

Article

# Controllable Fabrication of Heterogeneous p-TiO<sub>2</sub> QDs@g-C<sub>3</sub>N<sub>4</sub> p-n Junction for Efficient Photocatalysis

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**Abstract:** Photocatalytic technology has been considered to be an ideal approach to solve the energy and environmental crises, and TiO<sub>2</sub> is regarded as the most promising photocatalyst. Compared with bare TiO<sub>2</sub>, TiO<sub>2</sub> based p-n heterojunction exhibits a much better performance in charge separation, light absorption and photocatalytic activity. Herein, we developed an efficient method to prepare p-type TiO<sub>2</sub> quantum dots (QDs) and decorated graphitic carbonitrile (g-C<sub>3</sub>N<sub>4</sub>) nanocomposites, while the composition and structure of the TiO<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> were analyzed by X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis, transmission electron microscopy, X-ray photoelectron spectroscopy and UV-visible diffuse reflectance spectroscopy characterizations. The characterization results reveal the surface decorated TiO<sub>2</sub> quantum dots is decomposed by titanium glycerolate, which exhibits p-type conductivity. The presence of p-n heterojunction over interface is confirmed, and photoluminescence results indicate a better performance in transfer and separation of photo-generated charge carriers than pure semiconductors and type-II heterojunction. Moreover, the synergy of p-n heterojunction over interface, strong interface interaction, and quantum-size effect significantly contributes to the promoted performance of TiO<sub>2</sub> QDs@g-C<sub>3</sub>N<sub>4</sub> composites. As a result, the as-fabricated TiO<sub>2</sub> QDs@g-C<sub>3</sub>N<sub>4</sub> composite with a p/n mass ratio of 0.15 exhibits improved photo-reactivity of 4.3-fold and 5.4-fold compared to pure g-C<sub>3</sub>N<sub>4</sub> in degradation of organic pollutant under full solar spectrum and visible light irradiation, respectively.

**Keywords:** p-n heterojunction; g-C<sub>3</sub>N<sub>4</sub>; TiO<sub>2</sub>; charge separation; photocatalysis

## 1. Introduction

With the increasing concerns regarding the global environmental and energy-related crises over the past decades, photocatalytic technology has been considered to be an effective approach since the foundation of Fujishima-Honda effect in 1972 [1,2]. The key for an efficient photocatalytic process lies in the design and construction of highly active photocatalyst, which requires a wide light absorption edge, fast transfer and separation of photo-generated charge carriers, and quick surface redox reaction [3–7]. TiO<sub>2</sub> is regarded as the most promising photocatalyst due to the advantages such as earth abundance, low price, excellent thermal and chemical stability, and being environmentally friendly [8,9]. Unfortunately, the broad band gap (i.e., 3.2 eV for anatase) means TiO<sub>2</sub> can only be excited by ultraviolet (UV) light, which is less than 5% in the solar spectrum. Meanwhile, the fast

charge recombination rate in single TiO<sub>2</sub> also results in a low quantum efficiency. Therefore, it is an urgently necessary to promote the light absorption and charge separation efficiency of TiO<sub>2</sub> to meet the requirements of industrial applications [10,11].

Recently, many researchers have focused on the modification of TiO<sub>2</sub> towards an improved photocatalytic performance, including for: morphology modulation [12–14], metal or nonmetal doping [15–18], defect engineering [19–22], and fabrication of hetero/homojunction [2,23–27]. In our previous reports, we found that the introduction of titanium vacancies into TiO<sub>2</sub> will widen the valence band, which controls the mobility of holes inherently and thus increase charge separation efficiency. Moreover, the introduction of metal vacancies can alter TiO<sub>2</sub> from an n-type semiconductor to a p-type semiconductor [28]. Pan et-al. modified p-type TiO<sub>2</sub> with n-type TiO<sub>2</sub> quantum dots (QDs) to construct p-n homojunction, and the resulted p-n homojunction exhibits significantly high photo-activity compared with pure type TiO<sub>2</sub>, which is attributed to the formation of large electronic field over the interface [29]. Moreover, besides the influence of p-n homojunction, quantum sized TiO<sub>2</sub> can also enhance the charge separation due to the quantum size effect [13,30–32]. However, in these reports, both the titanium defected TiO<sub>2</sub> and TiO<sub>2</sub> QDs still absorb only UV light, which limits their applications under sunlight.

Graphic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is a promising metal-free photocatalyst in the field of H<sub>2</sub> production, organic pollutant degradation, CO<sub>2</sub> reduction, and artificial photosynthesis due to the suitable band structure (2.7~2.8 eV), excellent chemical and thermal stability [33–37]. Usually, g-C<sub>3</sub>N<sub>4</sub> is synthesized by thermal condensation of melamine, urea or other triazine derivatives, but the resultant product exhibits an irregular 2D aggregation structure, leading to a lower surface area and electrical conductivity, as well as an increased charge carrier recombination [38,39]. Both theoretical and experimental results suggest that nanosheet structured g-C<sub>3</sub>N<sub>4</sub> will exhibit a larger surface area and lower charge transfer resistance, so the exfoliation of bulk g-C<sub>3</sub>N<sub>4</sub> into nanosheets has been regarded as an effective approach to promote the photocatalytic performance of g-C<sub>3</sub>N<sub>4</sub> [40,41]. Wang et-al. applied a liquid exfoliation method on bulk g-C<sub>3</sub>N<sub>4</sub> to prepare layer g-C<sub>3</sub>N<sub>4</sub>, and the charge transfer resistance decreased by 75% according to the electrochemical impedance spectroscopy (EIS) results, indicating a lower charge recombination [42]. Cheng et-al. conducted an exfoliation treatment on bulk g-C<sub>3</sub>N<sub>4</sub> using a simple thermal oxidation etch method, and g-C<sub>3</sub>N<sub>4</sub> nanosheets with layer thickness of 2 nm and surface area of 306 m<sup>2</sup>/g were obtained. Compared with bulk g-C<sub>3</sub>N<sub>4</sub>, the charge carrier life in the as-prepared g-C<sub>3</sub>N<sub>4</sub> nanosheets is prolonged because of the quantum confinement effect [43]. Li and coworkers also reported the synthesizing of 6–9 atomic thick g-C<sub>3</sub>N<sub>4</sub> nanosheets by a thermal exfoliation approach, the photocatalytic degradation rate is 2.9 times higher than that of bulk g-C<sub>3</sub>N<sub>4</sub> [44]. Therefore, the exfoliation of bulk g-C<sub>3</sub>N<sub>4</sub> to nanosheets can effectively increase the surface area, and thus improve charge transfer and separation.

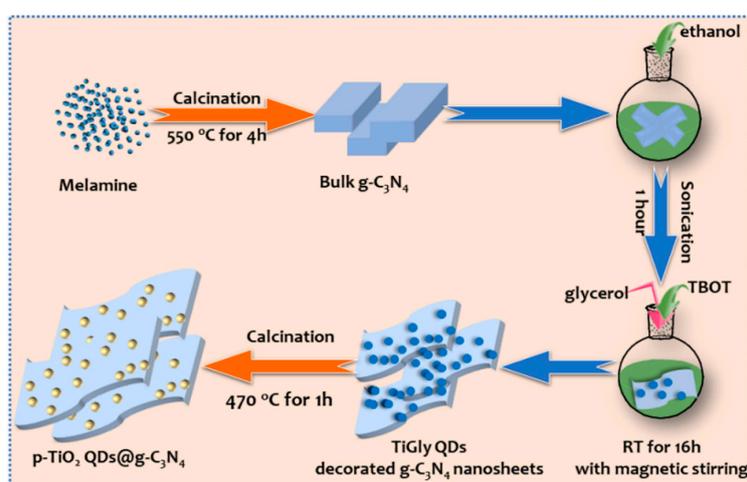
Construction of heterojunction is an effective approach to improve the photocatalytic performance by combining both the advantage of two semiconductors, and the electronic field will enhance the charge transfer and separation across the interface. Type II heterojunction with staggered band alignment is the most widely studied structure. Jiang et-al. placed 5.5 nm sized TiO<sub>2</sub> on g-C<sub>3</sub>N<sub>4</sub> nanosheets. Due to the formation of type-II heterojunction, the resultant composites exhibited a Rhodamine B (RhB) degradation rate of 2.5-fold compared to pure g-C<sub>3</sub>N<sub>4</sub> [25]. However, this is due to the fact that the work function of the same types semiconductor is closed to each other, which limits the driving force in type-II heterojunction. Instead, with different conductivity types semiconductor contacts, p-n heterojunction will be formed and the difference of the work function is large enough to realize a more efficient charge carrier separation [26,29]. For example, Wang et-al. reported that Cu<sub>2</sub>O/TiO<sub>2</sub> p-n junction exhibits a much better photoelectrochemical activity than that of pure TiO<sub>2</sub> and pure Cu<sub>2</sub>O [27].

In this work, based on the improvement of our previous work [26,28,29], nanosized titanium glycerolate (TiGly), precursors of p-type TiO<sub>2</sub> quantum dots, were successfully synthesized and in-situ deposited on the surface of g-C<sub>3</sub>N<sub>4</sub>. TiO<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> nanosheet p-n heterojunctions were then obtained after calcination in air. This p-n junction can achieve the function of killing three birds with one stone: p-type TiO<sub>2</sub> QDs for promoted charge separation, g-C<sub>3</sub>N<sub>4</sub> nanosheets for lower charge resistance and p-n junction for enhanced charge transfer over interface. Therefore, compared with pure g-C<sub>3</sub>N<sub>4</sub>

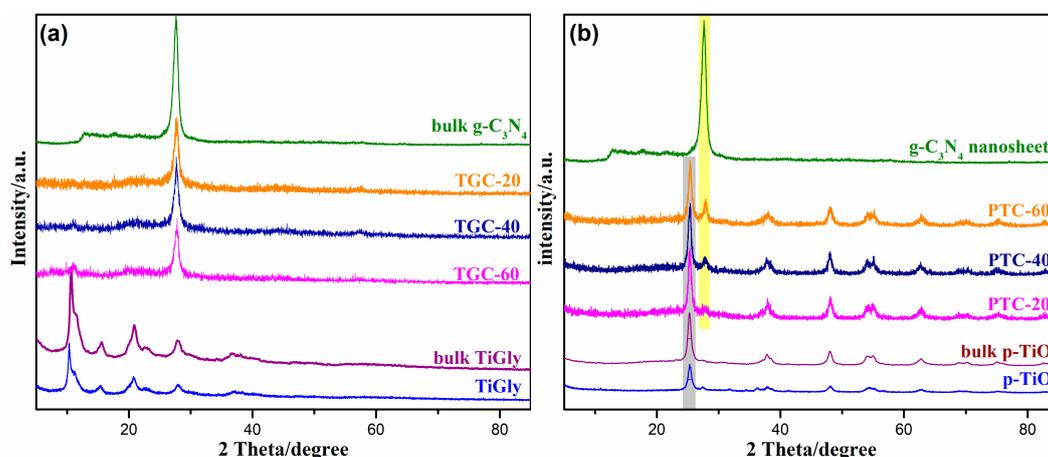
and  $\text{TiO}_2/\text{g-C}_3\text{N}_4$  type-II heterojunction,  $\text{TiO}_2$  QDs@ $\text{g-C}_3\text{N}_4$  p-n heterojunctions exhibit promoted electron-hole separation efficiency and excellent photocatalytic performance in degradation of organic pollutant and hydrogen evolution.

## 2. Results and Discussion

The synthesizing process of bulk  $\text{g-C}_3\text{N}_4$  and  $\text{TiO}_2$ @ $\text{g-C}_3\text{N}_4$  p-n heterojunctions were diagrammatically presented in Scheme 1. Consistent with the literature reported, melamine was calcined in air at  $550^\circ\text{C}$  and then bulk  $\text{g-C}_3\text{N}_4$  were obtained. Previously, we have demonstrated that titanium glycerolate (TiGly) is the precursor of p-type  $\text{TiO}_2$ , the organic groups will be gradually removed after calcination, and titanium vacancies ( $V_{\text{Ti}}$ ) will be introduced into  $\text{TiO}_2$  during the conjunction process of the remaining Ti-O-Ti parallel lattice chains. Herein, in order to fabricate  $\text{TiO}_2$ @ $\text{g-C}_3\text{N}_4$  p-n heterojunction, bulk  $\text{g-C}_3\text{N}_4$  is synthesized firstly, and then TiGly nanoparticles were in-situ deposited on the surface of  $\text{g-C}_3\text{N}_4$  and labeled as TGC- $x$  according to the added  $\text{g-C}_3\text{N}_4$ . After calcination in air,  $\text{g-C}_3\text{N}_4$  was exfoliated and TiGly nanoparticles were decomposed to p-type  $\text{TiO}_2$  QDs (labeled as PTC- $x$ ). The sharp peak at about  $27.4^\circ$  in the X-ray diffraction (XRD) pattern of TGC- $x$  (Figure 1a) can be attributed to the periodic accumulation of layers of conjugated aromatic systems in bulk  $\text{g-C}_3\text{N}_4$  [45]. In the sample TGC-20 and TGC-40, a weak peak appearing at about  $10.2^\circ$ , which is the characteristic peaks corresponding to TiGly [28], indicating the presence of TiGly nanoparticles. As for TGC-60, the content of TiGly is too low to be detected.



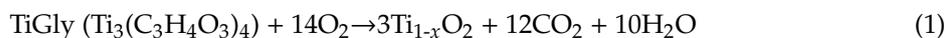
**Scheme 1.** Schematic fabrication procedures of  $\text{g-C}_3\text{N}_4$  and  $\text{TiO}_2$ @ $\text{g-C}_3\text{N}_4$  p-n heterojunctions.



**Figure 1.** (a) XRD pattern of bulk  $\text{g-C}_3\text{N}_4$ , bulk and nanoparticle TiGly and TGC- $x$  before calcination; (b) XRD pattern of  $\text{g-C}_3\text{N}_4$  nanosheets, bulk and nanoparticle p- $\text{TiO}_2$  and PTC- $x$  after calcination.

After being calcined at 470 °C for 1 h, TiGly nanoparticles will be decomposed into anatase p-type TiO<sub>2</sub>. As shown in Figure 1b, no diffraction peaks of TiGly can be observed, only anatase TiO<sub>2</sub> (JCPDS No. 21-1272) and g-C<sub>3</sub>N<sub>4</sub> (JCPDS No. 87-1526) can be observed in PTC-*x*, with no other visible phases or impurities. Notably, the full-width at half maxima (FWHM) of peaks at 25.3° corresponding to (101) planes of p-type TiO<sub>2</sub> nanoparticles is broadened from 0.57 to 0.65 compared with bulk p-TiO<sub>2</sub>, so the average particle size of the TiO<sub>2</sub> nanoparticles is smaller than the bulk p-TiO<sub>2</sub> according to Scherer Equation. The same phenomenon can also be observed in bulk g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> nanosheets, the peak at 27.4° corresponding to (002) plane of g-C<sub>3</sub>N<sub>4</sub> nanosheets is broadened and drastically weakened from PTC-60 to PTC-20, which is due to the decreased thickness of nanosheets during the thermal exfoliation process [39]. Moreover, we also calculated the lattice constant of the p-type TiO<sub>2</sub> nanoparticles based on XRD patterns, the results indicate that  $a = b = 3.793 \text{ \AA}$ , slightly larger than normal anatase TiO<sub>2</sub> ( $a = b = 3.785 \text{ \AA}$  for JCPDS No. 21-1272), whereas the *c* axis shrinks from 9.514 Å to 9.488 Å, which is identical with that of titanium defected TiO<sub>2</sub> [28].

Thermogravimetric (TG) tests were conducted to quantify the relative content of TiO<sub>2</sub> QDs in the as-prepared samples. As shown in Figure 2, the weight loss of the samples below 80 °C is due to the removal of surface absorbed water, whereas the weight loss between 80 °C and 400 °C is attributed to the decomposition of titanium glycerolate as shown in Equation (1) [28,29]. Since bulk g-C<sub>3</sub>N<sub>4</sub> exhibits almost no weight loss in this range, the weight loss of TGC-*x* can all assigned to the decomposition of TiGly. As shown in Figure 2, the weight loss is 20.03%, 9.77% and 7.98% for TGC-20, TGC-40 and TGC-60, respectively. Therefore, according to Equations (2) and (3), the mass content of TiGly in TGC-*x* can be calculated as 43.7%, 21.3% and 17.4%, respectively, corresponding to a p-type TiO<sub>2</sub> QDs mass content of 29.6%, 12.8% and 10.2% in PTC-20, PTC-40 and PTC-60, respectively. Additionally, there is a slight weight increase after 80 °C for all the samples, which may be due to the impurity in the sample gas used in TG tests, but this deviation will not affect the calculated QDs content in the samples.



$$y_{\text{TG}} = \frac{W_s}{W_{\text{TG}}} \quad (2)$$

$$y_{\text{TiO}_2} = \frac{m_{\text{TiO}_2}}{m_{\text{TiO}_2} + m_{\text{g-C}_3\text{N}_4}} = \frac{y_{\text{TG}}(1 - W_{\text{TG}})}{y_{\text{TG}}(1 - W_{\text{TG}}) + 1 - y_{\text{TG}}} = \frac{y_{\text{TG}} - y_{\text{TG}}W_{\text{TG}}}{1 - y_{\text{TG}}W_{\text{TG}}} \quad (3)$$

Among these figures:  $y_{\text{TG}}$  is the calculated content of TiGly, %;  $W_s$  is the weight loss of TGC-*x*, %;  $W_{\text{TG}}$  is the weight loss of pure TiGly, %;  $m_{\text{TiO}_2}$  is the calculated mass of TiO<sub>2</sub> in unit mass of PTC-*x*, g;  $m_{\text{g-C}_3\text{N}_4}$  is the calculated mass of g-C<sub>3</sub>N<sub>4</sub> in unit mass of PTC-*x*, g;  $y_{\text{TiO}_2}$  is the calculated mass content of p-type TiO<sub>2</sub> QDs in PTC-*x*, %.

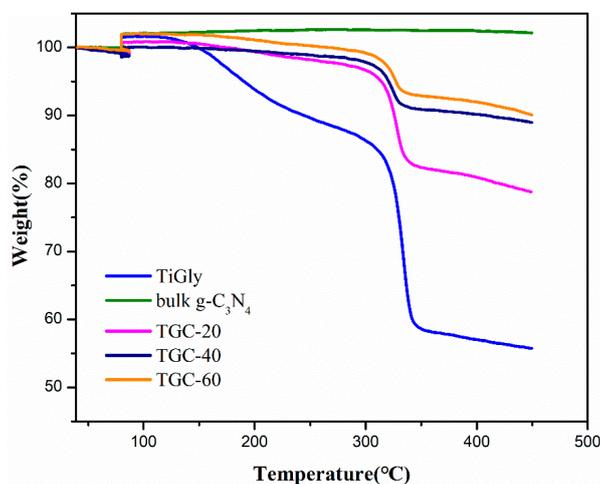
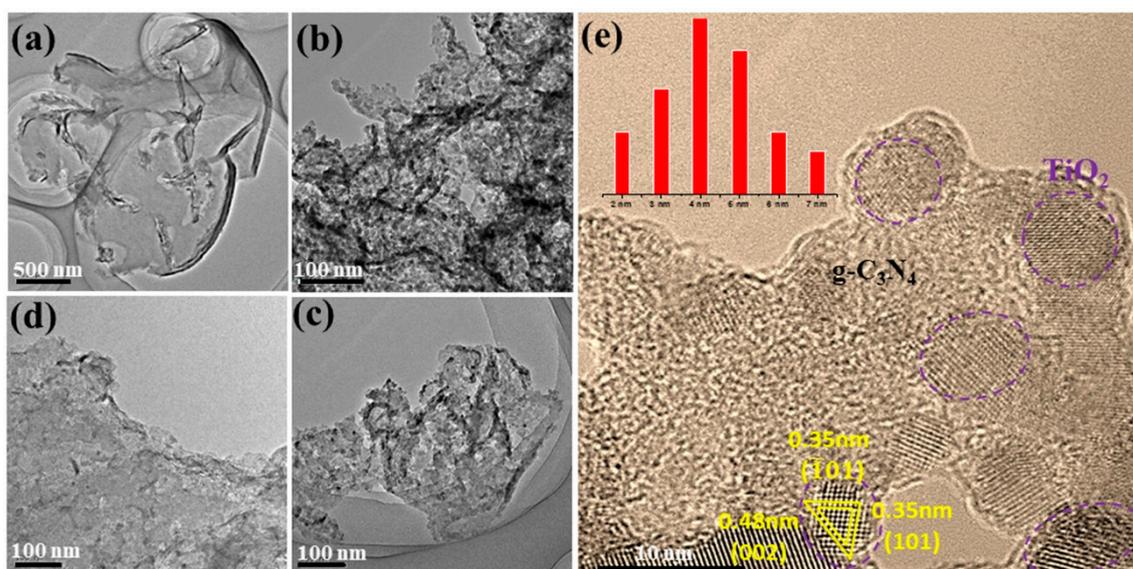


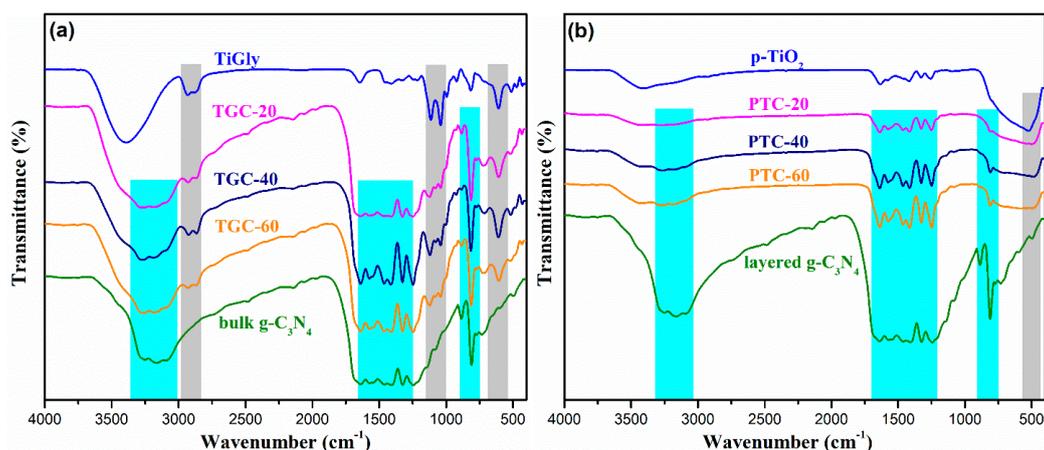
Figure 2. TG profiles of bulk g-C<sub>3</sub>N<sub>4</sub>, TiGly and TGC-*x*.

High resolution transmission electron microscopy (HRTEM) analyses were conducted to reveal the morphology and composition of the samples. Unlike the densely packed bulk  $g\text{-C}_3\text{N}_4$  reported in literatures [39], the as-prepared  $g\text{-C}_3\text{N}_4$  exhibits a nanosheet structure, the edges are curled and rough due to the minimizing surface energy (Figure 3a), which provides a lower resistance pathway for charge transfer. As shown in Figure 3b–d, the light contrast nanosheets are  $g\text{-C}_3\text{N}_4$  nanosheets whereas the dark contrast are the p-type  $\text{TiO}_2$  nanoparticles decomposed from TiGly. Figure 3e shows the lattice fingers of 0.35 nm and 0.48 nm in the dark contrast, corresponding to the (101) and (002) planes of anatase  $\text{TiO}_2$ , which reveal the exposure of (010) facet of anatase, consistent with the XRD results [31]. The typical size of  $\text{TiO}_2$  nanoparticles is 4–5 nm according to the particle size distribution result shown in the inset of Figure 3e, which is accordance with the characteristic size of quantum confinement effect. It is noteworthy that when the p-type  $\text{TiO}_2$  QDs are in-situ grown on the surface of  $g\text{-C}_3\text{N}_4$ , there is a strong interaction that exists between them so that the  $\text{TiO}_2$  QDs cannot be peeled off even after a 30 min ultra-sonication process. Moreover, the strong interaction implies an obvious interface heterojunction between  $\text{TiO}_2$  QDs and  $g\text{-C}_3\text{N}_4$ , which will enhance the transfer of photo generated electrons and holes [25]. In addition, in agreement with the TG results, the relative content of  $\text{TiO}_2$  QDs decreases from PTC-20 to PTC-60.



**Figure 3.** TEM images of (a)  $g\text{-C}_3\text{N}_4$  nanosheets, (b) PTC-20, (c) PTC-40 and (d) PTC-60, (e) is the enlarged image of PTC-40, inset: size distribution of  $\text{TiO}_2$  QDs in PTC-40.

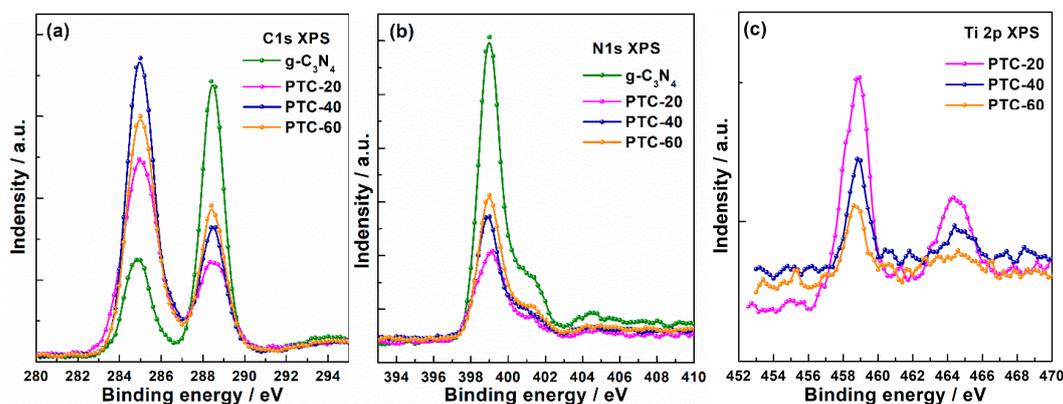
In order to further investigate the composition and interaction between p-type  $\text{TiO}_2$  QDs and  $g\text{-C}_3\text{N}_4$  in the as-prepared composites, Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) characterizations were conducted. As shown in Figure 4a, for the TGC- $x$ , there are three characteristic bands corresponding to  $g\text{-C}_3\text{N}_4$ , namely the broad peaks located at  $3000\text{--}3400\text{ cm}^{-1}$  assigned to the stretching of N–H bonds, the strong peaks at  $1250\text{--}1650\text{ cm}^{-1}$  due to the stretching vibration of C=N heterocycles and C–N bonds, and the band around  $808\text{ cm}^{-1}$  related to the ring vibration of s-triazine [45–48]. Moreover, besides the above three peaks, another three peaks related to TiGly appearing in TGC- $x$ , the peaks located at around  $1000\text{--}1150\text{ cm}^{-1}$  were attributed to the alcoholic Ti–O–C stretching mode, the apparent peak at  $611\text{ cm}^{-1}$  was indexed to the stretching mode of Ti–O bonds, and the bands located at  $2855\text{--}2927\text{ cm}^{-1}$  were assigned to the glycerol C–H stretching vibration [49]. Besides, the broad peak over  $3000\text{--}3600\text{ cm}^{-1}$  was attributed to the presence of physically adsorbed water and glycerol O–H stretching mode. Therefore, by combining with the XRD, TG and FT-IR results, it is proved that the as-prepared TGC- $x$  samples is composed by TiGly and  $g\text{-C}_3\text{N}_4$ .



**Figure 4.** (a) FT-IR patterns of bulk  $g\text{-C}_3\text{N}_4$ , TiGly and TGC- $x$  before calcination; (b) FT-IR patterns of layered  $g\text{-C}_3\text{N}_4$ , p-TiO<sub>2</sub> and PTC- $x$ .

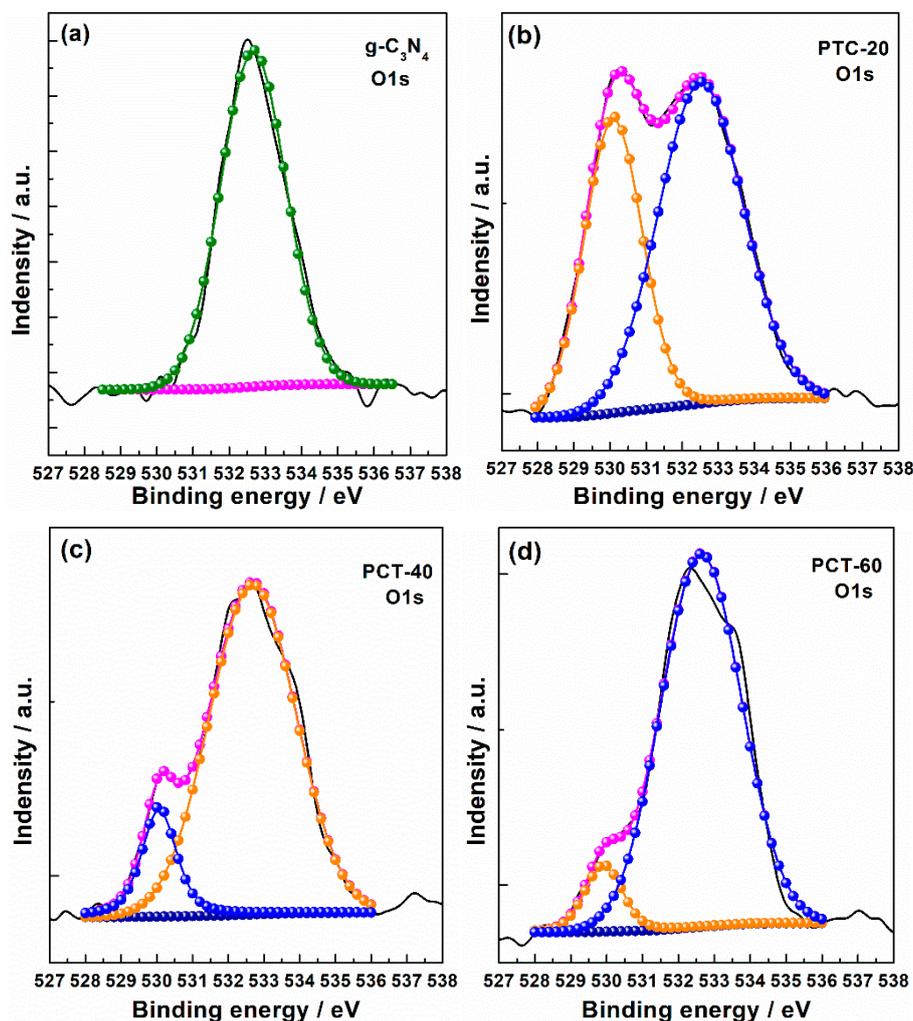
Upon calcination, the major FT-IR peaks of  $g\text{-C}_3\text{N}_4$  almost all remained in PTC- $x$  samples (Figure 4b). However, the bands assigned to C–H and O–H in TiGly disappeared, while only the stretching band of Ti–O remained, indicating the transformation of TiGly to TiO<sub>2</sub>, further confirming the formation of TiO<sub>2</sub> QDs@ $g\text{-C}_3\text{N}_4$  heterojunction. Moreover, with the decrement of  $g\text{-C}_3\text{N}_4$  content from PTC-60 to PTC-20, the intensity of s-triazazine ring vibration  $808\text{ cm}^{-1}$  also decreases, which is in agreement with the above TG results. It is noteworthy that the stretching vibration of Ti–O–Ti shifted significantly towards a lower wavenumber in PTC- $x$  composites, suggesting a strong interaction exists between p-TiO<sub>2</sub> QDs and  $g\text{-C}_3\text{N}_4$  [25], which is in favor of charge transfer across the interface and thus promotes the photocatalytic performance of the heterojunction.

XPS spectra were recorded to study the status of the C, N, Ti and O elements in the composites. Figure 5a shows the C1s XPS spectra of the samples, there are two main peaks located at 284.8 eV and 288.5 eV, respectively. The peak located at higher binding energy is attributed to the  $\text{sp}^3$ -bonded C of  $\text{N-C=N}_2$  in  $g\text{-C}_3\text{N}_4$ , and the peak located at 284.8 eV is due to the surface contaminated carbon during XPS test and  $\text{sp}^2$ -hybridized carbon atoms presented in graphic domains [29]. In the N1s XPS spectra (Figure 5b), an asymmetric profile can be observed in all the samples, with a main peak at 401 eV and a shoulder peak at lower binding energy, the main peak is due to the  $\text{sp}^2$ -hybridized nitrogen (C–N–C), while the shoulder peak is usually attributed to amino functional groups with a hydrogen atom (C–NH) and  $\text{sp}^3$ -hybridized nitrogen (N-[C]3) [25,39]. For the Ti 2p XPS spectra of the PTC- $x$  (Figure 5c), the binding energy of Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> are observed at 458.9 eV and 464.4 eV, respectively, suggests the existence of TiO<sub>2</sub> in the samples. Notably, compared with the Ti 2p binding energy of 458.4 eV in n-type TiO<sub>2</sub> [29], the Ti 2p binding energy in the as-prepared samples shifted towards a higher binding energy, indicating the existence of titanium vacancies ( $V_{\text{Ti}}$ ) and p-type properties of the TiO<sub>2</sub> QDs [28].



**Figure 5.** (a) C1s, (b) N1s and (c) Ti 2p XPS spectra of layered  $g\text{-C}_3\text{N}_4$ , p-TiO<sub>2</sub> and PTC- $x$ , respectively.

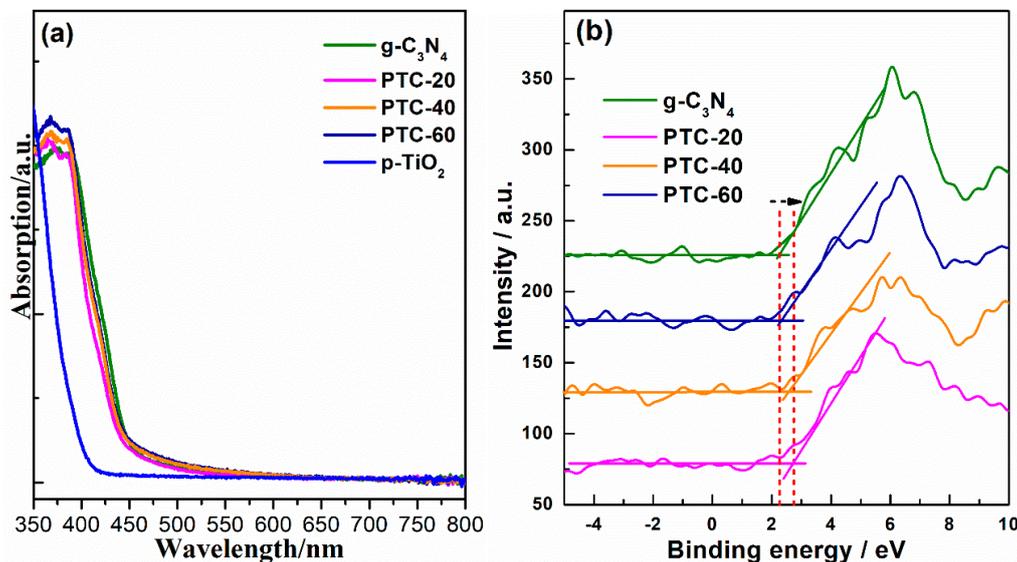
The O1s XPS spectra are shown in Figure 6, there is only one symmetrical peak at around 532.7 eV appearing in pure g-C<sub>3</sub>N<sub>4</sub>, which is attributed to the loosely bonded oxygen species on the surface (O<sub>2</sub>, H<sub>2</sub>O or OH groups), no peaks corresponding to C–O and N–C–O appeared at 531.4 eV, indicating that no O doping process occurred in g-C<sub>3</sub>N<sub>4</sub> during the calcination process [38]. As for the TiO<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> composites, the O1s peaks split into two peaks located at 532.7 eV and 529.8 eV, respectively. The lower binding energy is assigned to the oxygen anions (O<sup>2-</sup>) in the crystal lattice of anatase [28], and the concentration of TiO<sub>2</sub> QDs is proportional to the intensity of this peak. As shown in Figure 6b–d, from PTC-20 to PTC-60, the intensity of this peak becomes obviously weak, confirming the gradually decreased content of TiO<sub>2</sub> QDs in the composites. These results are in good agreement with the TEM, TG and FT-IR results, indicating that the composites are composed of g-C<sub>3</sub>N<sub>4</sub> and p-type TiO<sub>2</sub> QDs, and that the content of TiO<sub>2</sub> QDs decreases from PTC-20 to PTC-60.



**Figure 6.** Fitted O1s XPS spectra of (a) layered g-C<sub>3</sub>N<sub>4</sub>, (b) PTC-20, (c) PTC-40 and (d) PTC-60, respectively.

The light absorption properties of the as-prepared samples were characterized by UV-visible diffuse reflection spectrum (UV-vis DRS). As illustrated in Figure 7a, pure g-C<sub>3</sub>N<sub>4</sub> can absorb light from UV region to visible light up to 465 nm, while p-type TiO<sub>2</sub> only absorb UV light up to 400 nm. As for the TiO<sub>2</sub> QDs@g-C<sub>3</sub>N<sub>4</sub> composites, there is a remarkable absorption edge extension to the visible region compared with single TiO<sub>2</sub> [39]. Moreover, with the increasing content of g-C<sub>3</sub>N<sub>4</sub> from PTC-20 to PTC-60, the optical absorption edge of p-n heterojunction shifts towards a longer wavelength, indicating a stronger light absorption in the visible light region, which is beneficial for the improvement of photocatalytic performance. Meanwhile, the quantum-size effect of the p-type TiO<sub>2</sub>

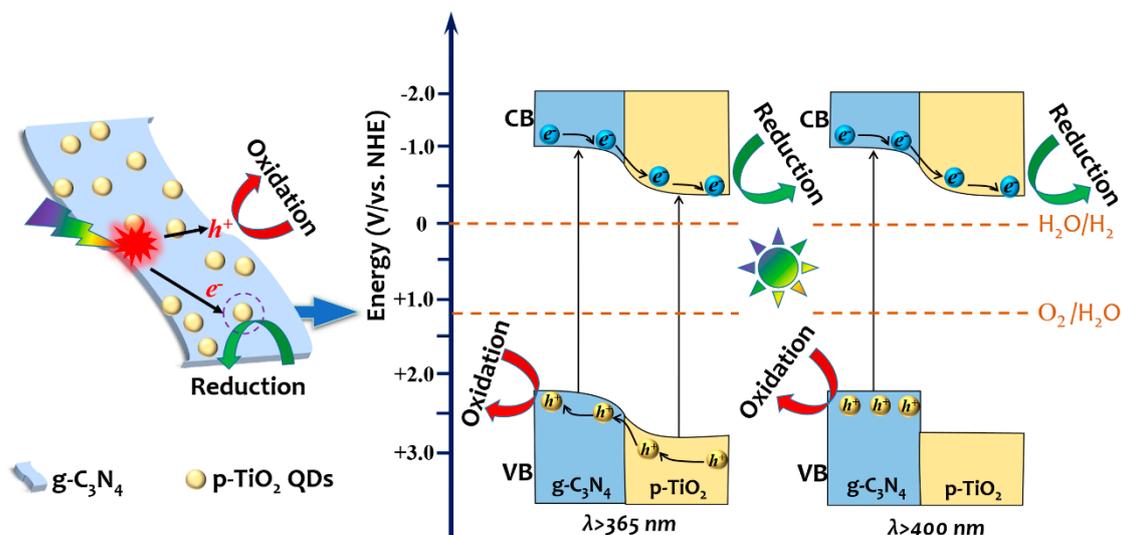
QDs is illustrated by VB XPS spectra. As shown in Figure 7b, a blue shift of VB edge is observed in the as-prepared heterojunctions due to the existence of TiO<sub>2</sub> nanoparticles, and this tendency becomes more and more obvious with the increment of TiO<sub>2</sub>, confirming the quantum dots nature of the surface decorated p-type TiO<sub>2</sub> nanoparticles [31].



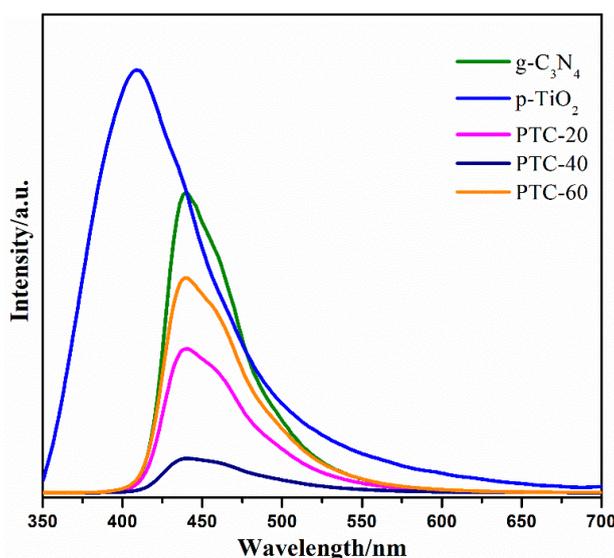
**Figure 7.** (a) UV-vis DRS spectra and (b) valence band density of states (DOS) of layered g-C<sub>3</sub>N<sub>4</sub>, PTC-20, PTC-40 and PTC-60.

As mentioned above, we have demonstrated that the surface deposited TiO<sub>2</sub> QDs is abundant in titanium vacancies, while both experimental and density functional theoretical (DFT) results have indicated that metal defected TiO<sub>2</sub> is p-type semiconductor [28]. In general, g-C<sub>3</sub>N<sub>4</sub> exhibits n-type conductivity, therefore, p-n heterojunctions will be formed across the interface, which can afford a large electrical field and more efficient charge separation. Therefore, according to the band gap and valence band (VB) position of pure g-C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub>, the band alignment of the p-n heterojunction (PTC-40) is diagrammed in Scheme 2. Both TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> can be excited under  $\lambda > 365$  nm, charge redistribution process will occur to equilibrate the Fermi level ( $E_f$ ) due to the large difference of  $E_f$  between p-type TiO<sub>2</sub> and n-type g-C<sub>3</sub>N<sub>4</sub>, the consequence is that the photogenerated electrons migrate to the conduction band (CB) of TiO<sub>2</sub> and holes to the g-C<sub>3</sub>N<sub>4</sub> VB. However, only g-C<sub>3</sub>N<sub>4</sub> can be excited under visible light irradiation ( $\lambda > 400$  nm), and the photogenerated electrons will still transfer to the CB of TiO<sub>2</sub>, while the holes tend to keep stay in the VB of g-C<sub>3</sub>N<sub>4</sub>. In both cases, an efficient electron-hole spatial separation can be realized and the lifetime of charge carriers can also be prolonged, these separated electrons can react with O<sub>2</sub> or H<sub>2</sub>O to form reactive oxygen species ( $\cdot\text{O}_2^-$ ) or H<sub>2</sub>, while the holes will oxidize an organic pollutant or sacrificial agent directly. In addition, the presence of metal vacancies will enlarge the width of VB, which controls the mobility of holes inherently [28], and thus the synergy influence of metal vacancies, quantum confinement effect, and nanosheet structure can effectively promote the charge transfer and separation across the interface.

The facilitated charge separation by the p-n heterojunction was confirmed by photoluminescence (PL) spectra. As shown in Figure 8, pure g-C<sub>3</sub>N<sub>4</sub> has an emission peak around 450 nm, whereas p-TiO<sub>2</sub> exhibits a signal at around 400nm, which is due to the band-band transition, namely the energy corresponding to the emission is close to the excitation energy of g-C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub>, respectively [25,29]. The PL intensity of PTC-*x* is much lower than pure p-type TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>, indicating a promoted electron-hole separation by the p-n heterojunction. Notably, PTC-40 exhibits the lowest PL intensity among the samples, suggesting a higher charge separation efficiency and a better photocatalytic performance, which also indicates that there exists an approximate p/n ratio between the p-type TiO<sub>2</sub> and n-type g-C<sub>3</sub>N<sub>4</sub> in the heterojunction.

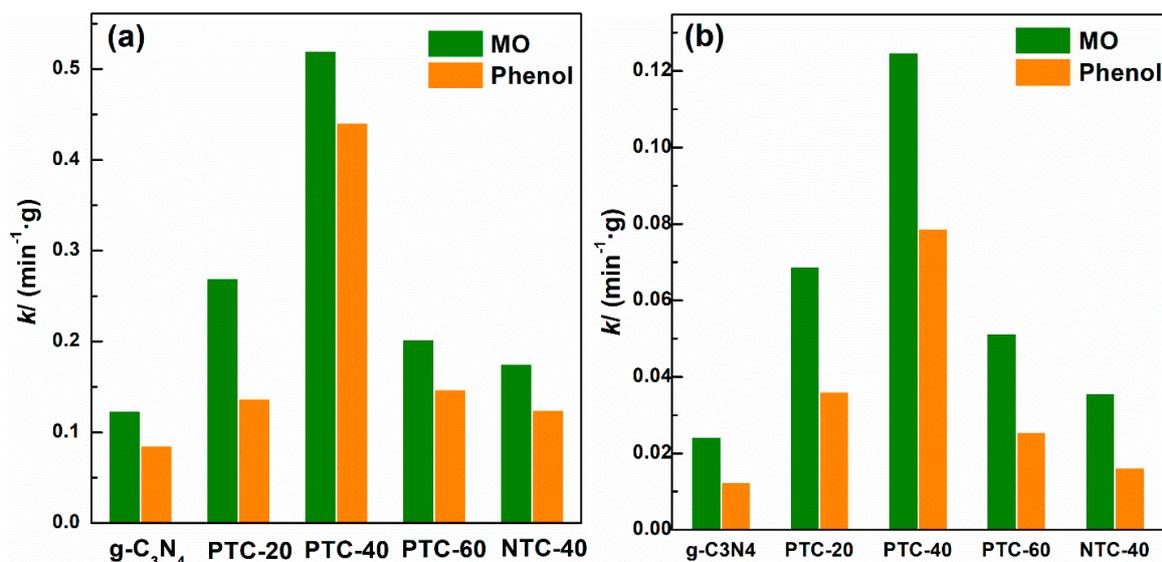


**Scheme 2.** Schematic illustration of TiO<sub>2</sub> QDs@g-C<sub>3</sub>N<sub>4</sub> p-n heterojunction and the pathway for electron-hole transfer and separation over the junction under simulated solar irradiation ( $\lambda > 365$  nm) and visible light irradiation ( $\lambda > 400$  nm).



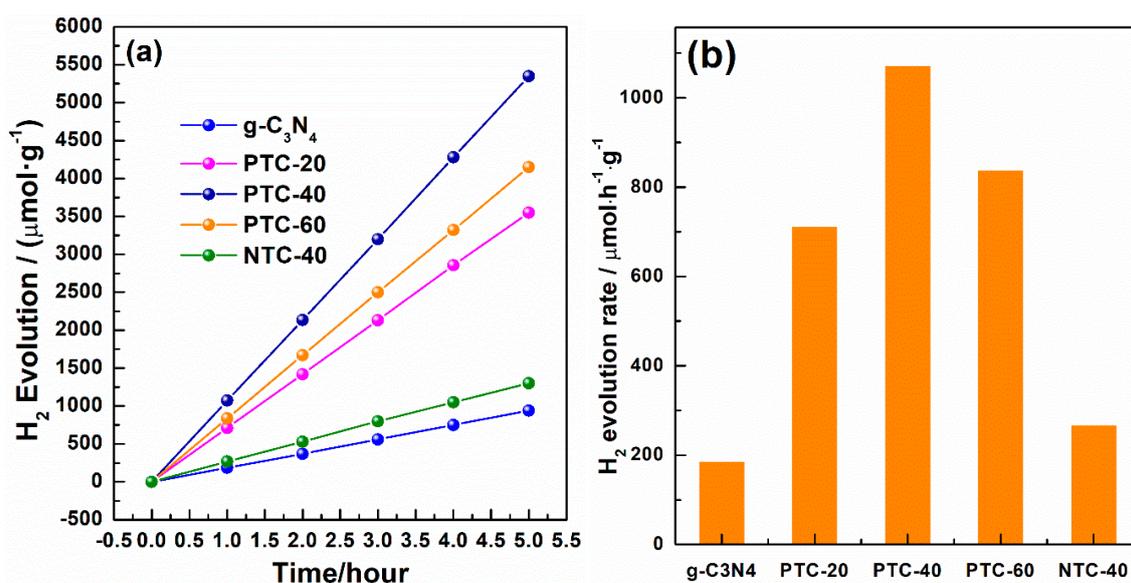
**Figure 8.** Steady state PL spectra of layered g-C<sub>3</sub>N<sub>4</sub>, PTC-20, PTC-40 and PTC-60.

Photocatalytic degradation of organic pollutants and photocatalytic water splitting were conducted to evaluate the performance of as-prepared TiO<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> p-n heterojunctions. Figure 9a shows the photodegradation rate of the samples based on pseudo-first-order reaction mode. Under simulated sunlight irradiation ( $\lambda > 365$  nm), the degradation rate of MO for PTC-40 with a TiO<sub>2</sub> (p) to g-C<sub>3</sub>N<sub>4</sub> (n) mass ratio of 0.15 is  $0.52 \text{ min}^{-1} \cdot \text{g}^{-1}$ , which is the highest among the PTC-*x* and is 4.3-fold higher than that of pure g-C<sub>3</sub>N<sub>4</sub>. Moreover, we also tested the photoactivity with a cut-off filter of  $\lambda > 400$  nm to evaluate the visible light photocatalytic performance, the reaction rate exhibits the same trends with that under simulated solar spectrum (Figure 9b), and the reaction rate for MO degradation of PTC-40 is  $0.125 \text{ min}^{-1} \cdot \text{g}^{-1}$ , 5.4-fold higher than pure g-C<sub>3</sub>N<sub>4</sub>. This result confirms that p-n heterojunction exhibits a better photocatalytic performance than single photocatalyst and that the as-prepared TiO<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> is active under visible light.



**Figure 9.** Pseudo-first-order reaction rate in degradation of methyl orange (MO) and phenol under: (a) full solar spectrum and (b) visible light ( $\lambda > 400$  nm).

The photocatalytic H<sub>2</sub> evolution reaction rate is shown in Figure 10a, the H<sub>2</sub> release rate for g-C<sub>3</sub>N<sub>4</sub>, PTC-20, PTC-40 and PTC-60 is 186  $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ , 712  $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ , 1072  $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$  and 838  $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ , respectively. It is clearly that the H<sub>2</sub> evolution rate of PTC-40 is the fastest, which is 5.8-fold of pure g-C<sub>3</sub>N<sub>4</sub>, 1.5-fold of PTC-20 and 1.3-fold of PTC-60. Combining with the PL results and photoactivity, we can get the conclusion that PTC-40 has the most efficient electron-hole separation, and thus exhibits the best photocatalytic performance among the as-fabricated samples. Meanwhile, this phenomenon also indicates that a suitable p/n ratio is required to construct the best p-n heterojunction. In comparison, we also loaded n-type TiO<sub>2</sub> QDs on the surface of g-C<sub>3</sub>N<sub>4</sub> to construct a type-II heterojunction and found that the promotion in photoactivity is far from that by p-n heterojunction (1.44-fold vs. 5.8-fold in H<sub>2</sub> evolution), illustrating that p-n heterojunctions are more effective in accelerating photogenerated charge carrier separation and promoting the photocatalytic performance.



**Figure 10.** (a) Time course of hydrogen evolution and (b) hydrogen generation rate of the samples.

### 3. Experimental

#### 3.1. Materials

Ethanol, glycerol, melamine and methyl orange (MO) were all purchased from Tianjin Jiangtian Fine Chemical Research Institute. Titanium butoxide ( $C_{16}H_{36}O_4Ti$ , TBOT), triethanolamine (TEOA) and phenol were purchased from J&K chemical. Milli-Q ultra-pure water with a resistivity larger than  $18.2 M\Omega\cdot cm$  was used in all experiments. All the chemicals were reagent grade and used as received.

#### 3.2. Preparation of Bulk $g-C_3N_4$

Bulk  $g-C_3N_4$  was synthesized by thermal annealing melamine under air atmosphere. Typically, 5 g of melamine was put into an airtight crucible, then the crucible was placed into a muffle furnace and calcined at  $550\text{ }^\circ C$  for 4 h with a ramping rate of  $5\text{ }^\circ C/min$ . After being cooled down to room temperature naturally, the obtained yellow powder is bulk  $g-C_3N_4$ .

#### 3.3. Preparation of $TiO_2$ QDs@ $g-C_3N_4$ p-n Heterojunction

As shown in Scheme 1, for the fabrication of  $TiO_2$  QDs@ $g-C_3N_4$  p-n heterojunction,  $x$  ( $x = 20, 40, 60$ ) mg  $g-C_3N_4$  was dispersed in 148 mL ethanol and sonicated for one hour. After that, 5 mL glycerol was added into the solution. After being stirred for another 20 min, 400  $\mu L$  TBOT was dropwisely into the solution and then titanium glycerolate (TiGly) was in-situ grown on the surface of  $g-C_3N_4$ , the solution was stirred at room temperature for 16 h. The resulted powders (labeled as TGC- $x$ ) were washed with water and absolute ethanol for several times, and dried at  $70\text{ }^\circ C$  overnight. After calcination of TGC- $x$  in air at  $470\text{ }^\circ C$  for 1 h,  $TiO_2$  QDs@ $g-C_3N_4$  p-n heterojunctions were obtained and labeled as PTC- $x$  ( $x = 20, 40, 60$ ). As a reference, n-type  $TiO_2$  QDs deposited  $g-C_3N_4$  was synthesized with the same procedure ( $x = 40$  mg) except that glycerol was replaced by 233  $\mu L$   $NH_3\cdot H_2O$  for the purpose of triggering the nucleation of  $TiO_2$  on  $g-C_3N_4$  as previously reported (the reference sample was labeled as NTC-40) [29].

#### 3.4. Characterization of Photocatalysts

The calcination temperature for the decomposition of titanium glycerolate and the content of  $TiO_2$  was determined by thermogravimetric analysis (TGA Q500, TA Instruments, DE, USA) with air gas flow at 50 mL/min in a range of  $30\text{--}500\text{ }^\circ C$  ( $5\text{ }^\circ C/min$ ). In order to obtain the composition of the samples, Fourier transform infrared spectroscopy (FT-IR, Bruker Tensor-27 spectrum, Bavaria, Germany) was conducted before and after calcination, the FT-IR spectra were acquired in the range of  $400\text{--}4000\text{ cm}^{-1}$  with a resolution of  $1\text{ cm}^{-1}$ .

All the samples were characterized with an X-ray diffractometer (XRD-6100, Shimadzu, Kyoto, Japan) to determine the crystalline properties. The X-ray diffractometer was equipped with a  $Cu\ K\alpha$  radiation at 40 kV and 30 mA at a scanning rate of  $5^\circ/min$ . The diffraction patterns were determined over 2 theta range of  $5^\circ\text{--}90^\circ$  with a resolution of  $2^\circ/min$ . To obtain the average size of the crystalline size, Scherrer equation was used ( $D = 0.9\lambda/\beta\cos\theta$ ), whereas the lattice constants was calculated according to Bragg equation of  $2dhklsin\theta = \lambda$ , where  $\lambda$  is the applied wavelength,  $\theta$  is the Bragg angle and  $\beta$  is the FWHM value.

The chemical states of the as-prepared samples were characterized by X-ray photoelectron spectroscopy (PHI-1600, ULVAC-PHI, Kanagawa, Japan) with  $Al\ K\alpha$  radiation, and the binding energy was calibrated by the  $C1s$  peak (284.8 eV) of the contamination carbon. High resolution transmission electron microscopy (HRTEM) analysis was carried out using a Tecnai  $G^2$  F-20 transmission electron microscope (FEI, OR, USA) with a field-emission gun operation at 200 kV.

The band gap and the light absorption properties of the samples were determined with a UV-vis diffuse reflectance spectrum (U-3010, Hitachi Ltd., Lbarakiken, Japan) with a 60 mm diameter integrating sphere using  $BaSO_4$  as the reflectance sample. Steady-state photoluminescence spectra (PL) spectra were measured by a Fluorolog3-21 (Horiba JobinYvon, NJ, USA) with the excitation light at 325 nm.

### 3.5. Photocatalytic Degradation and Hydrogen Evolution

Photodegradation of organic pollutants (phenol and MO) was conducted in an opening quartz chamber (150 mL) vertically irradiated by a 300 W high-pressure xenon lamp (PLS-SXE300, Beijing Perfect Light Co. Ltd., Beijing, China) located on the upper position. The irradiation area was about 20 cm<sup>2</sup>. The light density was measured using a radiometer (Photoelectric Instrument Factory, Beijing Normal University, Model UV-A, Beijing, China), and the results indicate that the light density at 365 nm and 400 nm was 34.7 mW/cm<sup>2</sup> and 32.5 mW/cm<sup>2</sup>, respectively. Reaction conditions included the following: a temperature of 25 °C, solution volume of 100 mL, C<sub>0</sub> (phenol) of 400 μmol·L<sup>-1</sup>; C<sub>0</sub> (MO) of 120 μmol·L<sup>-1</sup>; photocatalyst of 0.1 g·L<sup>-1</sup>. Prior to the reaction, the suspension was stirred without irradiation for 20 min to achieve an adsorption equilibrium. Samples were withdrawn, centrifuged and analyzed using a U-3010 UV-vis spectrometer.

Photocatalytic hydrogen production was carried out in a Pyrex top-irradiation reaction vessel connected to closed glass gas system. 10 mg catalyst dispersed in 120 mL aqueous solution containing TEOA (30 vol.%). The temperature of reaction solution was maintained at 0 °C. The resultant hydrogen was analyzed using an off-line gas chromatography (Bruker 450-GC, CA, USA) equipped with a thermal conductive detector (TCD), 5 Å molecular sieve column, and N<sub>2</sub> as carrier gas.

## 4. Conclusions

In this work, p-TiO<sub>2</sub> QDs@g-C<sub>3</sub>N<sub>4</sub> p-n heterojunctions were fabricated by in-situ decorating titanium-defected TiO<sub>2</sub> QDs on the surface of g-C<sub>3</sub>N<sub>4</sub>, in which TiO<sub>2</sub> QDs bring up p-type conductivity and g-C<sub>3</sub>N<sub>4</sub> affords for n-type conductivity. The as-prepared p-n heterojunction exhibits higher charge separation efficiency and photocatalytic performance in H<sub>2</sub> evolution reaction and degradation of organic pollutant than pure g-C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> type-II heterojunction under both UV-light and visible light irradiation, which can be ascribed to the synergy of a large electrical field over interface, a strong interface interaction, and the quantum confinement effect. In all the samples, PTC-40 with a p/n mass ratio of 0.15 exhibits the best photocatalytic performance. This work demonstrates that the construction of p-n heterojunction is an effective pathway to accelerate the electron-hole separation that is the key for a highly efficient photocatalyst.

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