3N_4$ (5), CQD/ $g-C_3N_4$ (10) and CQD/ $g-C_3N_4$ (15) composites was 2.68 eV, 2.65 eV and 2.59 eV respectively, indicating that the increase of CQD weight percentage in the composite would lead to the reduction of band gap energy for improved visible light absorption. Figure 3(b) summarized that the light harvesting capability of photocatalysts follows the sequence of CQD/ $g-C_3N_4$ (15) > CQD/ $g-C_3N_4$ (10) > CQD/ $g-C_3N_4$ (5) >  $g-C_3N_4$ .

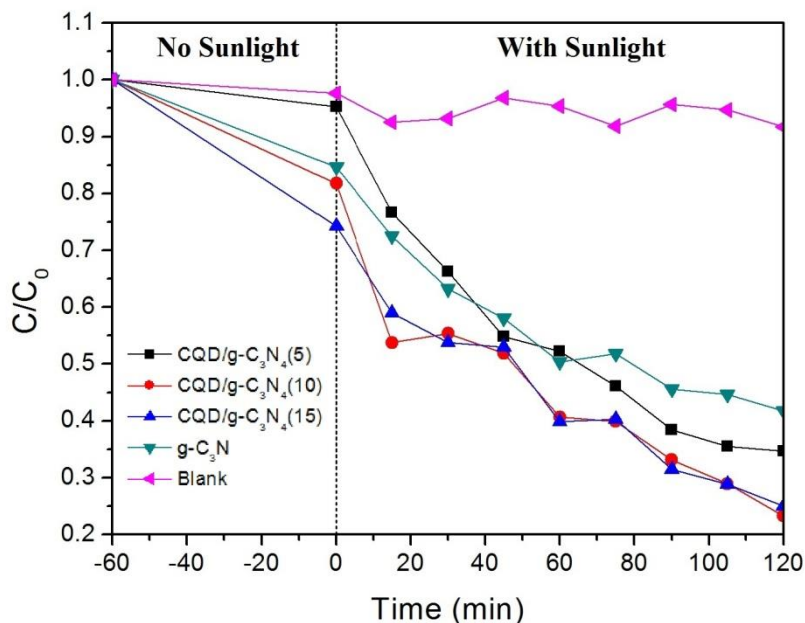


**Fig. 3.** (a) UV-visible Diffuse Reflectance Spectra of  $g-C_3N_4$ , CQD/ $g-C_3N_4$ (5), CQD/ $g-C_3N_4$ (10) and CQD/ $g-C_3N_4$ (15); (b) Tauc Plots of  $g-C_3N_4$ , CQD/ $g-C_3N_4$ (5), CQD/ $g-C_3N_4$ (10) and CQD/ $g-C_3N_4$ (15).

### 3.3 Photocatalysis

Figure 4 shows the degradation rate of 2,4-DCP solution from the beginning of dark adsorption process (1 h) to the end of photocatalysis process (2 h) with the aid of the as-prepared photocatalysts. The photodegradation efficiency of various catalysts was observed to be: CQD/ $g-C_3N_4$ (10) > CQD/ $g-C_3N_4$ (15) > CQD/ $g-C_3N_4$ (5) >  $g-C_3N_4$  > Blank. In the absence of photocatalyst, not much change was observed in term of concentration of 2,4-DCP solution for the blank solution under sunlight irradiation. Generally, the CQD/ $g-C_3N_4$  samples demonstrated improved photocatalytic capability compared to pure  $g-C_3N_4$ . On the other hand, the pure  $g-C_3N_4$  exhibited lower removal rate, calculated to be 49.30%. The relatively weak result of  $g-C_3N_4$  was mainly due to their short optical range absorption ability and fast recombination of  $e^-h^+$  pairs. The introduction of CQD onto  $g-C_3N_4$  in the hydrothermal process boosted the photoactivity efficiency.

CQD/ $g-C_3N_4$ (10) recorded the highest photocatalytic removal rate of 2,4-DCP which was 71.53%, followed by CQD/ $g-C_3N_4$ (15) CQD/ $g-C_3N_4$ (5) which recorded 66.26% and 63.57% degradation rate respectively. The improvement of photocatalytic ability of CQD/ $g-C_3N_4$  samples was mainly contributed by the broadening of the light absorption from UV region to near infrared region [9]. Secondly, enhanced photoactivity could be explained by reducing charge carriers recombination rate. The CQD prevented photogenerated electron-hole pairs from recombining by serving as electron reservoir, so that more charge carrier could be involved in the photodegradation process [9].



**Fig. 4.** Photocatalytic degradation of 2,4-DCP solution under irradiation of sunlight in the presence of various photocatalyst.

## 4 Conclusion

The CQD doped g-C<sub>3</sub>N<sub>4</sub> was successfully synthesized via green and sustainable method without expensive doping agent and complicated procedures. The as-prepared CQD/g-C<sub>3</sub>N<sub>4</sub> exhibited enhanced catalytic activity, effectively degrading 2,4-DCP up to 71.53% under sunlight. The factors that contributed to the improved properties of the composite included the reducing of electron-hole pairs recombination rate and increase in the light absorption range.

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