


Dimensionality-Driven CQD/TiO₂-g-C₃N₄ Ternary Composites for Boosting Photocatalytic and PEC Performance

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Original Research

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Abstract:

Photocatalysis and photoelectrochemical (PEC) water splitting are hindered by challenges such as rapid electron-hole recombination, limited visible light absorption, and inefficient charge transport. To overcome these limitations, a ternary composite CQD/TiO₂-g-C₃N₄ was engineered by combining 0D carbon quantum dots (CQDs), 1D TiO₂ nanorods, and 2D g-C₃N₄ nanosheets. This multidimensional structure significantly improves charge separation and transfer that enhances both photocatalytic and PEC efficiency. X-ray diffraction confirmed successful integration of TiO₂ and g-C₃N₄, with crystallite sizes ranging from 8.1 to 9.3 nm. SEM and TEM analyses showed uniform dispersion of TiO₂ nanorods on g-C₃N₄ sheets, while CQDs (~5–6 nm) were attached to surface, establishing strong interfacial contact for efficient charge movement. UV-vis exhibited a redshift, indicating a narrower band gap, and PL analysis showed reduced electron-hole recombination. Under visible light, composite with 15.0 mL CQD displayed excellent photocatalytic activity, achieving 96.0% degradation of mixed dyes (MO + BPB) with clear linear degradation indicating constant reaction rate and delivering a high PEC photocurrent density (~33 mA/cm²). CQDs enhance charge separation and lower band gap while multidimension (0D–1D–2D) structure boosts charge transfer. The 0D–1D–2D architecture enhances charge mobility and light utilization, making this material highly effective for environmental cleanup and sustainable energy applications.

Keywords: Dimensionalities; Synergistic role; CQDs; Ternary composite; 2D g-C₃N₄

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1. Introduction

The photocatalysis has emerged as a highly capable method to eliminate organic contaminants and split water to produce hydrogen in an eco-friendly and sustainable way [1, 2]. Effective photo catalysts should be cost effective, chemically stable and have high photocatalytic activity. N-type semiconductors such as TiO₂ and WO₃ etc are considered prototype photo-catalysts due to their exceptional chemical stability and conduction band edge at suitable potential level [3, 4]. Meanwhile, these materials practical applicability are limited since they absorb UV light in the complete solar spectrum and UV light increases efficiency of photo-generated excitons fast recombination.

Graphitic carbon nitride (g-C₃N₄) with low band gap was proposed as a next-generation photo-catalyst. g-C₃N₄ is a prominent organic polymeric semiconductor made entirely from non-metallic elements known for its non-toxic nature, strong chemical stability and effective utilization of visible light, due to its 2.7 eV band gap. Compared to other narrow band-gap semiconductor materials, it shows favorable valence and conduction band potentials of +1.6 eV/NHE and -1.1 eV, respectively [1]. These properties indicate that g-C₃N₄ is a highly effective, capable and functional for environmental cleaning and water splitting [5]. Despite its settlements, g-C₃N₄ has numerous limitations, like smaller precise surface area, fast charge carriers recombination rate, and the potential for H₂O₂ formation from opposing two-

electron reactions, which can disturb the photocatalytic efficiency for water splitting and hydrogen evolution [6]. Efforts to overcome these deficiencies have led to the development of effective methodologies, including g-C₃N₄ nanosheets, to increase the surface space [7]. Earlier studies have highlighted the benefits of heterojunctions in decreasing electron-hole recombination rates. For example, Wang et al. and Panimalar et al. established hydrogen production driven by visible light consuming MnO₂ and reforming carbon nanotubes with g-C₃N₄ composites [8, 9]. Similarly heterojunction of g-C₃N₄ with TiO₂ is extremely observed for attractive photocatalytic performance. Because TiO₂ band gap supports graphitic carbon nitride, allowing exchange of electrons from the conduction band of TiO₂ to g-C₃N₄, whereas VB of TiO₂ transports holes to g-C₃N₄ to drive redox reactions [10, 11]. To improve solar energy consumption, researchers have concentrated on improving its visible-light absorption through several approaches, such as structural amendment and morphological modification [12]. Therefore, adding TiO₂ with g-C₃N₄ to produce a porous nanocomposite with a large surface area is an inspiring strategy for improving photocatalytic performance [6]. TiO₂/g-C₃N₄ combinations with enhanced visible-light sensitivity have apprehensive escalating consideration in latest years [13, 14]. Several techniques have been discovered to achieve these improvements, such as stirring, bubbling, and the use of chemical agents, while fabrication of these heterostructures has been successfully employed through co-calcination and hydrothermal treatment method [15]. Besides, various heterojunction arrangements have been reported, including 0D/2D [6], 1D/2D [16], and core-shell structures [12]. These well-made heterojunctions may not only expand absorption of visible light but enhance the separation of photo induced excitons and downturn their recombination [7]. However, for TiO₂/g-C₃N₄ heterojunctions, interface electron-hole pairs traffic crowding has continued an in-expressive issue that blocks effective charge transport [8].

Additionally, the use of CQDs for their up-conversion fluorescence provides an opportunity to improve photo catalysis by expanding light absorption into ultraviolet or near-ultraviolet arrays. CQDs constitute a new group of carbon nanomaterials with outstanding qualities, including great bio-compatibility, size-dependent effects, strong solubility, transport abilities and effective electron acceptance. These prospects, linked with their cost-effectiveness, have led to their universal application in the photocatalyst strategy [17]. Owing to their nanoscale size, CQDs can generate close-fitting connections within photocatalysts, which support charge carrier recombination rates by enabling the transfer of photogenerated charges through various semiconductors [17, 18]. Earlier studies have confirmed that CQDs are capable of receiving electrons from other semiconductors and increasing light absorption. For example, CdS/CQD/g-C₃N₄ composites have greater degradation under visible, near-infrared (NIR) light when Z-structure charge transfer system is applied [19].

On the basis of a review of the present literature, we established a new graphitic carbon nitride nanocomposite

(CQDs/TiO₂-g-C₃N₄) combination that is both light and cost-effective for photocatalysis. These composites were precisely constructed to increase the degradation of methyl orange [19, 20] and bromo-phenol blue as well as to expand the electrochemical (PEC) performance [21, 22]. The integration of 0D CQDs into the TiO₂/g-C₃N₄ medium strongly affects the water splitting reaction. CQDs improve the solidity at potentials and in electrolyte situations, which provides better PEC interpretation even at small applied potentials. This could be linked to a reduction in the number of effective sites offered for the PEC water splitting system [23]. In these composite assemblies, TiO₂ uses solar light efficiently due to its band gap i.e. 3.2 eV. The variation in g-C₃N₄ by the CQDs extends the absorption spectrum into the ultraviolet region ($\lambda < 380$ nm), potentially facilitating the induction of TiO₂ through photon-generated carriers [22, 24]. Our plan also integrates up-conversion fluorescence to spread visible light consumption, thereby facilitating successful chemical catalysis for the degradation of MO and BPB.

This research motivated the formation of unique multidimensional (0D/1D/2D) structure where 0D CQDs serve as rapid electron acceptors, 1D TiO₂ nanostructures act as charge transport pathways and 2D g-C₃N₄ sheets enable broader light absorption capabilities which creates a synergistic effect that maximizes interfacial charge separation and transfer. This hierarchical integration not only accelerates surface redox reactions but also broadens absorption range and minimizes charge recombination losses. Such cooperative interactions between multiple dimensionalities represent key innovation of this work and fundamental mechanism driving superior photocatalytic and PEC performance.

2. Experimental methods

2.1 2D graphitic carbon nitride (g-C₃N₄) fabrication

To synthesize graphitic carbon nitride nanosheets, combination of 6.0 g urea and thiourea in 1:1 ratio are used as precursors in a controlled thermal process. To prevent exposure to air, the crucible was tightly covered with Al foil. The crucible is then subjected to thermal treatment in a furnace, where it is heated to 400 °C for 1 h. This method ensures the production of nanosheets with the desired structural properties through a controlled chemical annealing process.

2.2 1D TiO₂ fabrication

To fabricate 1D TiO₂ nanomaterials, 50 mL of NaOH solution and 5.0 mL of tetra butyl titanate (TBT) precursor were mixed. PH was carefully driven to 10 by gradually mixing with sodium hydroxide (NaOH) while stirring for 1.5 h. The combination was then treated hydrothermally in an autoclave at 160 °C for 4 h. Subsequently, the product was isolated by washing and centrifugation several times to remove impurities. After washing, the product was dried and calcined in an incinerator at 60 °C. Finally, calcined material was ground to produce a fine, white TiO₂ powder.

2.3 0D CQD fabrication

1.0 g of citric acid was melted in 40.0 mL of deionized water, stirred for 30 min to prepare the CQDs [25]. Citric acid was used as the carbon precursor in the hydrothermal synthesis of the CQDs. The subsequent solution was heated in hydrothermal instrument (oven) at 160 °C for 3 h. Compared to conventional high-temperature or vacuum-based techniques, the hydrothermal process uses a lot less energy and runs for a few hours at moderate temperatures (160 – 200°C) [22, 25]. The solution was examined in UV light, and a purple glow was observed. This indicates the successful formation of CQDs. This luminescence confirmed that the CQDs were ready for subsequent utilization.

2.4 Co-precipitation method for ternary composites

The fabrication of ternary composites, including g-C₃N₄, TiO₂, and CQDs, was achieved through a chemical method [26]. First, a binary nanocomposite of TiO₂ and g-C₃N₄ was fabricated by dissolving a specific amount of g-C₃N₄ with 2.0% TiO₂ in ethanol (40.0 mL). The mixture was sonicated for 40 min and then washed with ethanol for 30 min under centrifugation at 4000 rpm. The combination was subsequently dried at 70 °C for 3 h. The composite was subsequently partitioned into five equal parts. Four samples were combined with different proportions of CQDs (5.0, 10.0, 15.0, and 20.0 mL) and prepared (CQD/TiO₂-g-C₃N₄) ternary composites. These combinations were dehydrated by a hot plate, crushed into fine powders, and investigated for their photocatalytic activity. The fifth part is a binary composite for comparison with the ternary composites [25, 26]. The synthetic route of CQD/TiO₂-g-C₃N₄ nanocomposite is labelled in Scheme 1.

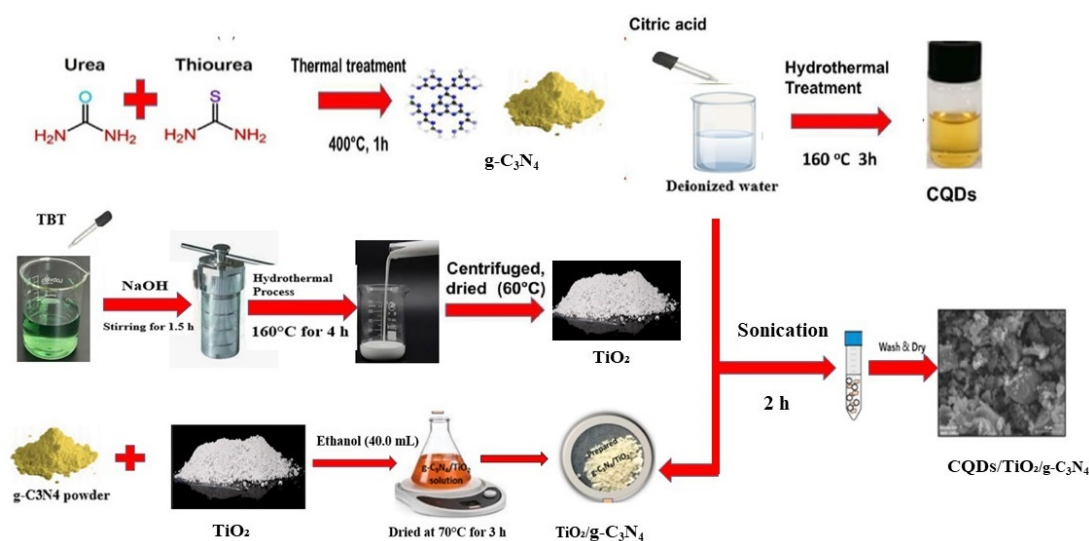
2.5 Photo catalysis experiment

The photocatalytic reactions of the fabricated composites were analyzed to degrade a mixed dye solution containing MO and BPB, each at a concentration of 10 mg, resulting in a total dye concentration of 20 mg/L. To determine the ideal dose, catalyst concentrations of 0.05 g are evaluated

in 50 mL of dye solution [23, 26]. In a similar vein, various dye concentrations (10 mg/L, 20 mg/L, and 30 mg/L) were examined; These dye concentrations of 10 mg/L, 20 mg/L and 30 mg/L, have been widely reported in literature for photocatalytic degradation studies using g-C₃N₄ and composite-based photocatalysts [4, 12]. For each experiment, 0.05 g of the synthesized photo catalyst either TiO₂-g-C₃N₄ or CQD/TiO₂-g-C₃N₄ was added to 50 mL dye solution in a beaker. Photocatalytic degradation procedure was determined by initially keeping the solution in dark room for 30 min to simplify photocatalyst adsorption. After this adsorption period, samples (4.0 mL) were removed at 1h intervals under the radiation of a 1000 W xenon spotlight and immediately filtered to remove photocatalyst particles. It is significant to remember that the 1000 W xenon lamp applied in this research was only used as a laboratory light source to repeat ordinary lighting condition a controlled environment [4, 16]. Measured the absorption of the remaining contaminant and degradation percentage using UV-Vis Shimadzu 2700 spectrophotometer by detecting the absorbance peak specific to the dye which allowed the determination of variations in the absorbances of solutions corresponding to the concentrations of MO and BPB [18]. This process determines the photocatalytic ability over time. Every experiment was repeated three times, and deviation for each run was ±3%.

2.6 Photoelectrochemical measurements

Photoelectrochemical experiments were performed using a work station (Correst potentiostat) with three-electrode classification, adjusting a standard calomel electrode (SCE), working electrode and a platinum counter electrode as a reference. The reversible hydrogen electrode (RHE) potential was measured via SCE analyses. To formulate the catalyst for the working electrode, 1.0 mg of the sample was liquefied in 10.0 mL of ethanol, subjected to ultrasonication for 1 h to attain a constant distribution, and then placed on fluorine-doped tin oxide (FTO) as a thin film substrate. Polarization bends were obtained via linear sweep



Scheme 1. Schematic diagram of CQD/TiO₂/g-C₃N₄ nanocomposite.

voltammetry (LSV) at 0.3 V versus NHE in a 0.5 M KOH electrolyte, which was sustained at a pH of approximately 12 and irradiated with $\lambda > 420$ nm. The photogenerated electrochemical cyclic voltammetry (CV) was implemented over five rounds at a scan rate of 20.0 mV/s. Furthermore, electrochemical impedance spectroscopy (EIS) was used to evaluate the system's proficiency under similar electrolyte and radiation atmospheres.

3. Characterization techniques

The sample morphology and composition were reviewed via SEM (JEOL-JAD 2300). Structural examination was conducted with X-ray diffraction using a Rigaku D/Max diffractometer with Cu K α radiation (wavelength = 1.54 Å) functioned at 40 kV and 100 mA to determine the crystal structures. FT-IR spectra were recorded between 400 and 4500 cm⁻¹ with a Model IR Tracer 100 spectrometer. UV-visible diffuse absorption and reflectance spectra were analyzed using a Shimadzu 2700 spectrophotometer. PL spectra were captured at ambient temperature with a Horiba Fluoromax-4 spectrofluorimeter. Raman spectra were obtained via a Horiba scientific Xplora spectrometer with a 532.0 nm YAG laser. PEC performance was assessed in a 3-electrode terminal cell with FTO glass coated with CQD/TiO₂-g-C₃N₄ composites using a standard calomel electrode (SCE) as the reference and a platinum counter as the working electrode, a saturated platinum electrode as the counter electrode, and 0.5 M KOH as the electrolyte. Photocurrent densities were measured at 100 mW/cm² from a 1000 W xenon arc lamp with an AM 1.5 G filter.

4. Results and discussion

4.1 Role of nanodimensionalities

The traditional systems usually include binary combinations such as CQDs/TiO₂ or TiO₂-g-C₃N₄, which often suffer from restricted charge separation and lacking light absorption. In difference, the CQD/TiO₂-g-C₃N₄ composite used a multidimensional structure combining 0D carbon quantum dots, 1D TiO₂ nanorods, and 2D g-C₃N₄ nanosheets. This architecture strategy proposed several benefits such as, 2D g-C₃N₄ provides large surface area for catalytic reactions, improving the charge transfer efficiency. 0D CQDs act as electron mediators, trapping electrons and facilitating their transfer while also extending visible-light absorption through upconversion photoluminescence. This multidimensional synergy optimizes light harvesting, minimizes charge recombination, and significantly enhanced the photocurrent density (~ 33 mA/cm²), than usually stated in the literature study. Therefore, this composite used as a photocatalyst not only surpasses old-fashioned TiO₂ structures in photocatalytic degradation but also indorse greater performance in photoelectrochemical water splitting.

4.2 X-ray diffraction (XRD) analysis

XRD was performed to calculate crystalline phases and structures of synthesized nanomaterials, as shown in figure 1 (A). The XRD results revealed distinctive peaks for g-C₃N₄, with prominent signals at 27.4° matching the (002)

plane and a small intensity peak at 11.9° for the (100) plane. The result agrees well with prior findings by Wang et al., and Zhang et al. [27, 28]. This figure illustrates the materials interplanner stacking of the periodic tri-azine units and aromatic rings, respectively [29, 30]. The XRD graph of titania (anatase phase in Fig. 1 (A)) typically shows its most intense diffraction peak at $2\theta \approx 25.3^\circ$, corresponding to the (101) plane, along with characteristic peaks at 37.8° (004), 48.0° (200), and 55.1° (211). These sharp peaks confirm the crystalline anatase structure of TiO₂. In the binary combination of TiO₂/g-C₃N₄ (Fig. 1 (A)) and CQD/TiO₂/g-C₃N₄ composites (Fig. 1 (B)), supplementary peaks for TiO₂ are detected at 27.4° (101), 33.3° (009), 37.5°, 40.8°, 45.5°, 53.4° (220), and 78.0° that endorse the effective combination of the components, as maintained in the literature using (PDF JCPDNo. 21-1272) [31], and other specific angles. However, their intensity decreases, possibly because of their low content or weak diffraction. In particular, the distinctive peak at 45.0° in CQD/TiO₂/g-C₃N₄ samples with 15.0 and 20.0 mL CQDs is attributed to the high content of CQDs in composites specify a unique structural phase not generally detected in earlier studies. This is allocated to induced interface by the amplified CQD content. It distinguished them from other samples. The diffraction peaks of the CQDs in the other samples are not detected because of their low contents. For the (002) plane, the main peak intensity is slightly reduced. The XRD patterns also display a shift in the (100) peak of g-C₃N₄ to a small intensity compared with the intensified peaks at 64.0° and 78.2°, credited to the combination of TiO₂. The absence of CQD peaks in some samples suggests their low concentration. The Scherrer formula was used to determine the crystallite size of the composites which are given in Table 1.

4.3 Raman spectroscopy

Raman spectroscopy was used to measure the phase characteristics and structural changes in TiO₂/g-C₃N₄ binary and CQD/TiO₂-g-C₃N₄ ternary composites. A significant upfield shift in the vibration band occurred at the same point at 1044 cm⁻¹ for both composites (Fig. 1 (C)) [32]. Similarly, peaks at 1276 and 1303 cm⁻¹ were observed for both TiO₂/g-C₃N₄ and 15.0 mL-CQD/TiO₂-g-C₃N₄ composites. The shifts are linked to the interactions among the sigma bonds of g-C₃N₄ and oxygen vibrations of TiO₂ in composite [33]. Additionally, the TiO₂/g-C₃N₄ spectra exhibit prominent D and G band peaks at 1427 cm⁻¹ and 1470 cm⁻¹, respectively, which signifies defects in the g-C₃N₄ carbon network [34]. The observed downfield shift in the ternary composite suggests the formation of new bonds or modifications in existing bonds, indicating that g-C₃N₄ may be integrated into the TiO₂ matrix rather than simply existing as a physical blend.

4.4 FTIR spectroscopy

FTIR spectroscopy, illustrated in figure 1 (D), was used to characterize functional groups present in the g-C₃N₄, TiO₂/g-C₃N₄ binary composite, and CQD/TiO₂-g-C₃N₄ ternary composites. FTIR investigation revealed the existence of g-C₃N₄, with characteristic peaks naturally observed in the 800 – 1900 cm⁻¹ range. The major peaks

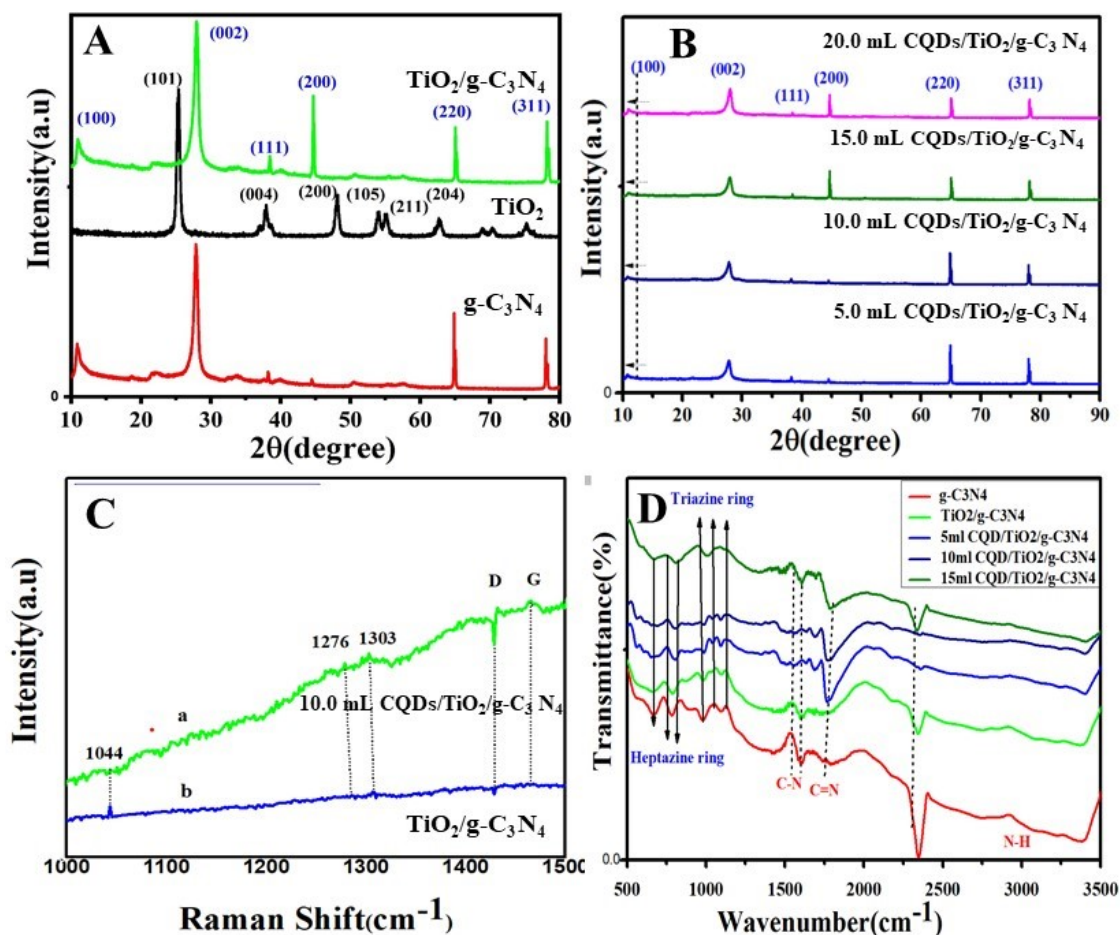


Figure 1. (A) XRD arrays of samples of 2D-g-C₃N₄, TiO₂ and TiO₂/g-C₃N₄ binary composites. (B) 5.0 mL-CQDs/TiO₂-g-C₃N₄, 10.0 mL CQDs/TiO₂-g-C₃N₄, 15.0 mL-CQDs/TiO₂-g-C₃N₄ and 20.0 mL-CQDs/TiO₂-g-C₃N₄. (C) Raman analyses of samples of the TiO₂/g-C₃N₄ binary composite and 15.0 mL-CQD/TiO₂/g-C₃N₄ ternary composite. (D) FT-IR spectra of various pure and binary and ternary composites.

at 500 – 700 cm⁻¹ were observed for Ti-O and Ti-O-Ti stretching modes [35]. Remarkably, spectra show distinctive vibrational modes connected with g-C₃N₄, containing the heptazine ring breathing mode at approximately 750-808 cm⁻¹ and additional peaks between 809 and 1200 cm⁻¹. These results are in consistent with the triazine group's vibrations as reported in earlier research studies [36]. Extending vibrations were apparent between 1200 and 1650 cm⁻¹, with definite peaks at 1540 cm⁻¹ and 1650 cm⁻¹ related to C-N and C=N bond broadening, respectively with previous documented [35, 37]. The peak at 2363 cm⁻¹ was attributed to CO₂ molecules on the surface. N-H broadening was detected between 2830

and 3500 cm⁻¹, associated with NH₂ or NH groups at defective sites in aromatic ring [38]. These explanations support presence of g-C₃N₄ in samples. However, the FTIR data alone do not elucidate whether g-C₃N₄ is simply mixed with TiO₂ or has been integrated into the TiO₂ lattice.

4.5 Optical studies

To evaluate the light absorption efficiency, diffuse reflectance spectroscopy was utilized, and results are shown in figure 2 (A). TiO₂ exhibited light absorption primarily below 375 nm, which is consistent with earlier research [39]. In contrast, the incorporation of g-C₃N₄ into TiO₂ extended absorption wavelength to 470 nm. This finding indicates

Table 1. Crystalline sizes and bandgaps of the pure, binary and ternary composites.

Composites	Crystallite Size (nm)	Bandgap (hc/λ) eV
g-C ₃ N ₄	9.0	2.75
TiO ₂ /g-C ₃ N ₄	8.1	2.63
5.0 mL CQDs-TiO ₂ /g-C ₃ N ₄	8.8	2.59
10.0 mL CQDs-TiO ₂ /g-C ₃ N ₄	8.6	2.43
15.0 mL CQDs-TiO ₂ /g-C ₃ N ₄	8.7	2.27
20.0 mL CQDs-TiO ₂ /g-C ₃ N ₄	9.3	2.33

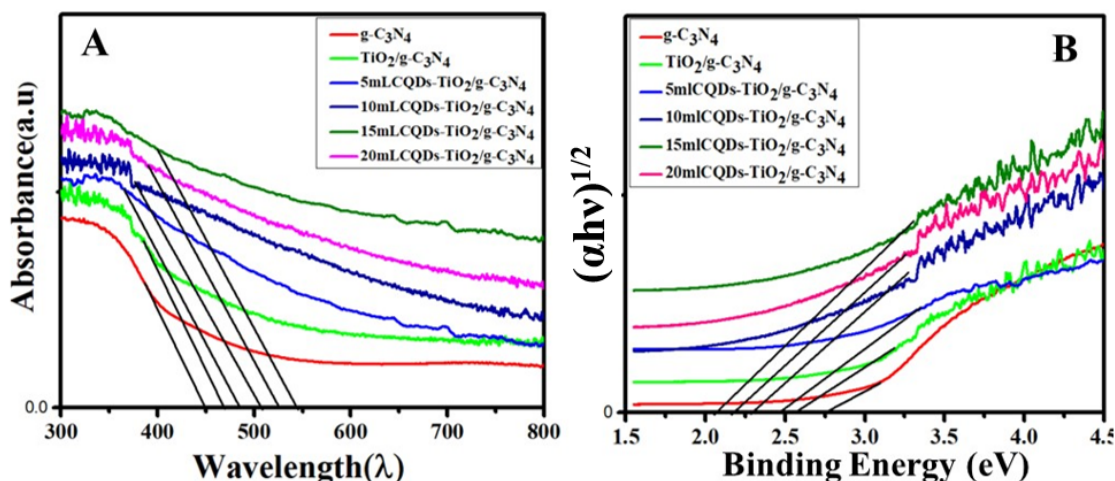


Figure 2. (A) UV-visible DRS absorbance spectra, (B) corresponding bandgap photon energy values of 2D-g-C₃N₄ and TiO₂/g-C₃N₄ binary composites, 5.0 mL-CQDs/TiO₂-g-C₃N₄, 10.0 mL CQDs/TiO₂-g-C₃N₄, 15.0 mL-CQDs/TiO₂-g-C₃N₄ and 20.0 mL-CQDs/TiO₂-g-C₃N₄ ternary composites.

that heterojunction between two materials enhances light absorption. Furthermore, the addition of CQDs to TiO₂/g-C₃N₄ led to an increased absorption edge that extended into the infrared region [40]. This redshift in the absorption spectrum suggests a reduction in the photocatalyst bandgap, as shown in Fig. 2 (B). This is linked to redox potential of the photogenerated charge carriers. CQDs act as electron acceptors and do not influence the VB directly. They contribute to a broader conduction band (CB) by shrinking the band gap [41]. This adjustment reduces the electron capacity for reduction in the conduction band but is offset by enhanced visible light absorption which is agreed with pervious report of Y. Deng et al. that CQDs showed up-conversion materials absorbing visible light, which initiates TiO₂ to produce electron-hole pairs [40]. This mechanism improves degradation efficiency of pollutants under both UV and visible light irradiation. Consequently, a redshift of the absorption edge within a specific range can improve photocatalytic performance by increasing efficiency of light utilization and enhancing overall photocatalytic activity. The photocatalytic efficiency decreased when the redshift effect could not be effectively counterbalanced by increased light absorption [42]. The optimal photocatalytic activity for TiO₂/g-C₃N₄ composites altered with CQDs was observed at 15.0 mL and 20.0 mL, where the enhanced visible light absorption sufficiently mitigated the redshift effect. However, at CQD loadings exceeding 15.0 mL, the redshift effect offset the benefits of increased visible light absorption, leading to reduced catalytic performance. Bandgap analysis via the Tauc plot method in Fig. 2 (B) indicated that g-C₃N₄, TiO₂/g-C₃N₄ and CQDs-TiO₂-g-C₃N₄ (5.0, 10.0, 15.0 and 20.0 mL concentrations of CQDs, respectively) have bandgaps of approximately 2.7, 2.6, 2.5, 2.4, 2.2 and 2.3 eV, respectively (Fig. 2 (B) and Table 1).

4.6 PL spectroscopy analysis

Photoluminescence (PL) spectra are dynamic for evaluating charge separation, recombination dynamics, and radiation mechanisms in photocatalysts, as displayed in Fig. 3. The PL spectra of g-C₃N₄ show two distinctive radiation peaks

at 439 nm and 479 nm, which are linked with sp³ C-N (σ) and sp² C-N (π) bond transitions, respectively which show similarity with the result reported earlier [43]. Upon the addition of TiO₂ and the CQDs, the PL intensity clearly decreases, with slight peak shifts. Certainly, integrating CQDs into TiO₂/g-C₃N₄ nanocomposites leads to strong PL quenching, which is generally visible in 15.0 mL of TiO₂/g-C₃N₄ composite. This outcome is attributed to intensified p-p interfaces and the creation of a type II van der Waals heterojunction, which efficiently decreases charge carrier recombination [44]. Moreover, a bathochromic shift in the PL spectra results in the highest radiation peak changing from 429 to 432 nm and 479 to 474 nm in the 5.0 mL-CQDs/TiO₂/g-C₃N₄ sample, which is likely an overview of the subgap defects incorporated by the nanomaterials [44, 45].

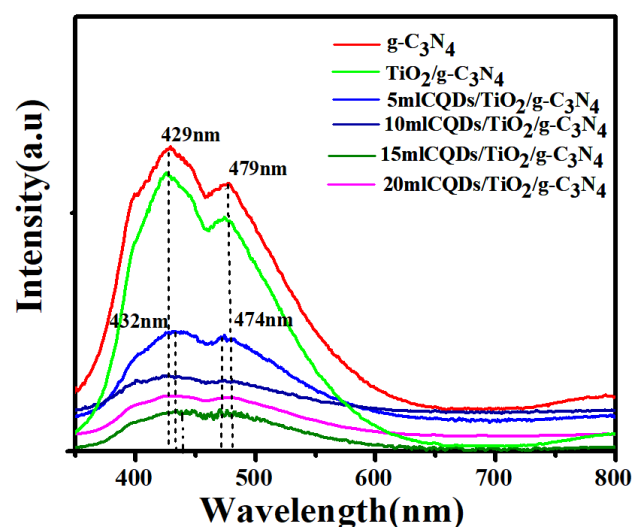


Figure 3. Photoluminescence composite spectra of 2D-g-C₃N₄ and TiO₂/g-C₃N₄ binary composites, 5.0 mL-CQDs/TiO₂-g-C₃N₄, 10.0 mL CQDs/TiO₂-g-C₃N₄, 15.0 mL-CQDs/TiO₂-g-C₃N₄ and 20.0 mL-CQDs/TiO₂-g-C₃N₄ ternary composite spectra at an excitation wavelength of 330 nm at standard temperature.

4.7 Morphology and composition analyses

Scanning electron microscopy and energy dispersive X-ray spectroscopy were used to analyze morphology and composition of samples. Figure 4 shows SEM images and EDX results for pure $g\text{-C}_3\text{N}_4$, revealing a non-uniform 2D nanosheet structure at scales of 1 μm and 500 nm. SEM images revealed the 2D sheet morphology of $g\text{-C}_3\text{N}_4$, which is crucial for optimizing its properties in composite formation. Figure 4 shows SEM images of the $\text{TiO}_2/g\text{-C}_3\text{N}_4$ composite, highlighting the integration of 1D TiO_2 rods within the 2D $g\text{-C}_3\text{N}_4$ sheets. The addition of 0D CQDs in $\text{TiO}_2/g\text{-C}_3\text{N}_4$ composite, as shown in Fig. 4, led to significant morphological changes, with a prominent stacked sheet-like structure visible in the 15.0 mL CQD/ $\text{TiO}_2/g\text{-C}_3\text{N}_4$ composite. The CQDs, which are difficult to detect because of their smaller size, are dispersed on the surface of $\text{TiO}_2/g\text{-C}_3\text{N}_4$ sheet, as

shown by black dots.

EDX spectroscopy was applied to examine the elemental arrangement of generated samples, as shown in Fig. 4. The EDX spectrum of 2D $g\text{-C}_3\text{N}_4$ nanosheets revealed the presence of carbon (C) and nitrogen (N) peaks, indicating the effective generation of $g\text{-C}_3\text{N}_4$ with no evident impurities. For the $\text{TiO}_2/g\text{-C}_3\text{N}_4$ binary composite and the 15.0 mL-CQD/ $\text{TiO}_2/g\text{-C}_3\text{N}_4$ ternary composition (Fig. 4), supplementary peaks for titanium (Ti) and oxygen (O) are detected. The EDX spectrum of ternary composite contains signals for C, N, O and Ti, confirming the integration of CQDs and TiO_2 . The differences in the spectra, particularly the existence of CQDs and TiO_2 peaks, confirm effective incorporation of these components. Table 2 presents the qualified elemental conformations of created samples.

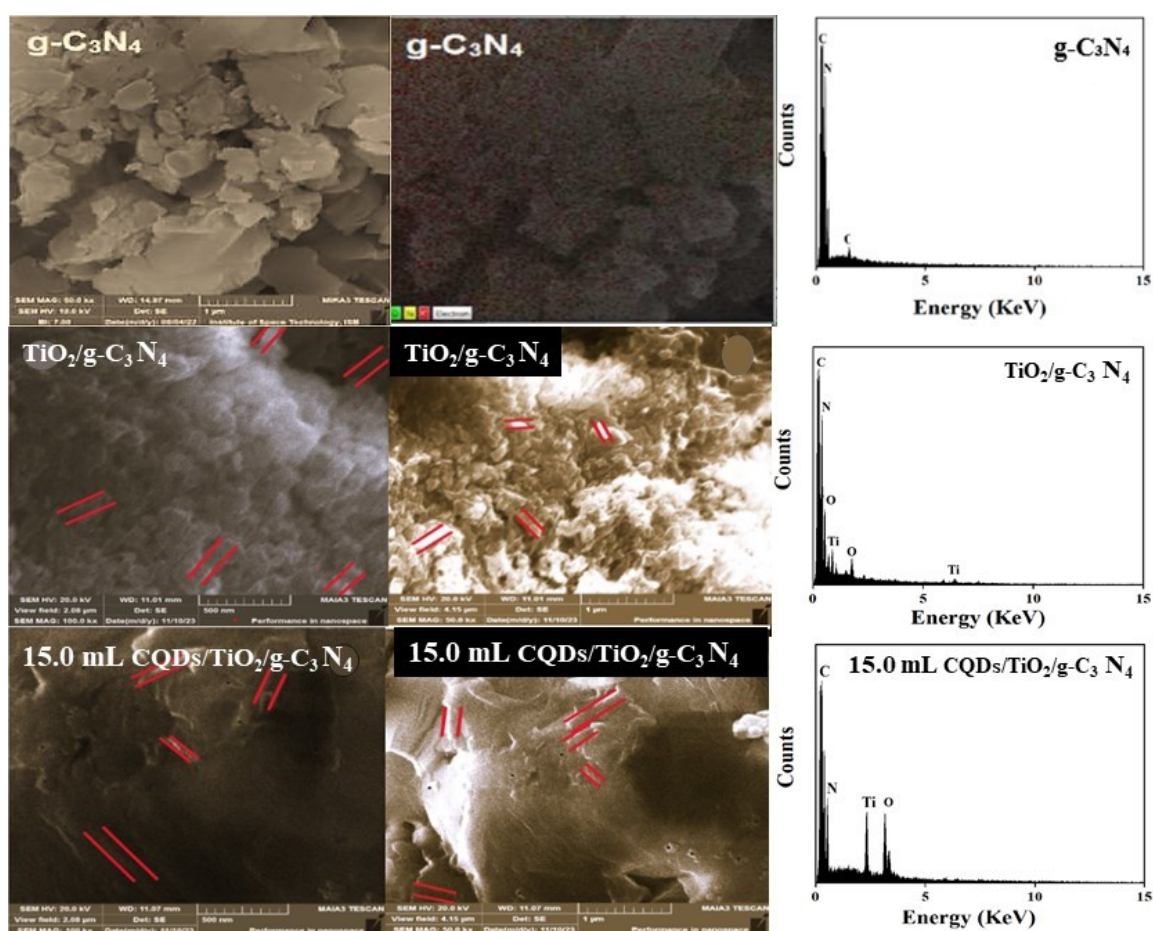


Figure 4. SEM images and EDS results of the prepared samples of the $g\text{-C}_3\text{N}_4$, $\text{TiO}_2/g\text{-C}_3\text{N}_4$ binary composite and 15.0 mL-CQD/ $\text{TiO}_2/g\text{-C}_3\text{N}_4$ ternary composite at different magnifications.

Table 2. Elemental composition of synthesized samples.

Composites Element	$\text{TiO}_2/g\text{-C}_3\text{N}_4$		15.0 mL CQDs/ $\text{TiO}_2/g\text{-C}_3\text{N}_4$	
	Weight %	Atomic %	Weight %	Atomic %
C	31.13	35.89	30.46	37.56
N	44.38	43.88	36.91	39.02
O	18.42	15.95	22.90	21.20
Ti	0.08	0.02	0.24	0.07

4.8 TEM analysis

The TEM images in Fig. 5 show the structure and morphology of the 15.0 mL-CQD/TiO₂-g-C₃N₄ heterojunction. The 2D g-C₃N₄ stacked nanosheets are shown in Fig. 5 (a,b). These regions appear as thin, sheet-like, or layered regions with extended planar dimensions. The faint, transparent, and slightly overlapping regions indicate the presence of 2D nanosheets or layered structures. On large scale lamellar structured aggregation is detected which is in agreement with the result [46]. There are dark regions and gray areas exist. The dark portion of the rod forms TiO₂, whereas the light gray area is allocated to the 2D g-C₃N₄ stacked sheet, confirming that the 1D TiO₂ are wrapped inside the g-C₃N₄ sheets. Moreover, TiO₂ is well dispersed on 2D g-C₃N₄ nanosheets, indicating that the presence of g-C₃N₄ suppressed the aggregation of TiO₂ [46]. In addition, the TiO₂ nanowires in the g-C₃N₄ sheet, which are openly dissimilar from TiO₂, indicate that the composites were effectively formed [31]. The CQDs that appear as small, bright, and well-defined nanoparticles are circled in the image to analyze the size distribution of the CQDs on the samples. According to the elemental mapping analysis, C, N, O and Ti were present in the 15.0 mL-CQD/TiO₂/g-C₃N₄ composite.

5. Photocatalytic activity

The photocatalytic degradation was determined by using the pure g-C₃N₄, binary and ternary photocatalysts under visible light. The catalysts consisted of 2D g-C₃N₄ nanosheets with TiO₂ and further altered with varying quantities of quantum dots (CQDs) (5.0, 10.0, 15.0 and 20.0 mL). To confirm

the highest absorption, each sample was originally placed in a dark chamber for 30 min before subjected to light intensity. The degradation efficiency of the photocatalysts was determined by the absorbance of the MO & BPB dyes. The results shown in Fig. 6 (A) reveal outstanding differences in the degradation of MO & BPB over different samples. In particular, the composites TiO₂-g-C₃N₄, and with 5.0, 10.0, 15.0, and 20.0 mL of CQDs displayed degradation profiles of 45.2, 67.5, 79.0, 96.0, and 82.0%, respectively. The composite with 15.0 mL of CQDs/TiO₂-g-C₃N₄ had the highest photocatalytic activity, resulting in maximum absorption and an excellent degradation ratio of 96.0%, as shown in Fig. 6 (B). Moreover, the maximum ratio of the ternary composites with 15.0 and 20.0 mL-CQDs was verified for the degradation of both MO and BPB, indicating their higher photocatalytic efficiency. Figure 6 (C) presents the degradation kinetic constant for all the samples. The 15.0 mL CQD/TiO₂-g-C₃N₄ composite displayed higher photocatalytic performance with the highest degradation kinetics. This investigation highlights the role of TiO₂ and CQDs in increasing photocatalytic proficiency through the optimization of electron-hole pair recombination rates and improved fluorescence responses. This observed performance supports well with the work reported that the composites of TiO₂/g-C₃N₄ heterojunction structures for active degradation of dyes [47]. The g-C₃N₄ serves as the foundational photocatalyst in photocatalytic activity, primarily due to its suitable medium bandgap (2.7 eV), which enables strong visible-light absorption, and excellent chemical stability, thus making it an effective material for heterojunction

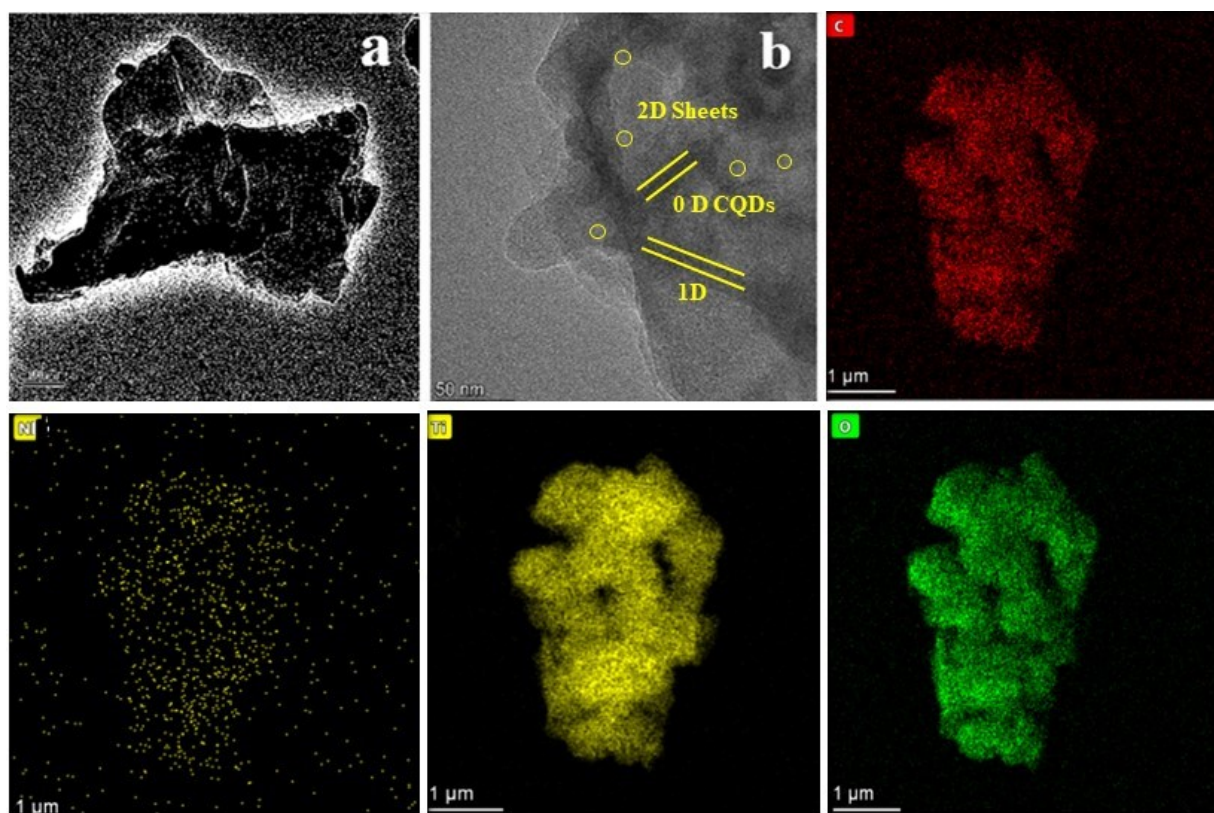


Figure 5. TEM image of 15.0 mL CQD/TiO₂-C₃N₄ heterojunctions at different nanoscales (a, b) and elemental mapping of 15.0 mL CQD/TiO₂-g-C₃N₄ ternary composites.

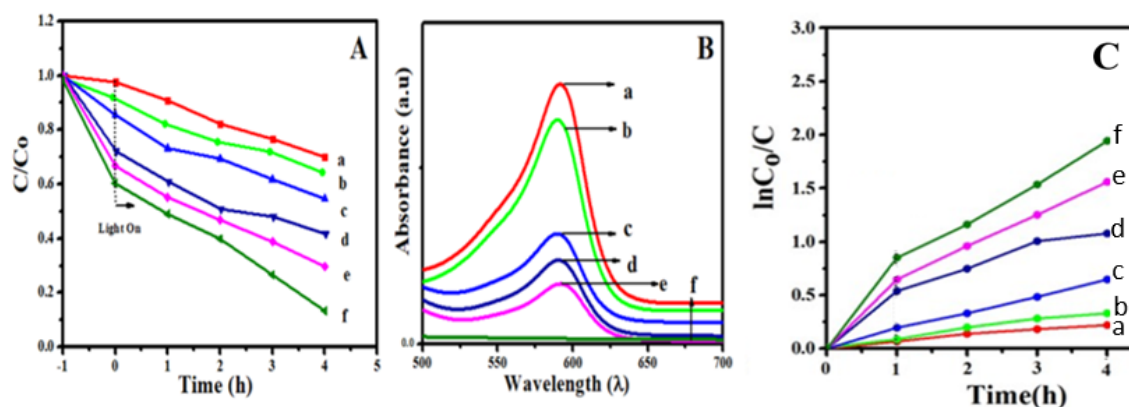


Figure 6. (A) Effect of the reactive photocatalyst on the simultaneous degradation of MO & BPB and time-dependent solar-driven catalytic degradation over (a) $g\text{-C}_3\text{N}_4$, (b) $\text{TiO}_2/g\text{-C}_3\text{N}_4$, (c) 5.0 mL of CQDs- $\text{TiO}_2/g\text{-C}_3\text{N}_4$, (d) 10.0 mL of CQDs- $\text{TiO}_2-g\text{-C}_3\text{N}_4$, (e) 20.0 mL of CQDs- $\text{TiO}_2-g\text{-C}_3\text{N}_4$ and (f) 15.0 mL of CQDs- $\text{TiO}_2-g\text{-C}_3\text{N}_4$, (B) UV visible absorption spectra of 15.0 mL of CQDs- $\text{TiO}_2-g\text{-C}_3\text{N}_4$ showing the highest degradation after five hours of the reaction process, and (C) kinetic study of synthesized samples for the degradation of dyes for 4 hours.

formation with TiO_2 and CQDs. Its 2D layered structure provide a vast surface area and active spots, whereas its nitrogen rich structure enables strong interaction with contamination. When $g\text{-C}_3\text{N}_4$ integrated with TiO_2 , forms a heterojunction that magnifies charge separation by stimulating the migration of photo induced charges-carriers in opposite direction, therefore reducing charge recombination [41, 47]. In combination CQDs supports the photocatalytic system by acting as electron mediators and contributing up-conversion photoluminescence, which permits the utilization of low energy photons that would otherwise be lost [40]. This amazing co-operation among $g\text{-C}_3\text{N}_4$, TiO_2 , and CQDs significant to effective charge transfer, sustained light absorption, and the generation of reactive oxygen species (ROS), remarkably enhance the degradation of contaminants or hydrogen production under visible light [48]. Generally, graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) works as an active visible light sensitizer and structural effective in CQDs/ $\text{TiO}_2-g\text{-C}_3\text{N}_4$ nanocomposites, making it significant component for photocatalytic efficiency booster. To increase the photocatalytic efficiency, quantum dots (CQDs) were integrated into $\text{TiO}_2/g\text{-C}_3\text{N}_4$ heterojunctions with quantities of 15.0 and 20.0 mL. This formation was deliberate to increase electron transmission inside the photocatalytic system [49]. The CQDs significantly increased the photocatalytic activity by increasing electron transfer and decreasing electron-hole recombination. These result are agreed well with the mechanism and performance enhancement reported in their study [50]. The addition of CQDs at specific concentrations thus proved essential for achieving the highest levels of photocatalytic activity, as shown in Fig. 6 (C). The photocatalytic degradation of MO and BPB followed pseudofirst kinetics, as clearly described by the following equation:

$$\ln\left(\frac{C_0}{C}\right) = k_{app} \times t \quad (1)$$

where C_0 denotes the primary concentration before radiation at $t = 0$, C is the concentration after radiation t represents the time in solution, and k_{app} signifies the apparent degradation rate.

A reliable study revealed that the existence of TiO_2 im-

proved the automatic properties of $g\text{-C}_3\text{N}_4$, thereby improving its photocatalytic performance [46]. Additionally, the combination of CQDs further increased this movement, with the 15.0 mL CQD composite displaying the best performance in environmental remediation applications over effective dye degradation [51, 63, 64]. The degradation proficiency of $g\text{-C}_3\text{N}_4$ composites was promisingly enhanced with the integration of CQDs, increasing from 28.0% to 96.0% as the CQD loading increased. When 15.0 mL of 0D-CQDs were integrated, the degradation ratio reached 96.0%. This degradation ratio subsequently decreased to 82% at a loading of 20.0 mL of CQDs. The maximum degradation efficiency of 96.0% was observed with 15.0 mL of CQDs added to the $\text{TiO}_2/g\text{-C}_3\text{N}_4$ composite, as represented in Fig. 6 (C).

The synthesized photocatalyst was used in this study to investigate various concentrations of MO & BPB pollutants (10, 20, and 30 ppm), as illustrated in Fig. 7 (A). The best concentration for assessing photocatalytic performance was found to be 20 ppm solutions of both MO & BPB, which demonstrated the maximum degradation efficiency among them. The best photocatalyst in this research study, 15.0 mL CQDs/ $\text{TiO}_2/g\text{-C}_3\text{N}_4$, was tested in triplicate to evaluate its stability and reproducibility. Figure 7 (B) illustrates the graph depicting the photocatalyst's consistent performance over repeated cycles. The catalyst retained the photoactivity of 83% after three cycles of reusability. Table 3 presents the comparison of the performance of various $\text{TiO}_2/g\text{-C}_3\text{N}_4$ -based nanocomposite for the photocatalytic degradation of different dyes and pollutants.

6. Catalytic mechanism

The photocatalytic performance of CQDs/ $\text{TiO}_2-g\text{-C}_3\text{N}_4$ of degradation of methyl orange (MO) and bromophenol blue (BPB) under visible light is governed by synergistic interacting among the 0D, 1D, and 2D components, which facilities superior light harvesting, charge carrier separation, and reactive oxygen species (ROS) generation. UV-vis diffuse reflectance spectroscopy (DRS) measurements confirm TiO_2 and $g\text{-C}_3\text{N}_4$ band gaps of approximately 3.38 and 2.72 eV, respectively [59]. Based on the empirical equations for

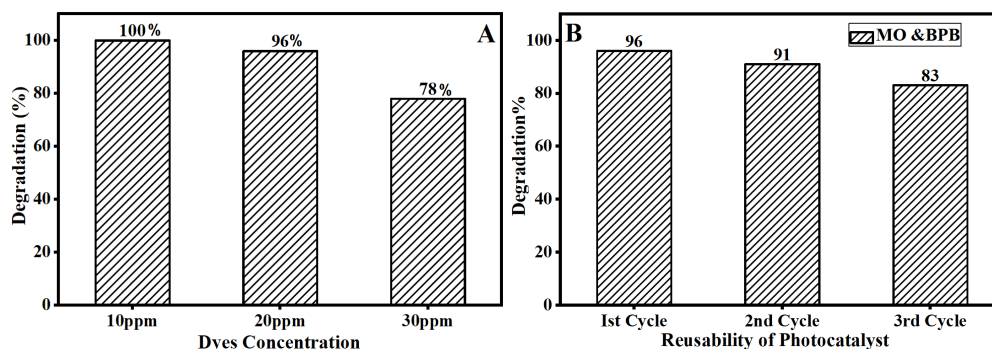


Figure 7. (A) Photocatalytic degradation of Dyes (MO & BPB) with changed dye concentration, (B) Reusability experiments of the most effective photocatalyst 15.0 mL CQDs/TiO₂/g-C₃N₄, over three cycles.

band edges position [65], TiO₂ possesses conduction band (CB) and valance band (VB) potentials of -0.43 and $+3.05$ eV, while g-C₃N₄ exhibits CB and VB positions at -1.44 eV and $+1.88$ eV, respectively. These band alignments from a type II heterojunction structure, where the CB electrons from g-C₃N₄ are energetically favorable to migrate to TiO₂, and the VB holes from TiO₂ shifts to g-C₃N₄. This spatial charge separation significantly reduces recombination rate of photogenerated electron hole pairs, which is one of major challenges in photocatalysis (Low J, et al.) [66]. The CB potential of TiO₂ is greater than that of g-C₃N₄, and negative ion (electron) transfer occurs from g-C₃N₄ to TiO₂. Conversely, holes transfer from TiO₂ to g-C₃N₄ due to the smaller VB potential of g-C₃N₄ than that of TiO₂. This effective transmission of photoinduced charge carriers decreases the recombination rate, thereby improving the photocatalytic activity. The inclusion of zero-dimensional (0D) CQDs further enhance the system by acting as efficient electrons mediators and photosensitizers. Their unique upconversion photoluminescence (UCPL) from properties

allow them to absorb long-wavelength visible light and emits shorter wavelength, thereby facilitating light absorption and efficiently transfer them to one-dimensional (1D) TiO₂, refining the charge mover confinement at the TiO₂/g-C₃N₄ edge [67]. Moreover, CQDs introduces abundant π -conjugated surface and surface functional groups that facilitate rapid electron transfer. Electrons can be captured from g-C₃N₄ by CQDs and then shuttled to TiO₂, minimizing recombination losses and promoting continuous redox reaction [14]. Upon visible light irradiation, both CQD and g-C₃N₄ are excited, the CQD/TiO₂-g-C₃N₄ composite producing electrons in the CB and holes in the VB. These charge carriers react with absorbed water (H₂O) and molecular oxygen (O₂) to form hydroxyl radicals (\bullet OH) and superoxide radicals (\bullet O₂⁻), which are the primary active species in the dye degradation. The VB potential of TiO₂ ($+3.05$ eV) is more positive than the oxidation potential of H₂O/ \bullet OH (2.68 eV), enabling the generation of \bullet OH radicals through hole oxidation [68]. Meanwhile, the CB of g-C₃N₄ (-1.44 eV) is more negative than the reduction potential of O₂/ \bullet O₂⁻

Table 3. Comparison of the performance of various TiO₂/g-C₃N₄-based nanocomposite for the photocatalytic degradation of different dyes and pollutants.

Photo catalyst	Pollutants	Initial concentration	Light source	Time (min)	Degradation (%)	References
g-C ₃ N ₄ /CQDs	Rh B	10.0 mg/L	300 W Xe lamp	60	90.9	[51]
Ag/g-C ₃ N ₄	AV-7 dye	20.0 mg/L	100 W Xe lamp	100	48	[52]
g-C ₃ N ₄ /TiO ₂	MO	10.0 mg/L	300 W Xe lamp	300	40.0	[53]
C-TiO ₂ /g-C ₃ N ₄	MO	10 mg/L	300 W Xe lamp	60	99.0	[54]
g-C ₃ N ₄ -TiO ₂ -GA	RhB	20.0 mg/L	500 W Xe lamp	60	98.0	[55]
TiO ₂ /rGO/g-C ₃ N ₄	RTB	10.0 mg/L	500 W Xe lamp	90	60.0	[56]
CdS/CQDs/g-C ₃ N ₄	RhBM	10.0 mg/L	300 W Xe Lamp	20	100.0	[57]
TiO ₂ /g-C ₃ N ₄ /RGO	RhB	10.0 mg/L	500 W Xe lamp	60	99.0	[58]
g-C ₃ N ₄ /TiO ₂ NTs	RhB	5.0 mg/L	300 W Xe lamp	150	99.0	[59]
TiO ₂ /C ₃ N ₄	Congo Red	10.0 mg/L	300 W Xe lamp	60	91.0	[35]
g-C ₃ N ₄ /TiO ₂ NTs	SMT	5.0 mg/L	450 W Xe lamp	300	100.0	[60]
g-C ₃ N ₄ -TiO ₂	MB	10.0 mg/L	300 W Xe lamp	180	80.0	[61]
TiO ₂ /C/g-C ₃ N ₄	MO	0.2 mol/L	Sunlight irradiation	180	93.6	[62]
CQDs/TiO ₂ /g-C ₃ N ₄	MO & BPB	20.0 mg/L	1000 W Xe lamp (Visible Light Source)	300	96.0	Present Work

(-0.33 eV), favoring superoxide radical formation via electron reduction [51, 69]. This charge transfer route involving CQDs helps maintain strong redox ability on both the TiO_2 and $\text{g-C}_3\text{N}_4$ sides, unlike simple type-II systems that often suffer from reduced oxidative/reductive potentials. CQDs also serves to trap and gradually release charge carriers, extending their lifetimes and increasing the reaction window for ROS generation. This mechanism explains the role of $\cdot\text{OH}$ radicals in the effective degradation of MO and BPB as shown in Fig. 8.

7. Useful application of degradation in different water sources

The influence of various water sources on the photocatalytic degradation of methyl orange (MO) and bromophenol blue (BPB) by applying prepared photocatalysts in the ternary composite $15.0\text{ mL-CQDs/TiO}_2\text{-g-C}_3\text{N}_4$ was investigated to understand their practical application for the purification of water. Water quality significantly affects photocatalytic efficiency. As depicted in Fig. 9 (A), the degradation ratios achieved with different water types were as follows: Drain water exhibited a 20.0% degradation rate, stream water 32.2%, river water 40.0%, tap water 49.0%, and underground water 80.3%. The associated degradation kinetic constants were 0.01057 , 0.01696 , 0.02268 , 0.04163 , and 0.05195 min^{-1} , respectively, as shown in Fig. 9 (B) for practical application. Water quality is the most important factor; therefore, different backgrounds of water were used and investigated for degradation of environmental pollutants (MO & BPB) by using the synthesized photocatalyst, which has the best performance in terms of catalytic activity in this study. The greatest inhibition effect on degradation occurred in the drain water, followed by the stream water, which revealed that several other pollutants exist, such as organic matter or anion inhibitors. Therefore, in this study, the degradation ratios decreased due to the addition of other or-

ganic or inorganic anions, as we revealed that underground water and tap water produced more pollutants than drain and stream water did. Thus, the maximum degradation is occurred for MO and BPB in terms of their photocatalytic activities in underground water and tap water. The reduced degradation process in certain water sources may be attributed to the presence of anionic inhibitors and/or competing organic substances, which likely interfere with the efficiency of the photocatalytic process.

8. Photo electrochemical activity

Due to quantum confinement, a reduced recombination rate of photogenerated electron-hole pairs enhances the reduction properties of samples according to their PL characteristics [45]. Photo-generated H_2 gas was evaluated by the use of $\text{CQDs/TiO}_2\text{-g-C}_3\text{N}_4$ under visible light. In OER, $\text{g-C}_3\text{N}_4$ and $\text{TiO}_2/\text{g-C}_3\text{N}_4$ display very poor performance, which might be due to the collection of H_2O_2 , which devalues plain catalysts and decreases the current concentration. A very minor improvement in the current concentration was detected for the $\text{CQDs/TiO}_2\text{-g-C}_3\text{N}_4$ (20.0 mL). The $\text{CQD/TiO}_2\text{-g-C}_3\text{N}_4$ (15.0 mL) composites were exposed to the excessive current. Similarly, photoinduced holes on the surface of $\text{g-C}_3\text{N}_4$ oxidize water to produce O_2 and H_2O_2 . CQDs offer a supplementary path and overturn rate of H_2O_2 molecules [70]. It is apparent from the spectra that the $\text{CQD/TiO}_2/\text{g-C}_3\text{N}_4$ (15.0 mL) composite has a more powerful photocurrent density than all the other composite materials. This highlights the new fabrication of photoinduced electrons and the greater departure rate of photoinduced electron-hole pairs, which was also realized in the PL investigation. This characteristic accounts for the enhanced performance of the samples in the photoelectrochemical and photocatalytic degradation of organic contaminants. LSV was used for the analysis of the HER of the samples in a 0.5 M KOH electrolyte. Figure 10 (A) depicts the HER polarization curves (current densities vs. reversible hydro-

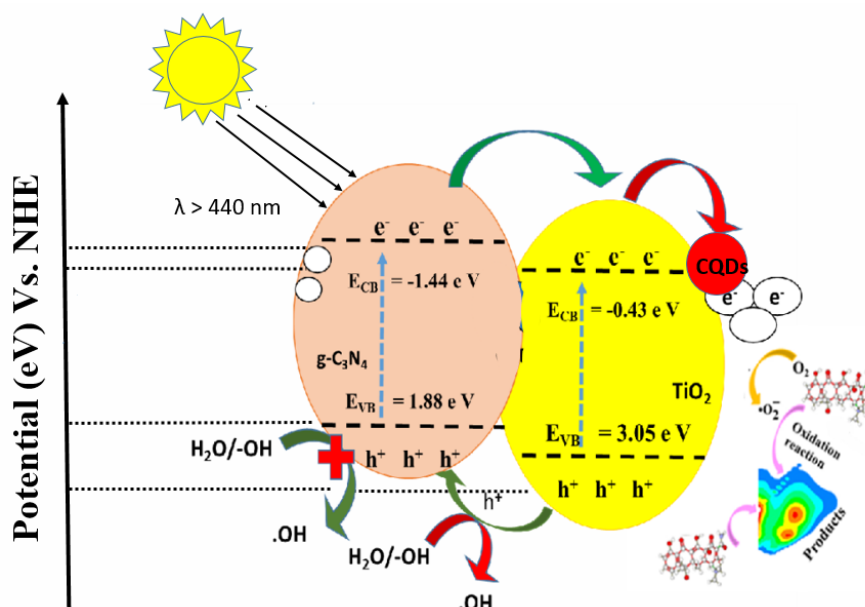


Figure 8. Hypothesized pathways for the photocatalytic degradation of MO & BPB on $\text{CQDs/TiO}_2\text{-g-C}_3\text{N}_4$ when exposed to visible light.

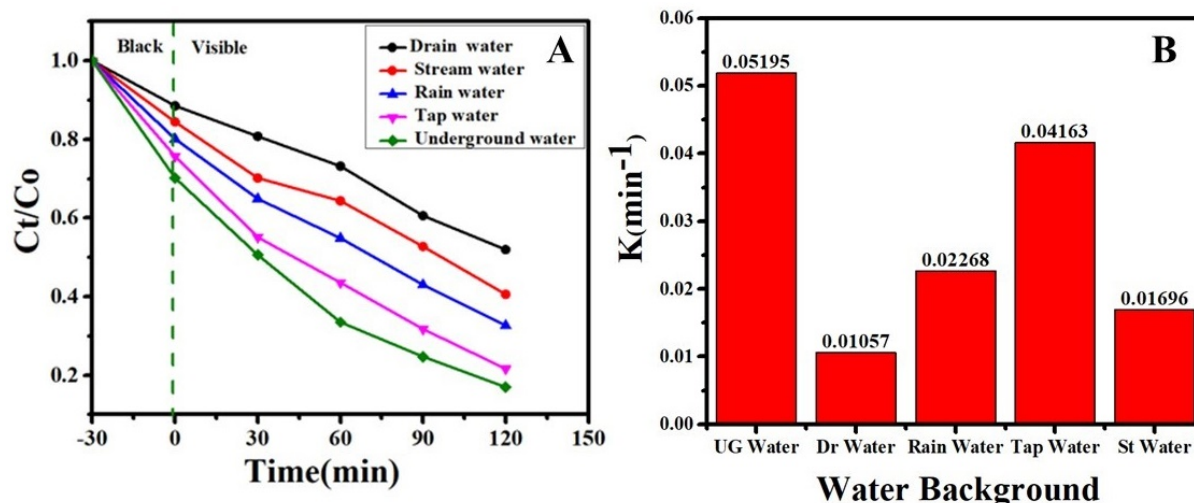


Figure 9. (A) The effect rates of different water background sources on water pollution (MO and BPB) breakdown by CQDs/TiO₂-g-C₃N₄ from different water sources. (B) shows the differences in the degradation kinetic constants for each water source.

gen electrode (RHE)) of electrodes based on TiO₂/g-C₃N₄ and TiO₂/g-C₃N₄ with concentrations of 10.0, 15.0 and 20.0 mL of CQDs, respectively. The results revealed that TiO₂/g-C₃N₄ produced a very low onset potential of -500 mV, corresponding to a very low current density of -2.7 mA/cm² for the HER. This catalyst is poor toward the HER. However, the pairing of CQDs with g-C₃N₄ is somewhat better because of the strong (spontaneous sp² and sp³ hybridization) electrostatic interactions between them [71, 72]. Clusters of Ti³⁺/Ti⁴⁺ ions and intraplanar and interplanar stacking structures of g-C₃N₄ are considered to cause H-O-H cleavage and provide active sites for the adsorption of hydrogen species [73]. The electrons of the delocalized π-conjugated network of CQDs effectively participate in the reduction process, leading to hydrogen production [74]. The sample with 15.0 mL of CQDs had a small onset potential (-370 mV) and greater current density (-33 mA/cm²) than the other samples did. Catalysts with 10.0 mL and 20.0 mL of CQDs generate onset potentials of -440 mV and -406 mV related to current densities of -4.8 and 17.0 mA/cm², respectively. A decrease in HER activity was

noted above 15.0 mL of CQDs. The catalyst can become saturated with a high amount of foreign material, and the active centers of the catalyst deteriorate, which reduces its efficiency. Figure 10 (B) shows the Nyquist plots of the samples. A very high charge transfer resistance (R_{ct}) was noted for TiO₂/g-C₃N₄ and TiO₂/g-C₃N₄ (20.0 mL). The samples with 10.0 and 15.0 mL of CQDs produced R_{ct} values of -831 Ω and -1032 Ω, respectively. A small value of R_{ct} is beneficial for conduction and reduction processes during photoelectrocatalysis. Figure 11 depicts a systematic approach for photoelectrochemical (PEC) water splitting on a TiO₂/g-C₃N₄ photoelectrode.

To assess the charge, transfer properties of the produced photocatalysts, electrochemical impedance spectroscopy (EIS) was used. According to the Nyquist plots (Fig. 10 (B)), the R_{ct} value of the 15.0 mL CQDs/TiO₂/g-C₃N₄ composite was approximately 1032 Ω, which was much lower than that of the TiO₂/g-C₃N₄ (~2700 Ω) and the 20.0 mL CQD-loaded sample (~2400 Ω). An intermediate R_{ct} of around 831 Ω was observed in the 10.0 mL CQD-loaded sample as shown in Table 4.

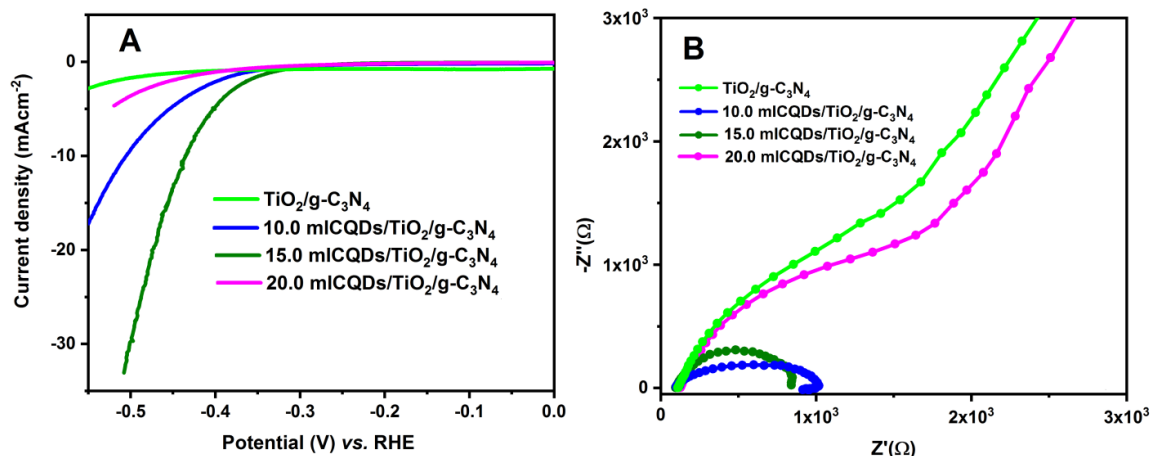


Figure 10. (A) Polarization curves of TiO₂/g-C₃N₄ and CQDs/TiO₂-g-C₃N₄ with concentrations of 10.0, 15.0 and 20.0 mL of CQDs obtained via LSV for the HER (0.5 M KOH) at a scan rate of 5 mV/s. (B) Corresponding Nyquist plots of the samples.

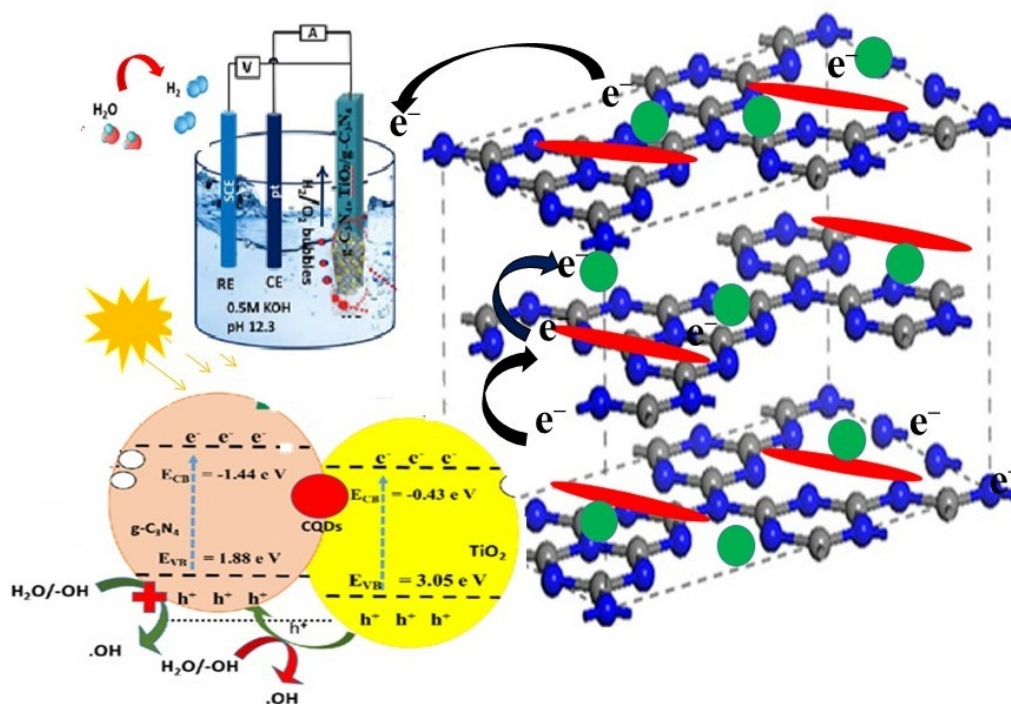


Figure 11. Systematic approach for photoelectrochemical water splitting on 2D $g\text{-C}_3\text{N}_4$ modified with 1D TiO_2 and CQD ($\text{CQD}/\text{TiO}_2/g\text{-C}_3\text{N}_4$) photoelectrodes.

Table 4. Quantitative comparison between the corresponding photocurrent densities derived from PEC measurements and R_{ct} (Ω) values:

Sample	R_{ct} (Ω)	Photocurrent Density (mA/cm^2)
$\text{TiO}_2/g\text{-C}_3\text{N}_4$	$\sim 2700 \Omega$	2.7
10.0 mL CQDs/ $\text{TiO}_2/g\text{-C}_3\text{N}_4$	$\sim 831 \Omega$	4.8
15.0 mL CQDs/ $\text{TiO}_2/g\text{-C}_3\text{N}_4$	$\sim 1032 \Omega$	33.0
20.0 mL CQDs/ $\text{TiO}_2/g\text{-C}_3\text{N}_4$	$\sim 2400 \Omega$	17.0

9. Conclusions

In summary, $\text{CQD}/\text{TiO}_2/g\text{-C}_3\text{N}_4$ ternary nanocomposites were successfully synthesized to exploit multidimensional (0D/1D/2D) heterostructures for enhanced photocatalytic and photoelectrochemical (PEC) performance under visible light. The incorporation of CQDs significantly improved visible absorption, suppressed electron-hole recombination, and facilitated charge transfer, as confirmed by photoluminescence (PL) quenching and UV-Vis DRS analysis. The 15.0 and 20.0 mL of the $\text{CQD}/\text{TiO}_2/g\text{-C}_3\text{N}_4$ composite achieved superior degradation efficiency of methyl orange (MO) and bromophenolblue (BPB) under visible light irradiation ($\lambda > 420$), reaching up to 96.0 and 82.0% outperforming $g\text{-C}_3\text{N}_4$ and binary composites. The MO & BPB are degraded in various sources of water, drain water, stream water, rainwater, and tap water as well. The PEC measurements showed a marked enhancement in photocurrent density, the optimized $\text{CQDs}/\text{TiO}_2-g\text{-C}_3\text{N}_4$ (15.0 mL) ($j^{1/4} \sim 33 \text{ mA}/\text{cm}^2$) exhibited a stable photoelectrocatalytic response throughout the PEC process due to improved charge separation and quick hole extraction. Moreover, effective CQD deposition onto the $\text{TiO}_2/g\text{-C}_3\text{N}_4$

heterostructure significantly improved the PEC performance, even at higher energy potentials and improved the chemical stability of TiO_2 -incorporated photocatalysts. The synergistic interactions between the CQDs and $\text{TiO}_2/g\text{-C}_3\text{N}_4$ heterostructure played a vital role in the boosting overall photocatalytic activity. This work takes advantage of electron mediator/transfer property of CQDs between the interface of the CQDs and $\text{TiO}_2/g\text{-C}_3\text{N}_4$ to improve the charge separation efficiency. The study demonstrates that the rational design of multidimensional heterojunctions ($\text{TiO}_2/g\text{-C}_3\text{N}_4$) with conductive CQDs to increase stability and visible light response can be used to create new CQD combinations that are connected with $g\text{-C}_3\text{N}_4$ frameworks. The 15.0 mL loading was found optimal as it ensured sufficient surface coverage and efficient charge transfer whereas excessive loading (20.0 mL) led to aggregation, limiting active sites. Moreover, this study acknowledges that further evaluation with real industrial wastewater is required to validate large-scale application. Future work will explore the optimization of CQDs loading, long term stability under solar conditions and application to real wastewater treatment and hydrogen generation system. Although the fabricated $\text{CQD}/\text{TiO}_2/g\text{-C}_3\text{N}_4$ composites'

photocatalytic performance was shown using prototypical organic dyes in an organized laboratory venue, further research applying real industrial wastewater models is crucial to entirely evaluate the developed photocatalysts' large-scale potential and actual applicability. This study is a component for practical potential on future research in evaluating considerable wastewater scenarios.

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Authors Contribution

Authors have contributed equally in preparing and writing the manuscript.

Availability of data and materials

The datasets generated and/or analyzed during the current study are available from the corresponding author on reasonable request. All data supporting the findings of this study are included within the article and its supplementary materials, where applicable.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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