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Facile Fabrication of TiO₂ Quantum Dots-Anchored g-C₃N₄ Nanosheets as 0D/2D Heterojunction Nanocomposite for Accelerating Solar-Driven Photocatalysis

Jin-Hyoek Lee^{1,†}, Sang-Yun Jeong^{1,†}, Young-Don Son² and Sang-Wha Lee^{1,*}

- ¹ Chemical and Biological Engineering Department, Gachon University, Seongnam-si 13120, Republic of Korea; 71in.cmsal@gmail.com (J.-H.L.); wjdtkddbs762@naver.com (S.-Y.J.)
- ² Department of Biomedical Engineering, College of IT Convergence, Gachon University, Seongnam-si 13120, Republic of Korea; ydson@gachon.ac.kr
- * Correspondence: lswha@gachon.ac.kr; Tel.: +82-10-2635-5360
- + These authors contributed equally to this work.

Abstract: TiO₂ semiconductors exhibit a low catalytic activity level under visible light because of their large band gap and fast recombination of electron–hole pairs. This paper reports the simple fabrication of a 0D/2D heterojunction photocatalyst by anchoring TiO₂ quantum dots (QDs) on graphite-like C_3N_4 (g- C_3N_4) nanosheets (NSs); the photocatalyst is denoted as TiO₂ QDs@g- C_3N_4 . The nanocomposite was characterized via analytical instruments, such as powder X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy, t orange (MO) under solar light were compared. The TiO₂ QDs@g- C_3N_4 photocatalyst exhibited 95.57% MO degradation efficiency and ~3.3-fold and 5.7-fold higher activity level than those of TiO₂ QDs and g- C_3N_4 NSs, respectively. Zero-dimensional/two-dimensional heterojunction formation with a staggered electronic structure leads to the efficient separation of photogenerated charge carriers via a Z-scheme pathway, which significantly accelerates photocatalysis under solar light. This study provides a facile synthetic method for the rational design of 0D/2D heterojunction nanocomposites with enhanced solar-driven catalytic activity.

Keywords: TiO₂ quantum dots; g-C₃N₄ nanosheet; 0D/2D heterojunction; solar-driven photocatalysis

1. Introduction

Photocatalytic systems that utilize solar-powered oxidation–reduction chemical reactions are attractive for a wide range of applications, including water purification, air purification, and the development of self-cleaning surfaces. In particular, semiconducting nanomaterials have been widely used in photocatalytic systems that harvest abundant solar radiation, thereby allowing the mitigation of environmental pollution [1–3]. For the effective application of semiconductors as photocatalysts, a reduction reaction involving photoexcited free electrons must be accompanied by an oxidation reaction involving photoinduced positive holes [4]. Therefore, the valence and conduction bands of a semiconductor photocatalyst should be located at an appropriate energy level (vs. NHE) to provide an ideal bandgap for the broad absorption of solar light [3,5,6].

The photocatalytic activity of TiO₂ semiconductors was first reported by Fujishima and Honda in 1970. Ever since then, TiO₂ materials have been used as the gold standard in fields related to the photocatalytic degradation of pollutants [7–10]. However, TiO₂ exhibits low visible-light photocatalytic activity levels because of the fast recombination of electron–hole pairs and the large bandgap (3.2 eV), which can only allow absorption in the ultraviolet (UV) region of the electromagnetic spectrum (\leq 387.5 nm) [11–13]. Improving the separation efficiency of photogenerated charge carriers is one of the main challenges limiting the rational design of visible-light-active TiO₂-based semiconductor photocatalysts.



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Conventional TiO₂ semiconductor photocatalysts have a typical diameter of 20–30 nm. In contrast, TiO₂ quantum dots (QDs) have a nanoscale diameter (\leq 57 nm) and a high surface-area-to-volume ratio; these properties make the TiO₂ QDs more effective at generating reactive oxygen species, owing to the increased number of active sites for photocatalytic reactions [14,15]. However, a high surface-area-to-volume ratio leads to high surface energy and causes TiO₂ QDs to easily form aggregates, consequently worsening their photocatalytic performance.

Among the different approaches, strategies based on the use of heterojunctions with 0D/2D or 2D/0D/2D dimensions are typically considered to be efficient methods for improving the performance of photocatalysts because they allow the uniform dispersion of 0D nanoscale particles on 2D materials [16–27]. Furthermore, the close contact between components of a 0D/2D composite accelerates charge transfer through the heterojunction interface and creates fast-moving channels from the interface to photoactive surface sites [28–33]. The ability of excited free electrons to move to a lower energy level inhibits the recombination of electron–hole charge carriers, enabling more efficient charge carrier separation [28,34]. In this regard, nanosized photoactive QDs deposited on the extensive 2D materials not only provide more available active sites, but it also suppress the fast recombination of photoexcited charge carriers.

This paper reports the simple fabrication of TiO₂ QDs-anchored graphite-like C_3N_4 (g- C_3N_4) nanosheets (NSs), denoted as TiO₂ QDs@g- C_3N_4 0D/2D heterojunction nanocomposite. In brief, TiO₂ QDs (3–5 nm) were synthesized via the hydrothermal method, and g- C_3N_4 NSs were prepared via the double calcination of urea in air at 550 °C for 2 h. Then, TiO₂ QDs were combined with thin g- C_3N_4 NSs via a sonication method, which established intimate contact between the two components of the heterojunction. The final composite was optimized by adjusting the amount of g- C_3N_4 NSs for a fixed amount of TiO₂ QDs. The optimized composite (TiO₂ QDs@g- C_3N_4) exhibited 5.7-fold and 3.3-fold higher photocatalytic activity levels than those of g- C_3N_4 and TiO₂ QD alone, respectively. The uniform distribution of the TiO₂ QDs, without severe aggregation, and the favorable electronic structure of the 0D/2D heterojunction effectively reduced the recombination rate of electron–hole pairs, significantly improving the photocatalytic performance of the heterojunction nanocomposite.

2. Materials and Methods

2.1. Chemicals

Titanium(III) chloride (TiCl₃, 12%), urea (CH₄N₂O, 98%), and ethanol (EtOH, >99.9%) were purchased from Sigma-Aldrich Corporation (St. Louis, MO, USA). Deionized (DI) water (HPLC grade) was purchased from J. T. Baker Chemical Company (Phillipsburg, NJ, USA). All reagents were of analytical grade and used without further processing.

2.2. Synthesis of TiO₂ QDs and g-C₃N₄ NSs

A total of 2.5 mL of TiCl₃ (12%) was added to 50 mL of ethanol; the mixture was stirred for 3 h until a transparent solution was obtained. The resultant solution was decanted into an autoclave reactor and maintained at 90 °C for 3 h. Finally, the product was collected and cleaned with anhydrous ethanol via centrifugation for 20 min at a speed of $7000 \times g$ rpm to purify the samples, thereby forming TiO₂ QDs. To prepare g-C₃N₄ NSs, urea (10 g) was finely ground using a mortar and transferred to a crucible, which was covered and wrapped in foil. The crucible was placed in a muffle furnace and was heated twice for 2 h at 550 °C in air [35,36]. The double heating process results in the production of thin g-C₃N₄ NSs.

2.3. Synthesis of the TiO_2 QDs@g-C₃N₄ Heterojunction

A simple sonication process was conducted to form a heterojunction between TiO_2 QDs and $g-C_3N_4$ NSs. Briefly, the as-synthesized TiO_2 QDs (100 mg) and $g-C_3N_4$ NSs (10 mg) were dispersed in 40 mL and 20 mL of ethanol under sonication for 30 min,

respectively. Two sample solutions were mixed in a beaker and sonicated for 2 h to facilitate the formation of the 0D/2D heterojunction nanocomposite. Zeta potentials of TiO₂ and g-C₃N₄ samples were measured as 1.05 ± 0.19 mV and -30.57 ± 0.95 mV, respectively, indicating the interplay of electrostatic interactions between them. Then, to purify the samples, the product was collected and cleaned with anhydrous ethanol via centrifugation for 10 min at a speed of $8000 \times g$ rpm. The final product of TiO₂ QDs combined with g-C₃N₄ NSs (so-called TiO₂ QDs@g-C₃N₄) was dried overnight at 60 °C. The whole fabrication procedure is illustrated in Scheme 1.



Scheme 1. Synthetic process for fabricating TiO_2 -QD-anchored g-C₃N₄ (TiO_2 QDs@g-C₃N₄) as 0D/2D heterojunction nanocomposite.

2.4. Photocatalytic Test

The photocatalytic properties of the as-prepared materials (TiO₂ QDs, $g-C_3N_4$, and TiO_2 QDs@g-C₃N₄) used for the decomposition of methyl orange (MO) were examined. All photocatalytic experiments were conducted at 25 °C under simulated solar light. For each of the materials, 30 mg of the photocatalyst sample was dispersed in 50 mL of an aqueous solution containing 10 ppm of MO dye. To equilibrate adsorption and desorption of MO on the catalyst, the solution was agitated in the dark for 30 min, followed by exposure to light (100 mW/cm^2) irradiated by a solar simulator (1000 W) equipped with Xe arc lamp with an air mass global 105 filter. At a predetermined time, 1.0 mL of sample was extracted from the reaction mixture, transferred to a vacant tube, and centrifuged at a speed of $10,000 \times g$ rpm in order to separate the photocatalyst. Two milliliters of DI water was added to 0.5 mL of the supernatant; a ultraviolet-visible (UV-Vis) spectrophotometer was used to detect the change in absorbance at 463 nm. To confirm the major active species in the degradation of MO dye, photocatalytic reactions were conducted in the presence of three different scavengers under solar light. Isopropyl alcohol (IPA, 1 mM), benzoquinone (BQ, 1 mM), and disodium ethylenediamine tetraacetate (EDTA-2Na, 1 mM) are scavenging agents for $^{\bullet}OH$, $^{\bullet}O_2^{-}$ and h+ species, respectively.

3. Results and Discussion

3.1. Preparation and Characterization of Samples

Scanning electron microscopy (SEM) images of $g-C_3N_4$ and TiO_2 QDs@ $g-C_3N_4$ samples are shown in Figure 1a,b. The morphology of $g-C_3N_4$ shows a sheet-like nanostructure, with an edge thickness of ~20 nm. Compared to $g-C_3N_4$ NSs, TiO_2 QDs@ $g-C_3N_4$ showed a rougher surface morphology, retaining the sheet-like structure, but possessing a thicker

edge because of the deposition of the TiO₂ QDs. The transmission electron microscopy (TEM) images in Figure 1c,d show the distinct surface morphology of g-C₃N₄ NSs and TiO₂ QDs@g-C₃N₄. The TEM image of g-C₃N₄ shows a thin sheet-like structure, confirming that it is a two-dimensional (2D) material. In the TEM image of TiO₂ QDs@g-C₃N₄, TiO₂ QDs are uniformly distributed over the g-C₃N₄ NS without severe aggregation; the size of the TiO₂ QDs is in the range of 3–5 nm. In order to confirm the structure of the heterojunction nanocomposite, elemental mapping analysis of TiO₂ QDs@g-C₃N₄ was performed using an energy-dispersive spectrometer (EDS). As shown in Figure 1e, the mapping images indicate the well-defined spatial distribution of Ti, O, C, and N components in the composite's structure. In addition, the co-existence of Ti and N indicates the formation of the TiO₂ QDs@g-C₃N₄ heterojunction. The EDS mapping of C components is more distinct than other components are because of the background substrate of carbon tape used for fixing the powder sample, as is usual for SEM-EDS measurements.



Figure 1. SEM (**a**,**b**) and TEM (**c**,**d**) images of the g- C_3N_4 NSs and TiO₂ QDs@g- C_3N_4 samples, respectively. (**e**) EDS mapping of elemental components (Ti, O, C, and N) of the TiO₂ QDs@g- C_3N_4 sample.

The crystalline phases and structures of the samples were evaluated via X-ray diffraction (XRD) conducted in the 2 θ range of 10°–80°, as shown in Figure 2. XRD peaks of pure g-C₃N₄ appeared at 2 θ = 13° (100) and 27° (002), which are consistent with the XRD peak positions of bulk g-C₃N₄. XRD patterns of TiO₂ QDs and TiO₂ QDs@g-C₃N₄ show the same characteristic diffraction peaks located at 2 θ = 25.28°, 37.80°, 48.05°, 53.89°, and 62.68°, which correspond to the (101), (004), (200), (105), and (224) crystal phases of anatase TiO₂, respectively [37]. However, the XRD pattern of TiO₂ QDs@g-C₃N₄ showed no peaks of g-C₃N₄ because of the relatively small amounts of g-C₃N₄ relative to the contents of TiO₂ QDs. The weight ratio of g-C₃N₄ (10 mg) to TiO₂ QDs (100 mg) was approximately 9.1 wt.% in the composite.



Figure 2. XRD patterns of the samples (TiO₂ QDs, g-C₃N₄, and TiO₂ QDs@g-C₃N₄).

X-ray photoelectron spectroscopy (XPS) was performed to examine the binding energy and chemical composition of TiO₂ QDs@g-C₃N₄. As shown in Figure 3a, the Ti 2p corelevel spectra exhibited two peaks located at 458.7 and 464.5 eV, respectively. These were assigned as $2p_{3/2}$ and $2p_{1/2}$ peaks, respectively, indicating the sole existence of Ti⁴⁺ because no signals were observed for Ti²⁺ and Ti³⁺ species [38,39]. In the O 1s core-level spectra shown in Figure 3b, the main peak at 530.0 eV was assigned to the Ti–O bonding of anatase TiO₂, and the shoulder peak at 531.1 eV was attributed to the –OH group on the sample's surface [40]. Figure 3c shows that the C 1s spectra de-convoluted into two peaks located at 284.9 and 287.5 eV, which correspond to the C–C and sp²-bonded N–C=N groups, respectively [41,42]. Figure 3d displays that the N 1s core-level spectra de-convoluted into three peaks at 398.0, 399.4, and 400.4 eV, which are assigned to the sp²-hybridized C=N–C in triazine rings, sp²-hybridized C–N(–C)–C or C–N(–C)-H, and C–N–H groups, respectively [43]. The XPS results confirmed the successful construction of a heterojunction nanocomposite of TiO₂ QDs and g-C₃N₄ NSs components.

The XPS spectra of TiO₂ QDs and g-C₃N₄ NSs were compared with those of TiO₂ QDs@g-C₃N₄ to investigate the influence of the interfacial effect between them. As shown in Figure S1a, the C 1s core-level spectra of the samples exhibited two distinct peaks at binding energies of 284.9 and 287.5 eV, corresponding to the C–C and sp²-bonded N–C=N groups, respectively [41]. The intensity of C 1s core-level spectra increased due to its binding with g-C₃N₄ on the surface of TiO₂ QDs. As shown in Figure S1b, the N 1s core level spectra for g-C₃N₄ show strong triple peaks centered at 398.2, 399.4, and 400.3 eV, corresponding to the sp²-hybridized C=N–C in triazine rings, sp²-hybridized C–N(–C)–C or C–N(–C)-H, and C–N–H groups, respectively [43]. TiO₂ QDs@g-C₃N₄ also exhibited N 1s core-level spectra at the same binding energy range of g-C₃N₄ provides a high-quality interface for TiO₂ QDs.

Brunauer–Emmett–Teller (BET) surface area analysis was performed to compare the surface area and pore size distribution of the TiO₂ QDs and TiO₂ QDs@g-C₃N₄ samples. Figure 4a shows the Type IV isotherm curves of both samples, indicating their mesoporous structures. The BET surface areas of TiO₂ QDs and TiO₂ QDs@g-C₃N₄ samples were measured as being 367.8, and 352.8 m²/g, respectively. The slight decrease in the surface area in the composite could be attributed to the substitution of g-C₃N₄ (ca. 9.1 wt.%) for high-surface TiO₂ QDs in the total mass. However, the g-C₃N₄-based heterojunction provides extensive 2D support for the dispersion of TiO₂ QDs, which is effective to prevent

the self-aggregation of TiO₂ QDs [44]. Figure 4b shows the pore size distributions of TiO₂ QDs (average pore diameter of 3.34 nm) and the TiO₂ QDs@g-C₃N₄ heterojunction (average pore diameter of 5.2 nm), respectively. This larger pore size of the composite can be ascribed to the heterojunction of TiO₂ QDs with g-C₃N₄ NSs, providing an additional interspace in the range of 20–100 nm. Moreover, TiO₂ QDs@g-C₃N₄ has a larger pore volume (0.46 cm³/g) than that of the TiO₂ QDs (0.32 cm³/g). Notably, the increases in the pore size and pore volume may induce the more uniform dispersion of TiO₂ QDs on g-C₃N₄ NSs, facilitating the separation of photo-excited charged carriers and leading to a high-performance heterojunction photocatalyst.



Figure 3. Core-level spectra of TiO₂ QDs@g-C₃N₄ by XPS: (a) Ti 2p, (b) O 1s, (c) C 1s, and (d) N 1s.



Figure 4. (a) N_2 absorption-desorption isotherms plot; (b) pore size distribution of the TiO₂ QDs and TiO₂ QDs@g-C₃N₄ samples.

3.2. Photocatalytic Activity and Mechanism

The photocatalytic activity of the samples was evaluated based on the degradation of MO dye under simulated solar light. During the photocatalytic reaction, the concentration of residual MO was calculated from the measurement of the time evolution of UV-Vis absorbance at 464 nm during the reaction time. We surveyed the mass fraction of carbon nitride in the heterojunction nanocomposite. According to Figure S2, the level of photodegradation (%) of MO dye was maximal at the optimal fraction of g-C₃N₄ (9.1 wt.%) in the composite, which was prepared by mixing 10 mg of g-C₃N₄ and 100 mg of TiO₂ QDs under sonication for 2 h. When the mass fraction of g-C₃N₄ in the composite is lower than the optimal value, the photocatalytic activity of the TiO₂ QDs@g-C₃N₄ is gradually decreased, while the photocatalytic activity of the TiO₂ QDs@g-C₃N₄ is probably because of the shielding effect of the excessive g-C₃N₄. Thus, TiO₂ QDs@g-C₃N₄ (9.1 wt.%) was used for further study.

According to the XPS elemental compositions of TiO₂ QDs@g-C₃N₄ (Table S1), the weight ratio of g-C₃N₄ to TiO₂ QDs is calculated as 8.47%, which is lower than 9.1% (in that all TiO₂ are loaded with g-C₃N₄). Basically, it is known that g-C₃N₄ has a molar C/N ratio of 0.75. However, urea-prepared C₃N₄ has often a lower molar C/N ratio (i.e., the carbon contents are relatively larger than the N contents are) [45]. For this reason, XPS elemental analysis underestimates the proportion of g-C₃N₄ in the composite. The actual proportion of g-C₃N₄ may be larger than the calculated value of 9.1% because some TiO₂ QDs are not fully loaded with g-C₃N₄ NSs. According to the XPS elemental compositions of urea-prepared C₃N₄ (Table S2), the C/N ratio is calculated as being 1.2 that is larger than 0.75 for the molecular structure of g-C₃N₄. Synthesized g-C₃N₄ is considered to be polymeric C₃N₄ (p-C₃N₄) with a significant loss of nitrogen atoms. The reason may be attributed to the significant destruction of the layered structure caused by two rounds of calcination at a high temperature (550 °C) for 2 h [46].

As shown in Figure 5a, the as-prepared samples exhibited different degradation efficiencies of MO dye after 120 min. The control solution without a photocatalyst showed no change in the MO concentration, indicating the negligible photolysis of MO under simulated solar light. In contrast, the MO concentration gradually decreased, owing to the catalytic action of $g-C_3N_4$ NSs, which exhibited a degradation efficiency of 40.6% after 120 min. TiO₂ QDs and TiO₂ QDs@g-C₃N₄ exhibited 30% equilibrium adsorption of MO under dark conditions. After solar light irradiation, TiO₂ QDs@g-C₃N₄ exhibited a degradation efficiency of 95.57%, which was higher than that of TiO₂ QDs (72.76%). The color of MO solution became colorless after 120 min irradiation, as shown in the inset, signifying the almost complete mineralization of MO dye. UV-vis spectra for MO degradation are shown in Figure S3.

A linear plot of $\ln(C_0/C)$ vs. reaction time is shown in Figure 5b according to the pseudo-first-order kinetics of $\ln(C_0/C) = kt$. The rate constants of g-C₃N₄ NSs, TiO₂ QDs, and TiO₂ QDs@g-C₃N₄ were fitted as $k = 4.19 \times 10^{-3}$, 7.31 $\times 10^{-3}$, and 2.38 $\times 10^{-2}$ min⁻¹, respectively. The rate constant for TiO₂ QDs@g-C₃N₄ was 5.7-fold and 3.3-fold larger than those of g-C₃N₄ and TiO₂ QDs, respectively. The electron–hole pair separation efficiency was determined via photoluminescence (PL) analysis at an excitation wavelength of 353 nm. As shown in Figure 5c, TiO₂ QDs@g-C₃N₄ exhibited the lower PL emission intensity as compared to those of the other samples (g-C₃N₄ and TiO₂ QDs), indicating an enhanced separation efficiency probably due to suitable band alignment of the 0D/2D heterojunction.

Pristine P25-TiO₂ was tested to assess the efficiency of the newly synthesized materials (TiO₂ QDs and TiO₂ QDs@g-C₃N₄). As shown in Figure S4, the photocatalytic activity of pristine P25-TiO₂ is higher than that of the TiO₂ QDs, but lower than that of TiO₂ QDs@g-C₃N₄, i.e., the degradation efficiencies of MO dye over P25 TiO₂, TiO₂ QDs, and TiO₂ QDs@g-C₃N₄ are 87%, 73%, and 75% after 120 min irradiation, respectively. This result indicates the superiority of the heterojunction photocatalyst over pristine P25 TiO₂, which is the gold standard for photocatalytic reactions.



Figure 5. (a) MO photodegradation rate of the as-prepared samples (TiO₂ QDs, $g-C_3N_4$, and TiO₂ QDs@ $g-C_3N_4$), (b) kinetic plot of the MO degradation by the samples, and (c) PL spectra of the samples (TiO₂ QDs, $g-C_3N_4$, and TiO₂ QDs@ $g-C_3N_4$). (d) Scavenger test of MO dye over the TiO₂ QDs@ $g-C_3N_4$.

The photocatalytic mechanism of the samples was determined by measuring the decomposition rate of MO and by adding three different scavengers (1 mM). Figure 5d shows the degradation efficiencies of MO dye (10 ppm) over TiO₂ QDs@g-C₃N₄ in the presence of isopropanol (IPA), disodium ethylenediamine tetraacetate (EDTA-2Na), and p-benzoquinone (BQ), which can intercept reactive species of •OH, h⁺, and •O₂⁻, respectively [47]. In relation to normalized MO degradation (100%) without a scavenger, the addition of BQ decreased the degradation efficiency by 83.3%, suggesting that •O₂⁻ is the dominant active species in the decomposition of MO under solar light. The addition of IPA and EDTA-2Na also led to decreases in the degradation efficiency of 29.7% and 67.5%, respectively, indicating that the positive hole (h⁺) is a more active radical species than •OH is. Figure 5d was replotted in the form of C/C₀ versus time with the kinetic plot from the scavenger test (Figure S5). It shows the pseudo-first order kinetics that were used to produce the rate constants of k = 1.0×10^{-3} , 1.89×10^{-3} , and 7.43×10^{-3} min⁻¹ for BQ, EDTA-Na, and IPA scavengers, respectively.

In summary, the TiO₂ QDs@g-C₃N₄ photocatalyst is strongly influenced by the presence of BQ ($^{\bullet}O_2^{-}$ scavenger) and EDTA-2Na (h⁺ scavenger). The heterojunction nanocomposite offers a facilitated migration path for excited charge carriers, allowing efficient separation through the heterojunction formation with a staggered electronic structure, which leads to the more activation of $^{\bullet}O^{2-}$ and h⁺ radicals.

In UV-Vis diffuse reflectance spectroscopy (DRS), absorption spectra of the samples were recorded within the UV-Vis region. According to the UV-Vis DRS results shown in Figure 6a, the absorption edge of TiO₂ QDs@g-C₃N₄ is shifted to a longer wavelength than that of the TiO₂ QDs ($\leq \sim$ 380 nm), generating more charge carriers via heterojunction formation. The products of absorption coefficient (α) and photon energy ($h\nu$) are plotted as a function of photon energy to provide information about the electronic and optical

properties of the samples (Figure 6b). Based on the Tauc plot, the optical bandgaps of the samples were calculated as 3.02, 3.23, and 3.19 eV for $g-C_3N_4$, TiO_2 QDs, and TiO_2 QDs@ $g-C_3N_4$, respectively. The lower bandgap of TiO_2 QDs@ $g-C_3N_4$ suggests that it has a higher capacity for light harvesting, bestowing the beneficial effect of the 0D/2D heterojunction toward expanding the wavelength of light absorption.



Figure 6. (a) UV-Vis DRS absorption spectra of the samples; (b) Tauc plot of the samples for calculating optical bandgaps.

The TiO₂ QDs@ g-C₃N₄ heterojunction with a staggered electronic structure exhibited more photoactivity than TiO₂ QDs and g-C₃N₄ did alone, signifying the interplay of facilitated transport of photo-excited charge carriers. Type-II and Z-scheme heterojunction are the main interfacial transport mechanism for the g-C₃N₄-based heterojunction [32,33,48]. Before establishing the photocatalytic mechanism, low-energy valence band XPS was performed to identify the valence band (VB) edge potentials of the TiO₂ and g-C₃N₄ components, which were estimated as 3.24 eV and 1.76 eV, respectively (Figure S6). In addition, scavenger tests indicated that $^{\circ}O_2^{-}$ and positive hole (h⁺) were determined as the main radical species in the decomposition of MO dye.

For the Type II heterojunction, photo-induced holes in the VB position of TiO₂ QDS are transferred to the VB position of the g-C₃N₄, and photo-excited electrons in the CB of g-C₃N₄ are transferred to the CB of TiO₂ QDs. In the case of Type II, the valence band edge potential is not sufficient to form hydroxyl radicals from water via a reaction with positive holes because the VB position of g-C₃N₄ is higher than the potential of the H₂O/•OH couple (2.8 V vs. NHE) [49]. In the Z-scheme, however, the photo-induced holes tend to stay in the more positive VB of TiO₂ QDs, which is sufficient to produce hydroxy radicals from water, and photo-excited electrons are accumulated in the more negative CB of the g-C₃N₄, which maintains the high redox powers of free charge carriers. In this regard, the Z-scheme mechanism is more appropriate to interpret the photocatalytic activity of TiO₂ QDs@g-C₃N₄ with highly enhanced photocatalytic activity.

In summary, the TiO₂ QDs@ g-C₃N₄ heterojunction system exhibited more enhanced photoactivity than TiO₂ QDs and g-C₃N₄ did alone. Photoexcited electrons in the conduction band (CB) of TiO₂ (0.01 eV vs. NHE) are transferred to the VB of g-C₃N₄ (1.76 eV vs. NHE) via a Z-scheme pathway and further excited to the CB of g-C₃N₄ (-1.28 eV vs. NHE) with high reducing power, whereas positive holes remained in the VB of TiO₂ QDs (3.24 eV vs. NHE), which can directly produce hydroxy radicals from water. The 0D/2D Z-scheme heterojunction causes the efficient separation of photogenerated charge carriers with high redox power, significantly enhancing solar-driven photocatalysis [8,32,33]. The photocatalytic mechanism underlying the solar-driven photocatalysis of TiO₂ QDs@g-C₃N₄ is illustrated in Figure 7.





Figure 7. Z-scheme mechanism underlying the photocatalysis of TiO_2 QDs@g-C₃N₄ with the 0D/2D heterojunction.

The photocatalytic stability of TiO₂ QDs@g-C₃N₄ was tested by measuring the degradation efficiency of MO dye after 120 min using recycled photocatalysts. The tested sample was collected via centrifugation after the reaction. After washing it with water and ethanol several times, the recovered sample was dried in an oven for the subsequent photocatalytic reaction. The photocatalytic results for a total of four cycles are shown in Figure S7. The photocatalytic activity decreased by 2.3% even after four recycling test. TiO₂ QDs@g-C₃N₄ exhibited photocatalytic stability under repeated solar light exposure, indicating the high structural stability of the heterojunction nanocomposite.

4. Conclusions

In this paper, we reported the facile fabrication of a TiO₂ QD-anchored g-C₃N₄ NSs, TiO_2 QDs@g-C₃N₄ 0D/2D heterojunction photocatalyst. In the TEM image of TiO₂ QDs@g- C_3N_4 , TiO₂ QDs (3–5 nm) were uniformly distributed over g- C_3N_4 NSs, without severe aggregation. The XRD results for TiO_2 QDs@g-C₃N₄ showed the same characteristic diffraction peaks at $2\theta = 25.28^{\circ}$, 37.80° , 48.05° , 53.89° , and 62.68° , corresponding to the (101), (004), (200), (105), and (224) crystal phases of anatase TiO₂, respectively. Furthermore, the EDS and XPS data confirmed the successful construction of the 0D/2D heterojunction nanocomposite and the coexistence of TiO_2 and $g-C_3N_4$ components. The performance of the as-prepared samples (TiO₂ QDs, g-C₃N₄ NSs, and TiO₂ QDs@g-C₃N₄) toward MO decomposition under simulated solar light was analyzed. The TiO₂ QDs@g-C₃N₄ photocatalyst showed MO degradation, with an efficiency of 95.57%, which was 3.3-fold and 5.7-fold higher than those of TiO₂ QDs and g-C₃N₄, respectively. The 0D/2D TiO₂ $QDs@g-C_3N_4$ photocatalyst possessed a staggered electronic structure that facilitated the efficient separation of charge carriers via a Z-scheme pathway, significantly enhancing solar-driven photocatalysis. The work proposed a simple method for fabricating highperformance 0D/2D heterojunction photocatalysts for environmental purification and energy conversion applications.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/nano13091565/s1, Figure S1: Core-level spectra of TiO₂ QDs, g-C₃N₄ and TiO₂ QDs@g-C₃N₄ by XPS (a) C 1s, (b) N 1s. Figure S2: Photodegradation rate of MO dye over the TiO₂ QDs@g-C₃N₄ with different g-C₃N₄ contents under simulated solar light. Figure S3: UV-absorbance of MO dye over TiO₂ QDs@g-C₃N₄ under simulated solar light. Figure S4: The comparison of photodegradation over as-prepared samples after 120 min irradiation. Figure S5: (a) Author Contributions: Conceptualization, J.-H.L. and S.-W.L.; methodology, S.-Y.J.; validation, S.-Y.J. and Y.-D.S.; formal analysis, J.-H.L. and Y.-D.S.; investigation, S.-Y.J.; data curation, J.-H.L., S.-Y.J. and Y.-D.S.; original draft, J.-H.L.; review and editing, S.-W.L.; supervision, S.-W.L.; funding acquisition, S.-W.L. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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