Title
Direct Electron Transfer from Upconversion Graphene Quantum Dots to TiO$_2$
Enabling Infrared Light-Driven Overall Water Splitting

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Abstract
Utilization of infrared light in photocatalytic water splitting is highly important yet challenging given its large proportion in sunlight. Although upconversion material may photogenerate electrons with sufficient energy, the electron transfer between upconversion material and semiconductor is inefficient limiting overall photocatalytic performance. In this work, a TiO$_2$/graphene quantum dots (GQDs) hybrid system has been designed with intimate interface, which enables highly efficient transfer of photogenerated electrons from GQDs to TiO$_2$. The designed hybrid material with high photogenerated electron density displays photocatalytic activity under infrared light (20 mW cm$^{-2}$) for overall water splitting (H$_2$: 60.4 μmol g$_{\text{cat.}}^{-1}$ h$^{-1}$, O$_2$: 30.0 μmol g$_{\text{cat.}}^{-1}$ h$^{-1}$). With infrared light well harnessed, the system offers a solar-to-hydrogen (STH) efficiency of 0.80% in full solar spectrum. This work provides new insight into harnessing charge transfer between upconversion materials and semiconductor photocatalysts, and opens a new avenue for designing photocatalysts toward working under infrared light.

MAIN TEXT
1. Introduction
The sun provides 173,000 TW energy every year, 9,000 times more than the annual world energy consumption. While the energy proportion of infrared (IR) light exceeds 50% in sunlight, the IR light has not been efficiently utilized for solar-to-chemical energy conversion by now due to the lack of related ideal materials to photogenerate electrons with sufficient energy and density. As a typical example, solar-driven water splitting, which can produce hydrogen with the energy density of 141.9 MJ/kg, possesses a 0.5 eV overpotential and requires the energy input of at least 1.8 eV corresponding to the photons at <688 nm. To implement IR or near-IR (NIR) (780~2526 nm) light in water splitting, two main strategies have been developed including localized surface plasmon resonance (LSPR)-induced hot electron injection and photon upconversion-induced electron injection. For instance, a CdS/Cu$_7$S$_4$ photocatalyst was employed for water splitting, in which LSPR-induced hot electrons from Cu$_7$S$_4$ were injected into CdS under NIR illumination (> 800 nm)
Similarly, other photocatalysts were demonstrated based on Au nanostructures with LSPR band in IR spectral region [4-6]. In parallel, photon upconversion is another strategy for utilizing NIR or IR light in solar energy storage and conversion. For instance, core-shell Pt@MOF/Au composites can convert NIR light to UV and visible light, driving photocatalytic hydrogen production under NIR irradiation [7]. Such an (N)IR-driven photocatalysis was also achieved by rare-earth upconversion materials [8-12]. Nevertheless, the energy conversion performance of the existing systems using NIR or IR light is unsatisfactory through the two strategies. The performance of two strategies relies on plasmonic hot electron generation or photon upconversion, and more importantly, their charge or energy transfer to semiconductor photocatalyst. As a matter of fact, the efficiency of these fundamental processes is relatively low, constituting the obstacle for overall performance.

Recently, graphene quantum dots (GQDs), as a class of zero-dimensional nanomaterials based on graphene, have attracted extensive attention owing to their advantages including low toxicity, high electron mobility (10,000 cm$^2$ s$^{-1}$), high carrier concentration (1,013 cm$^{-2}$), low cytotoxicity and facile surface grafting [15-18]. In addition, the quantum confinement and edge effect of GQDs endow them with more active sites [19, 20], wide optical absorption range [21], tunable band structure and (N)IR upconversion photoluminescence (PL) behavior [22]. In particular, a prevenient work has demonstrated that the energy difference between excitation light and emission light in the upconversion process is close to 1.1 eV because the p electrons are excited to a high-energy state (e.g., lowest unoccupied molecular orbital, LUMO) and then transition back to the s orbital [23]. We envision that such a upconversion material should be an ideal candidate for forming intimate interface with semiconductor given its facile surface chemistry, which would allow the direct transfer of multiphoton-generated electrons from upconversion GQDs to semiconductor photocatalyst (instead of emitting higher-energy photons) toward (N)IR-driven chemical reactions. Certainly, this opportunity based on upconversion GQDs remains largely unexplored in photocatalysis.

In this work, we demonstrate the concept that the electrons NIR-generated in GQDs through a multiphoton process can be directly transferred to semiconductor toward photocatalytic overall water splitting. As a model system, the surface of 2~3 layered GQDs is modified by reduction treatment and forms intimate bonding with TiO$_2$ nanotube photocatalyst, enabling efficient interfacial electron transfer. As a result, the GQDs can offer energy-sufficient electrons under IR irradiation for the photocatalyst to drive water splitting. While the composite displays a strong light absorption form UV region to IR region, the IR activity enhances the photocatalytic performance of overall water splitting to the solar-to-hydrogen (STH) efficiency of 0.80%.

2. Results

The GQDs are prepared through evolution from glucose, and are further treated to remove surface oxygen-containing groups through reduction with NaBH$_4$, producing r-GQDs. To demonstrate the importance of interface to charge transfer, the GQDs and r-GQDs with different surface conditions are both used for integration with TiO$_2$ nanotubes through the same hydrothermal process. Fig. 1a shows the XRD patterns of pure TiO$_2$, TiO$_2$/GQDs and TiO$_2$/r-GQDs composites. After integrated with
TiO$_2$, the intensity of the peaks corresponding to TiO$_2$ is evidently reduced. This suggests that the crystallinity of TiO$_2$ is lowered by the addition of GQDs (r-GQDs) or/and the TiO$_2$ is largely covered by the GQDs (r-GQDs). In addition, the average grain size of TiO$_2$ is calculated to be about 12 nm using Scherrer formula according to its XRD pattern. To gain surface information, Fourier transform infrared spectroscopy (FT-IR) is employed to characterize the samples. As shown in Fig. 1b, the oxygen groups such as OH (~3400 cm$^{-1}$) and C=O (~1400 cm$^{-1}$) in GQDs are obviously reduced after NaBH$_4$ reduction. In the meantime, it creates abundant dangling bonds of carbon, which then are bonded with oxygen atoms in TiO$_2$ [25, 26]. As a result, the Ti-O-C chemical bonds at 950 cm$^{-1}$ are observed in TiO$_2$/r-GQDs [27-29].

The formation of such Ti-O-C chemical bonds is also confirmed by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 1c, the XPS survey spectrum of TiO$_2$/r-GQDs composite demonstrates the existence of O, Ti and C elements. The C1s peaks at 284.6 eV, 285.6 eV and 288.7 eV are attributed to C-C, C=C and C-O-Ti bonds, respectively (Fig. 1d) [30]. The Ti-O-C bond is also detected by the peaks at 531.6 eV of O1s (Fig. 1e) and 457.8 eV of Ti2p (Fig. 1f) XPS spectra [23]. In comparison, the peaks for Ti-O-C bond have not been found for TiO$_2$ and TiO$_2$/GQDs (fig. S1). As such, the peak intensity change of TiO$_2$ in XRD should also be partially associated with the formation of Ti-O-C chemical bonding between TiO$_2$ and r-GQDs. This chemical bonding at the interface of TiO$_2$/r-GQDs surely will facilitate the interfacial electron transfer by lowering the potential barrier between TiO$_2$ and r-GQDs [31,32]. It is known that most composites are formed without intimate connection between two different components to leave gaps or defects at the interface, which forms a depletion layer to hinder the charge transfer to a large extent. A chemically bonded interface in the composite undoubtedly provides a better charge transfer path and enables efficient charge transfer from interface to surface.

![Figure 1. a) XRD patterns and b) FT-IR spectra of the obtained GQDs, TiO$_2$, TiO$_2$/GQDs and TiO$_2$/r-GQDs. XPS spectra of the TiO$_2$ and TiO$_2$/r-GQDs: c) survey, d) C1s, e) O1s and f) Ti 2p.](image-url)
To reveal the morphologies and microstructures, the samples are examined by transmission electron microscopy (TEM). Fig. 2a shows that the as-prepared GQDs have the size of about 2~3 nm. As indicated by Raman spectroscopy (Fig. 2b and fig. S2), both GQDs and r-GQDs are 2~3 layered thick. Meanwhile, the TiO$_2$ nanotubes that are used for integration with GQDs and r-GQDs have a width of ~7.4 nm and a length of several micrometers (Fig. 2c). High-resolution TEM (HRTEM, Fig. 2d) reveals that the TiO$_2$ nanotubes possess relatively smooth surface. Raman spectroscopy also confirms that the TiO$_2$ nanotubes are of anatase phase (fig. S3). After uniformly integrated with GQDs or r-GQDs, the one-dimensional morphology is well maintained as indicated by TEM and elemental mapping (Fig. 2e-2i). Despite the remained nanotubes, the samples display interesting characteristics in Brunauer Emmett Teller (BET) surface areas (the insets of Fig. 2c, 2e and 2g). The TiO$_2$ nanotubes and TiO$_2$/GQDs exhibit similar BET surface areas (93.8 m$^2$/g and 97.2 m$^2$/g) and pore size distributions (fig. S4). However, the BET area of TiO$_2$/r-GQDs reaches up to 275.3 m$^2$/g (Fig. 2g). Most likely, this feature is associated with the Ti-O-C chemical bonding between TiO$_2$ and r-GQDs, which induces the electronegativity change in both TiO$_2$ and r-GQDs promoting N$_2$ polarization and adsorption. The integrated composite structure of TiO$_2$/r-GQDs has also been resolved by HRTEM (Fig. 2j-2l), showing that hexagonal r-GQDs are loaded on the surface of TiO$_2$ nanotubes. Aberration-corrected TEM (AC-TEM, Fig. 2m and 2n) further confirms the existence of r-GQDs and TiO$_2$ at atomic resolution.

Figure 2. Morphology and microstructure characterization of the samples. a) TEM image and b) Raman spectrum of the obtained GQDs. The inset of a shows the size distribution. c) TEM image and d) HRTEM images of the obtained TiO$_2$ nanotubes. The inset of c shows the BET result. e) TEM image and f) elemental mapping profiles of the obtained TiO$_2$/GQDs (Scale bars are 10 nm). The inset of e shows the BET result. g) TEM image, h) elemental mapping profile, i) EDX spectrum, j-l) HRTEM images and m-n) AC-TEM images of the obtained TiO$_2$/r-GQDs. o) Valence-band spectra measured by XPS and p) band structures of the three samples.
The addition of GQDs and r-GQDs broadens the light absorption of TiO$_2$ nanotubes to visible region as shown in fig. S5. To determine band structures, valence-band spectra are measured by XPS (Fig. 2o). As depicted in Fig. 2p, GQDs lower the conduction band (CB) edge from -0.18 eV to +0.21 eV, which is unfavorable for hydrogen evolution through water splitting. However, r-GQDs can elevate the CB and valence band (VB) edges to -0.26 eV and +2.38 eV, respectively, which enable overall water splitting for hydrogen and oxygen production simultaneously. This highlights that the surface modification on GQDs has a significant impact on band structures, which may in turn alter charge dynamics.

To look into charge dynamics, we closely examine the PL behavior of samples. It is known that the capture centers for excitons are formed by surface oxidation, leading to surface-state-related fluorescence [33]. As shown in Fig. 3a, after reduction of GQDs, the PL emission of graphene quantum dots exhibits an obvious blue-shift from 433 to 418. This observation is similar to the finding in literature that the band gap is widened as a decreasing number of oxygen atoms are present in the structure, resulting in a PL blue-shift [34]. More importantly, multiphoton upconversion-induced emissions at 546 nm and 663 nm are detected for the GQDs-based samples under a 980 nm IR light excitation as shown in Fig. 3b. This upconverted PL property of GQDs should be attributed to the multiphoton active process similar to the previously reported carbon dots [35], indicating that GQDs should be a powerful energy-transfer component in photocatalyst design. The unchanged emission positions between GQDs and r-GQDs demonstrate that the emission should originate from carbon core rather than surface state. After GQDs are anchored on TiO$_2$, the sample displays the strengthened upconverted PL emission, suggesting that more active electrons are formed on surface. The time-resolved PL spectra (Fig. 3c) show that the average PL lifetimes of r-GQDs, TiO$_2$/GQDs and TiO$_2$/r-GQDs are 0.3 ns, 1.17 ns and 9.06 ns, respectively, proving that the photogenerated electrons of r-GQDs can be timely extracted by coupling with TiO$_2$.

This argument is also supported by photocurrent measurements as displayed in Fig. 3d. The photocurrents by TiO$_2$/r-GQDs are dramatically higher than those by TiO$_2$/GQDs and TiO$_2$, demonstrating that charge separation and transfer are better harnessed in TiO$_2$/r-GQDs. As a supplementary experiment, electrochemical impedance spectroscopy (EIS) measurements (Fig. 3e and 3f) are carried out at a 4 kHz frequency in dark and under 420 nm illumination. It shows that the arc radius under light irradiation is smaller than that in dark. As compared with TiO$_2$ and TiO$_2$/GQDs, the Nyquist plot of TiO$_2$/r-GQDs displays a substantially smaller radius under irradiation, which further proves the improved separation efficiency of electron-hole pairs in TiO$_2$/r-GQDs [36]. The enhanced charge separation in TiO$_2$/r-GQDs is also demonstrated by surface photovoltage spectroscopy (SPS) (fig. S6). It is known that distinct SPS signal can reflect the enhanced separation rate of photoinduced charge pairs [37]. Among these features, the high conductivity and strong electron transfer ability of r-GQDs facilitate the access to electrons and the electron diffusion process, effectively improving the charge transfer in the photocatalyst. Taken together, the r-GQDs possess the upconversion properties for harvesting IR photons and the electronic properties for efficient charge transfer, which should be a good candidate to offer high photocatalytic activity.

We are now in a position to evaluate the photocatalytic overall water splitting performance of the samples. The measurements are first carried out under
ultraviolet light without the addition of precious metal cocatalyst and sacrificial agent. As shown in Fig. 3g, pure TiO$_2$ and TiO$_2$/GQDs do not have the ability for overall water splitting due to their mismatched energy level structure or unsuitable band gap (Fig. 2p). In contrast, TiO$_2$/r-GQDs shows excellent photocatalytic performance for overall water splitting under UV light with the H$_2$ production rate of 358.8 μmol g$_{cat}^{-1}$ h$^{-1}$ and the O$_2$ production rate of 175.9 μmol g$_{cat}^{-1}$ h$^{-1}$. More importantly, TiO$_2$/r-GQDs also exhibits photocatalytic activity for overall water splitting under IR light. As shown in Fig. 3h, the photocatalyst offers the values of H$_2$ (60.4 μmol g$_{cat}^{-1}$ h$^{-1}$) and O$_2$ (30.0 μmol g$_{cat}^{-1}$ h$^{-1}$) production under IR light (>800 nm, 20 mW cm$^{-2}$). As such, the H$_2$/O$_2$ production rates of 128.3/64.1 μmol g$_{cat}^{-1}$ h$^{-1}$ are achieved in full spectrum (100 mW cm$^{-2}$). To better assess the overall performance, the STH efficiency is determined to be 0.80%. In addition, the apparent quantum efficiency (AQE) of TiO$_2$/r-GQDs under different illustration wavelengths (365 nm: 61 mW cm$^{-2}$, 455 nm: 45 mW cm$^{-2}$, 850 nm: 15 mW cm$^{-2}$) is measured respectively, as shown in Fig. 3i. The sample displays a 0.26% AQE even under 850 nm infrared light, which further confirms its outstanding ability for overall water splitting. The TiO$_2$/r-GQDs photocatalyst also shows high stability in cycling tests as shown in fig. S7-S9.

Figure 3. Charge dynamics behavior and photocatalytic performance. PL spectra of the samples with a) 340 nm and b) 980 nm excitation. c) Fluorescence lifetime spectra, d) transient photocurrent spectra, e-f) electrochemical impedance spectra of the TiO$_2$, TiO$_2$/GQDs and TiO$_2$/r-GQDs. g-h) Photocatalytic water splitting performance (UV light: 100 mW cm$^{-2}$; Sunlight: 100 mW cm$^{-2}$; IR light: 20 mW cm$^{-2}$). i) AQE values of TiO$_2$/r-GQDs under different illumination wavelengths.

Upon recognizing the performance, a question naturally arises how the upconversion r-GQDs participate in water splitting after harvesting IR light. To
decode the mechanism, we employ in-situ XPS to characterize the sample with trace water. As shown in Fig. 4a, the peaks located at 458.0 and 460.6, 455.3 and 463.7 eV are attributed to the Ti$^{4+}$ and Ti$^{2+}$ oxidation states, respectively. The peaks belonging to Ti$^{2+}$ show an increasing trend with the extension of irradiation time. At the same time, the common Ti$^{3+}$ peaks, such as that around 457.0 eV for Ti 2p$_{1/2}$, are not distinct [38, 39]. In comparison, only Ti$^{3+}$ is observed for TiO$_2$-based photocatalysts under light irradiation [40, 41]. This indicates that the electrons generated from the upconversion of r-GQDs can be directly transferred to TiO$_2$. In addition, a shift of C 1s peaks toward lower binding energies is observed in Fig. 4b, which should be due to the lowered electron density in carbon atoms after the electron transfer process and further demonstrates the electron transfer from r-GQDs to TiO$_2$ under illumination. In the meantime, the O 1s peaks assigned to TiO$_2$ and Ti-O-C (Fig. 4c) are unchanged. The water splitting process is also characterized by in-situ FT-IR spectroscopy. As shown in Fig. 4d, once the light is turned on, the peaks corresponding to C-H (1458 cm$^{-1}$), C-O stretching in carboxyl (1364 cm$^{-1}$), H-C-H (1340 cm$^{-1}$) and C-O-O-H (1148 cm$^{-1}$ and 878 cm$^{-1}$) are gradually strengthened [42, 43]. The appearance of these transient oxygen-containing species confirms the fact that the oxygen evolution reaction (OER) takes place on CQDs. Simultaneously, the crucial C-O-O-H intermediate detected in water splitting points out a single-site process of OER [38], which is known as the rate-limiting step. In this single-site process, firstly a -OH is bonded with carbon atom of CQD and then loses its hydrogen atom to form a C-O species. Further another -OH is added on C-O for -COOH formation, which finally releases an O$_2$ molecule. In addition, the peaks attributed to Ti-H are also found in the measurement (Fig. 4e and fig. S10), suggesting that hydrogen is produced at the Ti sites in TiO$_2$ [44, 45]. The efficient transfer of upconversion-generated electrons from r-GQDs to the Ti sites in TiO$_2$ is responsible for the IR-driven overall water splitting as illustrated in Fig. 4f.

It should be noted that such efficient transfer of upconversion electrons can also trigger photocatalytic CO$_2$ reduction with IR light. As shown in fig. S11-15, the TiO$_2$/r-GQDs sample shows 19.49 μmol g$_{\text{cat.}}$ h$^{-1}$ CO and 3.13 μmol g$_{\text{cat.}}$ h$^{-1}$ CH$_4$ production rates under full-spectrum light (100 mW cm$^{-2}$) as well as 0.45 μmol g$_{\text{cat.}}$ h$^{-1}$ CO and 0.03 μmol g$_{\text{cat.}}$ h$^{-1}$ CH$_4$ production rates under weak IR light (>800 nm, 20 mW cm$^{-2}$).
Figure 4. Electron transfer from r-GQDs to TiO₂ investigated by a-c) in-situ XPS, d) in-situ FT-IR and e) in-situ Raman measurements. f) Illustration of the electron transfer process in TiO₂/r-GQDs.

3. Discussion
In summary, reduced graphene quantum dots are integrated with TiO₂ photocatalyst by forming intimate interface, allowing the direct transfer of multiphoton-generated electrons from r-GQDs to TiO₂ toward IR-driven photocatalysis. The high electron density induced by such a direct electron transfer invests the sample with prominent photocatalytic abilities under infrared light for not only overall water splitting but also CO₂ reduction. Remarkably, the designed hybrid material achieves photocatalytic overall water splitting for H₂ at 60.4 μmol g⁻¹ h⁻¹ and O₂ at 30.0 μmol g⁻¹ h⁻¹ under infrared light (>800 nm, 20 mW cm⁻²). Such an IR activity makes an important contribution to the STH of 0.80%. This work provides new insights into photocatalyst design for harnessing low-energy photons.

4. Materials and Methods
Preparation of TiO₂ nanotubes. All the chemicals were of analytical grade. TiO₂ nanotubes were synthesized using an alkaline hydrothermal process according to the literature [24].

Preparation of GQDs and r-GQDs. Glucose was dispersed in 40 mL pure water. The solution was stirred in a magnetic stirrer for 10 min, then transferred to a Teflon lined autoclave (50 mL) and heated at 190 °C for 3 h. After the reaction, the autoclave was naturally cooled to room temperature. The brown solution was centrifuged for 20 min to remove the precipitate and retain the supernatant, namely GQDs. The aqueous suspension of GQDs (0.1-1 mg/mL) was added with 50 mg NaBH₄, and the reaction was under stirring at room temperature for 4 h. The resulted product was named as r-GQDs.

Preparation of TiO₂/GQDs and TiO₂/r-GQDs. The TiO₂/GQDs or TiO₂/r-GQDs composites were obtained by the hydrothermal method. 0.2 g TiO₂ and 40 mL GQDs or r-GQDs suspension were mixed. The mixture was continuously stirred at room temperature for 4 h to obtain a uniform suspension. TiO₂/GQDs or TiO₂/r-GQDs was collected by centrifugation, washed three times with distilled water and dried in vacuum overnight at 60 °C.
Acknowledgments

Author Contributions: P. Gao, D. M. Jia and Q. Q. Chi conceived the XPS experiments; D. M. Jia carried out the PL, In situ FT-IR and in situ XPS measurements. J. X. Low analyzed the XRD data. P. Deng and Y. K. Wang conducted the SEM and EDX measurements. W. B. Wu and K. L. Zhu analyzed the TEM measurements and supervised the optical measurements. X. D. Xu, G. Jia and M. Q. Xu analyzed and interpreted the HRTEM. P. Gao, W. Ye and Y. J. Xiong supervised the research. All authors have seen the paper, agree to its content, and approve submission.

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Conflicts of Interest
The authors declare that there is no conflict of interest regarding the publication of this article.

Supplementary Materials

Supplementary Methods

X-ray powder diffraction (XRD)

XRD characterization used a Cu-Kα radiation source with a wavelength of \( \lambda = 0.15405 \) nm. Voltage and current in the process of testing were 40 kV and 150 mA, respectively. The scanning speed was 10°s\(^{-1}\) and the scanning area was from 10° to 70°.

Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy with an energy dispersive X-ray (STEM-EDX) spectroscopy characterizations were performed on a FEI Talos F200X G2 transmission electron microscope with a field emission gun operated at 200 kV.

Aberration-corrected transmission electron microscopy (AC-TEM)

JEM-ARM300f was equipped with spherical aberration corrector independently developed JEOL. ETA (expanding trajectory error corrector) was a 12-pole spherical aberration corrector developed by JEOL at an accelerating voltage of 300 kV.

Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectra were recorded on a Perkin-Elmer 580B IR spectrophotometer using the KBr pellet technique.

In-situ FT-IR spectroscopy
In-situ FT-IR spectroscopic measurements for photocatalytic process in the presence of trace water were carried out on the Bruker TENSOR II FTIR spectrometer. Specifically, 30 mg of the photocatalyst was placed on the sample holder in the test chamber, and 100 μL of the H$_2$O was injected into the chamber. After the chamber was purged with Ar gas for 30 min, the background spectrum was recorded from 4,000 to 400 cm$^{-1}$. Subsequently, the test chamber was heated to 423 K for 30 min to achieve that the H$_2$O molecules were volatilized and adsorbed on the photocatalyst. After the excess vapor of H$_2$O was purged by Ar gas, the time-dependent DRIFTS spectra were recorded to monitor the photocatalytic process under the irradiation of Xe lamp and infrared lamp.

Brunauer Emmett Teller (BET) measurement

N$_2$ adsorption/desorption measurements were conducted with a Micromeritics TriStar 3020 to characterize the Brunauer Emmett Teller (BET) parameters of samples. The test temperature was 196.15 °C (liquid nitrogen temperature), and the samples were heated at 120 °C for 2 h before the test.

Raman spectroscopy

Raman spectra were taken using a Raman spectrometer (LABRAM HR800) with a 325 nm laser excitation. The samples were dispersed in ethanol for 30 min.

In-situ Raman spectroscopy

In-situ Raman spectroscopic measurements were performed at room temperature using a HORIBA LabRam spectrometer with a 785 nm excitation wavelength at 0.5 mW between 200 and 2500 cm$^{-1}$. To avoid laser-induced deintercalation and photochemistry, the laser power was kept below 0.5 MW and the laser spot size of 1 mm (Olympus LMPlanFl 50*, NA 0.50). A charge-coupled device was used to detect the signal after analyzing the signal via a monochromator. The spectrometer was calibrated in frequency using a HOPG crystal.

X-ray photoelectron spectroscopy (XPS)

XPS was used to characterize the atomic composition content and the chemical valence state, which was equipped with an excitation source of 1486.6 eV of AlKα target.

In-situ XPS

Samples were analyzed using the Thermo Scientific K-Alpha XPS equipped with MAGCIS (Monatomic and Gas Cluster Ion Source), and the Thermo Scientific ESCALAB 250 Xi XPS parallel images were collected using the ESCALAB 250Xi. The instrument was equipped with a monochromated Al Kα X-ray source, high energy resolution electron analyzer, parallel imaging detector, magnetic immersion lens for improved spatial resolution, and charge neutralization system for insulating sample analysis. The K-Alpha was used for other XPS analyses. Surface layers were removed by bombardment with 4 kV, 2000 atom, Ar gas clusters (8 nA beam current), and scanned over an area of 2 mm 4 mm. Advantage software was used for instrument control & data reduction. The wet catalyst containing water was dropped onto a very transparent silicon wafer. Subsequently, the samples were treated with argon plasma for 10 min and stored in argon atmosphere before further characterization. After the sample was sent to the analysis room, high-purity nitrogen was introduced. A partial pressure of up to 0.5 mbar was introduced into the analysis chamber in turn. A 300
W xenon lamp (PLS-SXE300, perfect light) was used to irradiate the catalyst on the silicon wafer. Ti2p, C1s and O2s spectra were obtained in situ every 5 min.

Photoluminescence (PL) spectroscopy

PL spectra were measured at an excitation wavelength of 320 nm by using a spectrophotometer (FLS 980) and a Xe lamp (450 W) as excitation sources. The time-resolved transient PL decay curve was mathematically described as the following biexponential function:

\[ I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \]

where \( \tau_1 \) and \( \tau_2 \) are fluorescence lifetimes, and \( A_1 \) and \( A_2 \) are corresponding amplitudes. The calculation formula for average fluorescent lifetime is described as follows:

\[ \tau_a = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \]

UV-vis reflectance spectroscopy

UV-vis reflectance spectra were collected by an ultraviolet spectrophotometer (UV2550, Shimadzu, Japan).

Electrochemical impedance spectroscopy (EIS)

EIS experiments, photocurrent density characterization and Mott-Schottky analysis were performed using a three-electrode system in a 0.5 M Na2SO4 solution with Pt foil and saturated Ag/AgCl as the counter electrode and reference electrode by an electrochemical workstation CHI 660D (Chen Hua, China). The calculation formula for carrier density is described as follows:

\[ N_d = \frac{2}{e_0 \varepsilon \varepsilon_0} \left( \frac{d(1/e^2)}{dV} \right) \]

Surface photovoltage (SPV) measurement

Surface photovoltage measurements were performed at room temperature using a CEL-SPS1000 spectrometer with a 500 W Xe lamp. The catalysts were suspended by a sonicated treatment and dropped on FTO glass.

Photocatalytic water splitting measurements

The photocatalytic experiments were performed in a 500 mL closed quartz flat-bottom container. Firstly, 50 mg catalyst was dispersed with 100 mL distilled water. A 300 W xenon arc lamp was used as a visible light source to trigger the photocatalytic reaction. The power density of the incident light was controlled as 100 mW cm\(^{-2}\), which was measured by a CEL-HFX300 Visible spectrophotometer. The amount of gas evolution was measured using an on-line gas chromatograph (SP7800, thermal conductivity detector (TCD), molecular sieve 0.5 nm, N\(_2\) carrier, Beijing Keruida Limited). The solar-to-hydrogen (STH) efficiency \( \eta_{STH} \) was determined by the following equation:

\[ \eta_{STH} = \frac{\text{Output energy as } H_2}{\text{Energy of incident solar light}} = \frac{n_{\pi_2} \Delta G_{\pi_2}}{P_{\text{min}} \times S} \]
where is the rate of hydrogen production, is the change in Gibbs free energy per mol of \( \text{H}_2 \) (at 25°C, \( G = 237 \text{ kJ mol}^{-1} \)), \( P_{\text{sun}} \) is the effective input energy flux of the sunlight (100 mW cm\(^{-2}\)) and \( S \) is the area of the reactor (4.5 cm\(^2\)).

Photocatalytic CO\(_2\) reduction measurements

The photocatalytic CO\(_2\) reduction was carried out in a top irradiation vessel connected to the glass gas circulation system of CEL-PAEM-D6 (Beijing China Education Au-Light CO., Ltd). The system was irradiated under an infrared light (>800 nm) with an intensity of 100 mW cm\(^{-2}\). Then 50 mg photocatalyst dispersed in 100 mL deionized water was added into the above system with constant magnetic stirring. The collected gas was analyzed by GC-7920 gas chromatography equipped with TCD and 5A molecular sieve column.

Apparent quantum efficiency (AQE) determination

The apparent quantum efficiency was measured using the photocatalytic reactor setup according to the following equations:

\[
\text{Apparent quantum efficiency (\%) = } \frac{\text{Moles of reacted electrons per unit time}}{\text{Moles of incident photons per unit time}} \times 100
\]

Mols of incident photons per unit time (NEinstein) = Number of incident photons per unit time/NA. Number of incident photons \( N_p \) per unit time can be calculated by:

\[
N_p = \frac{\text{Intensity (E)}}{\text{Photo energy (Ep)}}
\]

\( E = \text{Irradiance} \times \text{reactor area illuminated} \); and photon energy \( \text{(Ep)} = \frac{hc}{\lambda} \).

Analysis of grain size by XRD

\[
D_{hkl} = \frac{K \lambda}{(B_{hkl} \cos \theta)}
\]

where \( D_{hkl} \) is the crystallite size in the direction perpendicular to the lattice planes, \( hkl \) is the Miller indice of the plane being analyzed, \( K \) is a numerical factor frequently referred to as the crystallite-shape factor, \( \lambda \) is the wavelength of the X-rays, \( B_{hkl} \) is the width (full-width at half-maximum) of the X-ray diffraction peak in radians, and \( \theta \) is the Bragg angle.
Fig. S1. XPS spectra of the TiO$_2$/GQDs: a) survey, b) C 1s, c) O 1s and d) Ti 2p.

Fig. S2. Raman spectrum of the obtained r-GQDs.
Fig. S3. Raman spectrum of the obtained TiO$_2$.

Fig. S4. Pore size distributions of the TiO$_2$/GQDs and TiO$_2$/r-GQDs.

Fig. S5. UV–vis reflectance spectra and the optical band gaps of three samples.
Fig. S6. SPV spectra of three samples.

Fig. S7. IR light (>800 nm, 20 mW cm\(^{-2}\)) driven photocatalytic water splitting for \(\text{H}_2\) generation in 9 hours by the TiO\(_2\)/r-GQDs.
Fig. S8. IR light (>800 nm, 20 mW cm\(^{-2}\)) driven photocatalytic water splitting for H\(_2\) and O\(_2\) generation in 4 repeated cycles (5 h/cycle) by the TiO\(_2\)/r-GQDs.

Fig. S9. TEM image of the TiO\(_2\)/r-GQDs after photocatalytic water splitting, which maintains its one-dimensional structure.
Fig. S10. In-situ FT-IR spectra between 1480 and 1800 cm\(^{-1}\) of the TiO\(_2\)/r-GQDs sample, which clearly shows the peaks belonging to Ti-H.

Fig. S11. Simulated Sunlight (100 mW cm\(^{-2}\)) driven photocatalytic CO\(_2\) reduction for CO and CH\(_4\) generation in 9 hours by the TiO\(_2\)/r-GQDs.
Fig. S12. Simulated Sunlight (100 mW cm$^{-2}$) driven photocatalytic CO$_2$ reduction for CO and CH$_4$ generation in 4 repeated cycles (5 h/cycle) by the TiO$_2$/r-GQDs.

Fig. S13. Gas chromatography measurement for IR light (>800 nm, 20 mW cm$^{-2}$) driven photocatalytic CO$_2$ reduction for CO and CH$_4$ generation by the TiO$_2$/r-GQDs.
Fig. S14. IR light (>800 nm, 20 mW cm\(^{-2}\)) driven photocatalytic CO\(_2\) reduction for CO and CH\(_4\) generation in 9 hours by the TiO\(_2\)/r-GQDs.

Fig. S15. IR light (>800 nm, 20 mW cm\(^{-2}\)) driven photocatalytic CO\(_2\) reduction for CO and CH\(_4\) generation in 4 repeated cycles (5 h/cycle) by the TiO\(_2\)/r-GQDs.
References


