1 **Facile One-Step Hydrothermal Synthesis Toward Strongly Coupled**
2 **TiO₂/Graphene Quantum Dots Photocatalysts for Efficient Hydrogen**
3 **Evolution**

4 Shixiong Min^{a,*}, Jianhua Hou^a, Yonggang Lei^a, Xiaohua Ma^a, Gongxuan Lu^b

5 ^a School of Chemistry and Chemical Engineering, Beifang University of Nationalities,
6 Yinchuan, 750021, Ningxia Province, China.

7 ^b State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of
8 Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China.

9 *Corresponding author.

10 E-mail: sxmin@nwnu.edu.cn (S. Min)

11 Fax: 86-951-2067915

12 Tel: 86-951-2067917

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Abstract

The coupling of semiconductor photocatalysts with graphene quantum dots (GQDs) has been proven to be an effective strategy to enhance the photocatalytic and photoelectrical conversion performances of the resulted composites; however, the preparation of semiconductor/GQDs composites usually involves several time-inefficient and tedious post-treatment steps. Herein, we present a facile one-step hydrothermal route for the preparation of GQDs coupled TiO₂ (TiO₂/GQDs) photocatalysts using 1,3,6-trinitropyrene (TNP) as the sole precursor of GQDs. During the hydrothermal process, TNP molecules undergo an intramolecular fusion to form GQDs, which simultaneously decorate on the surface of TiO₂ nanoparticles, leading to a strong surface interaction between the two components. The effective coupling of GQDs on TiO₂ can effectively extend the light absorption of the TiO₂ to visible region and enhance the charge separation efficiency of TiO₂/GQDs composites as a result of GQDs acting as a photosensitizer and an excellent electron acceptor. These key advances make the TiO₂/GQDs photocatalyst highly active towards the H₂ evolution reaction, resulting in 7 and 3 times higher H₂ evolution rate and photocurrent response at optimal GQDs content than TiO₂ alone, respectively. This study provides a new methodology for the development of high-performance GQDs modified semiconductor photocatalysts for energy conversion applications.

Keywords

TiO₂; graphene quantum dots; hydrothermal synthesis; photocatalyst; hydrogen evolution

1. Introduction

Hydrogen (H_2) is a clean and high-density energy carrier proposed to solve the energy shortage and environmental pollution issues [1]. Photocatalytic H_2 evolution by using semiconductor photocatalysts and solar energy is a promising strategy for solar-to-fuel conversion [2-10]. Among the investigated photocatalysts so far that have shown sufficient capability for reducing water to H_2 , metal oxides especially titanium dioxide (TiO_2), has shown to be promising one because of its high activity, good photostability, chemical inertness, nontoxicity, and low cost [5]. However, the wide-band gap ($E_g=3.2$ eV) and high recombination rate of photogenerated charge carriers of TiO_2 greatly limit its practical implementations [7]. Recently, it has been demonstrated that the incorporation of conductive carbon nanomaterials [11], such as fullerene (C_{60}) [12-14], carbon nanotubes (CNTs) [15-17], and graphene [18-25], can greatly improve the photocatalytic activity of TiO_2 by providing a rapid electron transfer pathway for enhancing charge separation efficiency and introducing sensitization effect for extending light absorption towards visible light region.

“Molecule-like” graphene quantum dots (GQDs), as a newly emerging carbon nanomaterials of the graphene families [26-28], have received increasing attentions for photocatalysis and photoelectrochemical conversion owing to its combined merits of graphene and quantum dots, such as high electron reservation capability, tunable optical and electronic properties, and plentiful edge defects. Specifically, GQDs itself can be directly used as a metal-free photocatalyst for overall water splitting or to modified semiconductor photocatalysts with enhanced photocatalytic and photoelectrochemical performances [29-44]. For examples, Teng et al. [30] has reported that nitrogen-doped GQDs (NGO-QDs) with both p-type and n-type conductivity domains resulted in an internal Z-scheme charge transfer for water splitting reactions, as a result, the NGO-QDs showed visible light activity for overall water splitting to H_2 and O_2 . Gupta [32] and Chan et al. [33] have shown that GQDs infilled/modified TiO_2 nanotube arrays hybrid exhibits improved photocatalytic efficiency for degradation of dyes under UV light irradiation. Pan et al. [35] has observed an enhanced separation efficiency of electron-hole pairs in GQDs by forming heterojunctions with TiO_2 .

and the resulted composites showed a high activity for dye degradation. Guo et al. [36] has reported the utilization of GQDs as a green photosensitizer to functionalize ZnO nanowire arrays and enhanced photoelectrochemical water splitting activity was observed. Hus et al. [37] has observed an enhanced photoelectrochemical H₂ production activity on CdSe nanocrystals by loading GQDs, where a type-II vectorial charge transfer mechanism was proposed to responsible for enhanced performances of nanoheterostructures. Moreover, GQDs can be used as an electron transfer mediator in polymer and dye-sensitized photovoltaic devices [38-44]. In above studies for GQDs modified semiconductor materials, it is generally believed that when GQDs decorated on semiconductor surfaces, it can not only act as an electron acceptor but also as a photosensitizer, resulting in an enhanced charge separation efficiency along with an enhanced light utilization efficiency, thus leading to enhanced photocatalytic activity on semiconductor/GQDs photocatalysts [32-37]. However, tedious reactions and post-treatment steps are required for the preparation of those composites. Typically, the GQDs were first prepared and purified and then combined with semiconductors to form semiconductor/GQDs composite photocatalyst [35], where an additional hydrothermal treatment step is typically needed to achieve strong surface integrity between the two components [34-38], which cannot be accessible in one-step synthesis process. Therefore, development of more facile and rapid, as well as low-cost methods for synthesis of semiconductor/GQDs photocatalysts with strong interaction remains highly desirable in terms of their large-scale applications in photo(electro)catalysis.

In the present work, we demonstrate a facile one-step hydrothermal route to synthesis TiO₂/GQDs composite photocatalyst, where the 1,3,6-trinitropyrene (TNP) was chosen as the sole precursor of GQDs and transformed to GQDs on the surface of TiO₂ nanoparticles *via* intermolecular fusion of TNP catalyzed by alkaline species under mild hydrothermal conditions. The in-situ formation of GQDs on the surface of TiO₂ nanoparticles would ensure a strong chemical interaction between the TiO₂ nanoparticles and GQDs. Moreover, the GQDs content in TiO₂/GQDs can be easily tuned by simply varying the addition amount of TNP precursor during the preparation processes. By optimizing the amount of TNP, the

photocatalytic H₂ evolution performance and photocurrent response of the TiO₂/GQDs composite photocatalysts could be enhanced by a factor of 7 and 3 compared with that of pure TiO₂ nanoparticles under UV light irradiation. In addition, the composite photocatalyst exhibits excellent long-term photocatalytic stability for H₂ evolution. Based on the results of UV-vis, photoelectrochemical, and steady-state and time-resolved photoluminescence measurements, a possible mechanism was proposed and the enhanced performances could be attributable to the enhanced charge separation efficiency and utilization efficiency of incident light.

2 Experimental sections

2.1 Chemicals

All reagents were of analytical grade and used without further purification. Pyrene was obtained from Sigma-Aldrich. TiO₂ nanoparticles (P25, 20% rutile and 80% anatase) were purchased from Degussa. Sodium hydroxide (NaOH) were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized (DI) water was produced using an YL-100B-D water-purification system (resistivity>15 MΩ).

2.2 Preparation of TiO₂/GQDs photocatalyst

The 1,3,6-trinitropyrene (TNP) was prepared according to the method reported in the literature [35, 45]. In a typical synthesis of the TiO₂/GQDs photocatalyst, 15 mg of TNP was dispersed in 0.2 M NaOH aqueous solution (80 mL, 0.2 M) by ultrasonication (150 W, 50 kHz) for 4 h. Afterwards, 0.5 g of TiO₂ nanoparticles were added into above suspension and the resulting mixture was sonicated for additional 2 h before transferring into a Teflon-lined autoclave (100 mL). Next, the hydrothermal reaction was performed in an electric oven at 200 °C for 10 h. After cooling to room temperature, the product was collected by filtration through a 0.22 μm microporous membrane, washed with water and ethanol for several times, and dried in air for overnight. The resulted product was denoted as TiO₂/GQDs-15. Following similar preparation procedures for TiO₂/GQDs-15, the content of GQDs in TiO₂/GQDs photocatalysts was tuned by changing the addition amount of TNP from 5 to 30 mg, and the obtained samples were labeled as TiO₂/GQDs-5, TiO₂/GQDs-10, TiO₂/GQDs-20, and

TiO₂/GQDs-30, respectively. In addition, the exact same synthesis procedure was employed to produce GQDs in the absence of TiO₂.

2.3 Characterization of photocatalysts

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken with a Tecnai-G2-F30 field emission transmission electron microscope. X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku B/Max-RB diffractometer with a nickel filtrated Cu K α radiation operated at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed on a K-Alpha surface analysis (Thermo Scientific) using X-ray monochromatization. Fourier transform infrared spectroscopy (FT-IR) spectra were performed on Thermo Nicolet Avatar 380 FT-IR spectrometer. Raman spectra were recorded with a DXR2 Raman microscope (Thermo Scientific) with a 633 nm He–Ne laser as excitation source at room temperature. UV–vis diffuse reflectance spectra were recorded on a Shimadzu UV-3600 UV–vis-near-IR spectrophotometer equipped with an integrating sphere and BaSO₄ powders were used as a reflectance standard. UV–vis absorption spectra were obtained with a TU-1810 UV–vis spectrophotometer (Beijing Persee). Photoluminescence spectra were determined by a Horiba Scientific FluoroMax-4 spectrofluorometer spectrometer. The fluorescence decay times were measured using the Horiba Jobin Yvon Data Station HUB operating in time-correlated single photon counting mode (TCSPC) with the time resolution of 200 ps. Nano LED diode emitting pulses at 280 nm with 1 MHz repetition rate was used as an excitation source. Light-scattering Ludox solution was used to obtain the instrument response function (prompt). The time ranges are 0.055 ns/channel in 4096 effective channels. Horiba Jobin Yvon DAS6 fluorescence decay analysis software was used to fit the model functions to the experimental data.

2.4 Photocatalytic hydrogen evolution experiments

Photocatalytic hydrogen evolution experiments were performed in a sealed quartz flask (142 mL) with a flat window for light irradiation and a silicone rubber septum for sampling.

The light source was a 250 W high pressure mercury lamp. 20 mg of the photocatalyst was dispersed in 80 mL of 10% (v/v) ethanol aqueous solution. Prior to light irradiation, the reaction mixture was sonicated for 5 min and degassed by bubbling N₂ gas for 40 min. The amount of H₂ evolved was manually analyzed using a precalibrated gas chromatography (Tech comp; GC-7900) equipped with a molecular sieve 5 A column and a TCD detector, and N₂ was used as the carrier gas.

2.5 Photoelectrochemical measurements

Photoelectrochemical measurements were performed with an electrochemical analyzer (CHI660E) in a conventional three-electrode configuration. A Pt mesh (1 cm²) and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. The supporting electrolyte was 0.5 M Na₂SO₄ solution. A 300 W Xe lamp was used as a light source. The photocatalyst working electrodes were prepared by electrophoretic deposition on conducting glass supports (FTO) as following: 40 mg of photocatalyst powder and 10 mg of iodine were dispersed in 15 mL of acetone under stirring and sonicated for 5 min. After this process, two FTO electrodes (1.5 cm×2.5 cm) were inserted parallel with each other in the above homogeneous suspensions with *ca.* 8 mm of distance, and then 10 V of bias was applied between them for 3 min using the same potentiostat used for photoelectrochemical measurements. After that, the photocatalyst electrodes were dried at 100 °C for 12 h and store in dark prior to measurements. The unbiased anodic photocurrent was investigated with an amperometric current-time technique.

3. Results and Discussion

3.1 Preparation and characterizations of TiO₂/GQDs photocatalysts

It has been reported that TNP molecules can readily fuse to form single-crystalline GQDs with uniform size distribution under mild hydrothermal conditions in the presence of alkaline species such as OH⁻, NH₃, or N₂H₄ as catalysts [35, 45]. Inspired by this work, we selected TNP as the sole precursor of GQDs to prepare TiO₂/GQDs photocatalysts by using a one-step hydrothermal reaction in NaOH (0.2 M) aqueous solutions, as schematically illustrated in Fig. 1a. Prior to the hydrothermal reaction, the TNP was dispersed into NaOH (0.2 M) aqueous

195 solution containing TiO_2 nanoparticles with the aid of ultrasonication. During this process,
196 due to the presence of positively charged NO_2 groups on TNP molecules [45], the TNP can be
197 readily adsorbed onto the surfaces of negatively charged TiO_2 nanoparticles (isoelectric point:
198 5.8~6.8 depend on particle size [46-48]) at basic conditions via electrostatic interactions, and
199 consequently fused to form GQDs by subsequent hydrothermal treatment, resulting in a
200 strongly coupled TiO_2 /GQDs photocatalyst. The in-situ formation of GQDs on the surface of
201 TiO_2 nanoparticles would ensure a strong chemical interaction between GQDs and TiO_2 and
202 endow an improved charge transfer dynamics for photocatalytic H_2 evolution reactions.
203 Moreover, the GQDs content in the resulted TiO_2 /GQDs photocatalysts can be easily tuned by
204 varying the addition amount of TNP precursor, which would simplify the large-scale
205 preparation of GQDs functionalized semiconductor composite photocatalysts for desirable
206 purposes.

207 Figure 1b and c show the typical TEM and HRTEM images of as-prepared GQDs,
208 respectively. The obtained GQDs have a relatively uniform particle size and consist of almost
209 defect-free graphene domains with a clear interplanar spacing of 0.22 nm corresponding to
210 graphene (100) planes (see the inset image in Figure 1c) [35, 45]. The average lateral size was
211 statistically computed to be 2.6 ± 0.6 nm (Figure 1d). Figure 1e shows the low-magnification
212 TEM image of TiO_2 /GQDs-15 sample. It is found that the GQDs are uniformly distributed
213 throughout the surface of TiO_2 nanoparticles. HRTEM (Figure 1f) shows that the TiO_2
214 nanoparticles are firmly decorated with GQDs to form strongly coupled TiO_2 /GQDs-15
215 composite. HRTEM image (Figure 1g) also reveals the existence of the GQDs in the
216 TiO_2 /GQDs-15 composite, where a 0.21 nm lattice spacing for the graphene (100) planes
217 could also be identified [35].

218 Figure 2a shows the FT-IR spectra of the samples. In contrast to TiO_2 , several additional
219 vibration peaks arising from the GQDs appear in the spectrum for TiO_2 /GQDs-15 composite,
220 indicating the presence of GQDs. Besides the C=C vibration at 1530 and 1646 cm^{-1} , the
221 vibrations for C-OH/OH at 1358 and 3402 cm^{-1} could also be observed. In addition, a very
222 weak vibration band for C-N occurs at 1450 cm^{-1} . The existence of GQDs in the

TiO₂/GQDs-15 composite was further verified by Raman spectroscopy, as shown in Figure 2b. It can be seen that in the Raman spectrum of pure TiO₂ (Figure 2b), four strong peaks at 637, 514, 391, and 138 cm⁻¹ correspond to the E_{g(3)}, A_{1g}+B_{1g(2)}, B_{1g(1)}, and E_{g(1)} vibration modes of anatase TiO₂, respectively [35]. In the case of the pure GQDs, two obvious peaks at 1581 and 1355 cm⁻¹ are observable, which correspond to the G and D bands of GQDs, respectively [35]. In the Raman spectrum of TiO₂/GQDs-15 composite, except for the characteristic peaks arising from TiO₂, two characteristic peaks of the GQDs can also be identified at slightly higher Raman shifts, further confirming the presence of GQDs and indicating that there is a strong interaction between the two components. The chemical compositions of TiO₂/GQDs-15 and the interaction between the two components are studied by XPS analysis. As shown in Figure 2c in Supporting Information, the survey XPS spectrum of TiO₂/GQDs-15 sample shows strong signals of Ti 2p, C 1s, and O 1s, as well as negligible signal of N 1s. The Ti 2p and O 1s signals originate from TiO₂ and the presence of C 1s and N 1s signals confirm the existence of GQDs in the composite. The high-resolution C 1s spectrum (Figure 2d) reveals the strong signal of C=C at 284.8 eV, C-O/C-N peak at 286.9 eV, and the distinguishable C=O peak at 287.9 eV. The peaks at 529.5 and 531.0 eV in the O 1s XPS spectrum (Figure 2e) are assigned to the Ti-O and O-C/O=C bonding, respectively. Moreover, the Ti 2p_{3/2} and Ti 2p_{1/2} signals for TiO₂/GQDs-15 photocatalyst occur at 458.2 and 464.0 eV (Figure 2f), which are slightly higher than that for pure TiO₂, for which the Ti 2p_{3/2} and Ti 2p_{1/2} appear at 457.8 and 463.7 eV (Figure S1a, Supporting Information). At the same time, the O1s spectrum of TiO₂/GQDs-15 shown in [Figure S1b](#) exhibits higher binding energy as compared to TiO₂. These results indicate that there is a strong interaction between TiO₂ and GQDs in the composite, driven from the probable electron transfer from TiO₂ by crossing intimately contacted interface to GQDs [49, 50]. It has been extensively demonstrated that GQDs not only has large number of zigzag edges and thereby having the band-gap [11, 37], but also contains graphene microdomains that can serve as an electron acceptor [50-52]. Thus, in the TiO₂/GQDs composite, the electrons in the TiO₂ could transfer to GQDs upon UV light irradiation and participates in following photocatalytic reactions (*vide*

infra) [50].

The XRD patterns of samples in Figure 3a reveal that all the TiO₂/GQDs composites exhibit the similar XRD patterns with TiO₂, no additional diffraction peaks assigned to GQDs could be detectable, which might be due to the small amount and/or high dispersion of GQDs in the composites [35, 53]. The light absorption capability of TiO₂/GQDs composites was then studied by the UV-vis diffuse reflectance spectra (UV-vis-DRS). As shown in Figure 3b, pure TiO₂ exhibits no absorption in the visible light region, and only an abrupt absorption onset at 400 nm is observable. Compared with white pure TiO₂, the color of the TiO₂/GQDs samples changes from light yellow to brown (inset in Figure 3b) with the increasing GQDs contents. Meanwhile, the TiO₂/GQDs samples exhibits an enhanced absorption in the visible light region ranging from 400 to 800 nm, and the absorption intensity increases gradually with the increase of GQDs contents. More interestingly, it can be clearly seen that there is an obvious absorption peak at ~500 nm in the absorption spectra of TiO₂/GQDs composites. The enhancement in background absorption and appearance of the characteristic peak at ~500 nm could be attributed to the presence of GQDs, which exhibits a broad absorption in whole UV-vis region with three characteristic absorption peaks at 232, 371, and 503 nm (Figure S2). Moreover, it is also worthy to be noted that the absorption peak at ~500 nm for TiO₂/GQDs composites is more pronounced compared with the GQDs, which could be related to the strong chemical interaction between the TiO₂ and GQDs, as evidenced by the above XPS results. These results indicate that the strong coupling of GQDs onto the surface of TiO₂ nanoparticles will lead to enhanced light harvesting ability for resulted TiO₂/GQDs composites, which may render the formation of more charge carriers upon light irradiation, thus improving their photocatalytic activities of TiO₂/GQDs composites [43, 50].

3.2 Photocatalytic hydrogen evolution activity of TiO₂/GQDs photocatalysts

The photocatalytic H₂ evolution activities on TiO₂/GQDs photocatalysts from ethanol aqueous solution (10%, v/v) were evaluated under UV light irradiation at room temperature and ambient pressure. Figure 4a and b shows the time courses of H₂ evolution and the corresponding H₂ evolution rates on various photocatalysts, respectively. For comparison

purpose, the results obtained on pure TiO_2 are also included. Blank experiments under the exact same conditions indicate that no H_2 formation could be observed in the absence of any catalysts or light irradiation. The controlled experiment over the GQDs alone also shows no appreciable H_2 evolution [30, 35]. Pure TiO_2 alone can steadily produce H_2 but with an extremely low rate ($0.3 \mu\text{mol h}^{-1}$). After coupling with GQDs at a proper content, TiO_2/GQDs photocatalysts can effectively enhance the photocatalytic activity of H_2 evolution. The rate of H_2 production increases with the GQDs content and achieves a maximum on $\text{TiO}_2/\text{GQD-15}$ sample ($2.2 \mu\text{mol h}^{-1}$), which is higher than that of pure TiO_2 by up to 7 times. A further increase in GQDs content rather deteriorates the H_2 evolution activity. This can be explained by the fact that although these composites show stronger visible light absorption owing to higher GQDs doping level (Figure 3b), the formation of GQDs aggregates is inevitable [35], which may not only cause an indirect contact with TiO_2 nanoparticles, but also shield the TiO_2 nanoparticles from absorbing the incident light, thus leading to a decreased photocatalytic activity, similar to the observations over other carbon-based nanomaterials such as carbon black, graphene, carbon nanotubes, and fullerene coupled TiO_2 photocatalysts [12-20].

Figure 4a also reveals that the rate of H_2 evolution over each TiO_2/GQDs photocatalyst increases linearly with the irradiation time, indicating that the photocatalytic reaction proceeds steadily over TiO_2/GQDs photocatalysts. We also carried out a long-term photocatalytic stability experiment of the $\text{TiO}_2/\text{GQDs-15}$ photocatalyst. The photocatalytic reaction was allowed to precede for 32 h with intermittent evacuation every 8 h, as show in Figure 4c. The photocatalytic H_2 generation activity of $\text{TiO}_2/\text{GQDs-15}$ remains fairly stable and no obvious deactivation occurs in the repeated runs, revealing the high photocatalytic stability of our photocatalyst.

3.3 Photocatalytic mechanism for enhanced H_2 generation over TiO_2/GQDs photocatalysts

As shown in above discussions, the incorporation of GQDs is effective to enhance the photocatalytic activity of TiO_2 for H_2 evolution. On the one hand, it has been previously reported that the photosensitization of semiconductor photocatalysts with GQDs are believed

to be mainly responsible for the observed high photocatalytic activity on semiconductor/GQDs photocatalysts [30-37]. Note that our TiO₂/GQDs photocatalysts can absorb most of the visible light in the solar spectrum, which will maximum the light utilization efficiency. Given that the reported conduction band (CB) level of GQDs (-3.55~-3.09 eV vs. vacuum energy level) [35, 39-41] is less negative than that of TiO₂ (-4.2 eV vs. vacuum energy level) [35], thus the electrons generated in CB of GQDs upon the light irradiation will easily transfer to the CB of TiO₂ due to the large energy offset (0.65~1.11 eV) formed at contact interface, which would render an efficient electron-hole separation, and hence enhancing the photocatalytic activity of TiO₂/GQDs photocatalysts. On the other hand, it has been reported that the GQDs can also act as an electron collector to enhance the separation of the photogenerated charge carriers [50-52], which is similar to graphene-based materials [54-56]. In order to clarify this role of GQDs, photoelectrochemical and steady-state and time-resolved photoluminescence (PL) measurements were carried out. Figure 5a shows the transient photocurrent response for photocatalysts under UV-vis light irradiation at zero bias. It is clearly to see that the pure TiO₂ electrode shows a much lower photocurrent, most likely due to the fast recombination of electrons and holes. After coupling with GQDs, the photocurrent response of TiO₂/GQDs photocatalyst electrodes is greatly enhanced by 3 times as compared to pure TiO₂ at an optimal GQDs content. The observed enhancement in the photocurrent response indicates that the improved charge separation and transportation efficiencies could be obtained for TiO₂/GQDs composites due to the presence of GQDs. However, at the higher GQDs loadings, light absorption by GQDs adversely affects the effective excitation of TiO₂ nanoparticles, which leads to decreased photocurrent response.

In Figure 5b, the steady-state PL spectrum of pure TiO₂ exhibits an emission band in the wavelength range of 350 to 550 nm, which was assigned to the excitonic band edge emission of TiO₂. Compared with pure TiO₂, all the TiO₂/GQDs samples display a substantially decreased PL emission, and the quenching efficiency of PL emission increases with the increase of GQDs content. This observation reveals that charge recombination of TiO₂ was greatly retarded by combination with GQDs. To further understand the charge separation

dynamics, the time-resolved PL decay spectra of the pure TiO_2 and TiO_2/GQDs photocatalysts were recorded at room temperature, as shown in Figure 5c. It can be seen that the emission decays of the TiO_2/GQDs are much faster than that of pure TiO_2 , suggesting that the incorporation of GQDs provides a rapid electron transfer pathway for enhanced charge separation [37]. These results clearly indicate that the incorporation of GQDs improves, to some extent, the charge separation efficiency of TiO_2 , and consequently improving the photocatalytic activity of TiO_2/GQDs composite materials. However, the quenching efficiency and emission decay of PL of TiO_2 by GQDs for TiO_2/GQDs samples cannot be completely correlated to their photocatalytic performances, suggesting that the photocatalytic activity of TiO_2/GQDs was not simply related to the charge separation factor [57], and equally important, the transfer and the redox ability of charge carrier also play important roles for observed performances. Moreover, it has been demonstrated that GQDs itself can be directly used as a photocatalyst for H_2 evolution reaction without the addition of any cocatalysts such as Pt [30], suggesting that GQDs also can serve as a reaction center for H_2 evolution reaction. Overall, it can be concluded that the GQDs play synergistic roles in enhancing the photocatalytic activity of TiO_2/GQDs photocatalyst, that is, GQDs act as a photosensitizer for maximizing light absorption (Figure 6a), an electron acceptor for enhancing charge separation efficiency, and a reaction center for facilitating H_2 evolution reaction (Figure 6b).

4 Conclusions

In summary, we have developed a facile one-step hydrothermal method for synthesis of strongly coupled TiO_2/GQDs photocatalysts by in-situ intramolecular fusion of TNP on the surface of TiO_2 nanoparticles. The in-situ formed GQDs firmly decorated on TiO_2 nanoparticles due to the chemical interactions between the two components. The incorporation of GQDs has no effect on crystallographic structure of TiO_2 (P25) as confirmed by XRD analysis. UV-vis-DRS characterizations revealed that after coupling GQDs onto the surface of TiO_2 nanoparticles, the resulted TiO_2/GQDs composites exhibited enhanced visible light absorption in the range of 400 to 800 nm. The photoelectrochemical and PL measurements indicated that the GQDs can also act as an effective electron acceptor to

facilitate the charge separation of TiO₂. Significantly, compared with pure TiO₂ nanoparticles, the resulted TiO₂/GQDs photocatalysts display enhanced photocatalytic activity for H₂ evolution by 7 times and photocurrent response by 3 times. This enhancement could be attributable to the synergistic roles of GQDs that can act as a photosensitizer for improving the light utilization efficiency, but also act as an electron acceptor for reducing the recombination rate of charge carriers. Thus, it is a scalable and cost-effective route for the synthesis of GQDs modified semiconductors as efficient photocatalysts for the photocatalysis and photoelectrochemical conversion.

Acknowledgements

This work is supported by the National Science Foundation of China (21463001, 21263001), the Natural Science Foundation of Ningxia Hui Autonomous Region (NZ15102), the Scientific Research Projects of the State Ethnic Affairs Commission (No. 2066204), and the cultivation project of National Natural Science Foundation of China (2014QZP04).

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475 **Figure captions:**

476 **Figure 1.** (a) Schematic diagram for the preparation of TiO₂/GQDs photocatalyst by a
477 one-step hydrothermal reaction. (b-d) TEM and high-magnification TEM (HRTEM) images
478 of GQDs. The inset in panel c shows the HRTEM images of individual GQD. (e-g) TEM and
479 HRTEM images of TiO₂/GQDs-15 photocatalyst.

480 **Figure 2.** (a) FT-IR spectra of pure TiO₂ and TiO₂/GQDs-15 photocatalysts. (b) Raman
481 spectra of GQDs, pure TiO₂, and TiO₂/GQDs-15 composite. (c-f) XPS survey spectrum (c)
482 and High-resolution XPS spectra of C 1s (d), O 1s (e), and Ti 2p (f) core level for
483 TiO₂/GQDs-15 photocatalyst.

484 **Figure 3.** (a) XRD patterns of pure TiO₂ and TiO₂/GQDs photocatalysts. (b) UV-vis diffuse
485 reflection spectra of pure TiO₂ and TiO₂/GQDs photocatalysts. Inset is the optical photos of
486 photocatalysts on FTO substrate.

487 **Figure 4.** (a) Time courses for H₂ evolution over pure TiO₂ and TiO₂/GQDs photocatalysts. (b)
488 The rate of H₂ evolution over pure TiO₂ and TiO₂/GQDs photocatalysts. (c) Long-term
489 photocatalytic test of TiO₂/GQDs-15 photocatalyst during the repeated runs. Reaction
490 conditions: photocatalyst, 20 mg; ethanol aqueous solution, 100 mL, 10% (v/v); light source,
491 250 W high-pressure mercury lamp.

492 **Figure 5.** (a) Unbiased transient photocurrent response of pure TiO₂ and TiO₂/GQDs
493 photocatalysts electrodes in 0.5 M Na₂SO₄ at pH 7. (b) Steady-state PL spectra of pure TiO₂
494 and TiO₂/GQDs photocatalysts. Excitation wavelength: 280 nm. (c) Time-resolved PL
495 emission decay curves of pure TiO₂ and TiO₂/GQDs photocatalysts. Excitation wavelength:
496 280 nm; detection wavelength: 410 nm.

497 **Figure 6.** Proposed photocatalytic mechanism for enhanced activity of TiO₂/GQDs
498 photocatalyst. (a) photosensitization effect of GQDs and (b) as an electron acceptor and
499 reaction center.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

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574 **Graphical abstract**

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