A novel, in situ simultaneous reduction-hydrolysis technique (SRH) is developed for fabrication of TiO$_2$–graphene hybrid nanosheets in a binary ethylenediamine (En)/H$_2$O solvent. The SRH technique is based on the mechanism of the simultaneous reduction of graphene oxide (GO) into graphene by En and the formation of TiO$_2$ nanoparticles through hydrolysis of titanium (IV) (ammonium lactato) dihydroxybis, subsequently in situ loading onto graphene through chemical bonds (Ti–O–C bond) to form 2D sandwich-like nanostructure. The dispersion of TiO$_2$ hinders the collapse and restacking of exfoliated sheets of graphene during reduction process. In contrast with prevenient G-TiO$_2$ nanocomposites, abundant Ti$^{3+}$ is detected on the surface of TiO$_2$ of the present hybrid, caused by reducing agent En. The Ti$^{3+}$ sites on the surface can serve as sites for trapping photogenerated electrons to prevent recombination of electron–hole pairs. The high photocatalytic activity of G-TiO$_2$ hybrid is confirmed by photocatalytic conversion of CO$_2$ to valuable hydrocarbons (CH$_4$ and C$_2$H$_6$) in the presence of water vapor. The synergistic effect of the surface-Ti$^{3+}$ sites and graphene favors the generation of C$_2$H$_6$, and the yield of the C$_2$H$_6$ increases with the content of incorporated graphene. The work may open a new doorway for new significant application of graphene for selectively catalytic C–C coupling reaction.

1. Introduction

CO$_2$ is a greenhouse gas of growing concern, and its atmospheric concentration continues to rise from the ongoing burning of fossil fuels. One of the best solutions is to convert CO$_2$ into valuable organic products by means of solar energy. Thus many research efforts have been made to develop efficient heterogeneous photocatalysts for the reduction of CO$_2$.$^{[1–6]}$ Considerable photocatalysts have been explored including semiconductors, such as TiO$_2$,$^{[7–9]}$ ZnO,$^{[7,10]}$ CdS,$^{[7,11]}$ ZnGa$_2$O$_4$,$^{[12]}$ Zn$_2$GeO$_4$,$^{[13,14]}$ and metal-incorporated metal–organic frameworks.$^{[15]}$ Coupling of co-catalysts such as platinum, Cu$_x$O and RuO$_2$ enhances stability of the photocatalysts against photocorrosion, improves a higher separation of photogenerated charge carriers, and increases the CO$_2$ conversion efficiency. Different products have been obtained over various photocatalysts under light illumination in presence of CO$_2$ and H$_2$O, such as CO, CH$_4$, CH$_3$OH, HCOOH or others.$^{[5]}$ Due to complex multielectron transfer process, however, the understanding of the catalytic selectivity and mechanism is in its infancy.$^{[16–20]}$

Conversion C$_1$ species such as CH$_4$ to more valuable high-grade carbon species (C$_n$, n ≥ 2, such as ethane, C$_2$H$_6$) under mild condition is a fundamental but significant transformation of great industrial importance, because the produced ethane can in turn be conveniently converted to liquid fuels or ethene through metathesis and dehydrogenation, respectively.$^{[19]}$ To
date, coupling of CH₄ into C₂H₄ by thermal routes for activation of the strong C–H bond (104 kcal mol⁻¹) requires high temperatures and multistep processes, and therefore they are energy-consuming and inefficient.⁴⁰ Compared to methods powered by thermal energy, techniques that use photonic energy to directly drive C–C coupling of CO₂ at room temperature undoubtedly have substantial advantages, such as the capacity to minimize coking.⁴¹

Graphene, a 2D honeycomb-like network of carbon atoms, has been used as a support for fabricating various nanohybrids with semiconductors, in which graphene is widely recognized to serve as an electron collector and transporter to efficiently hinder electron-hole recombination and lengthen the lifetime of the photo-generated charge carriers from semiconductor nanoparticles.²¹ Besides those properties, exploring and advancing the graphene-relevant new performance is greatly important to expand the range of applications.²² For instance, graphene can prevent CdS from photocorrosion during visible-light photocatalytic H₂ production.²³ Graphene is also able to promote CdS photocatalyst in selective oxidation of a range of alcohols to corresponding aldehydes under mild conditions.²⁴

The conducting band of TiO₂ around −4.21 eV³⁷ and the work function of graphene of −4.42 eV³⁸ allow the charge transfer from TiO₂ to graphene. Thus, hybrid of graphene and TiO₂ (abbreviate as G-TiO₂) has drawn intense attention in the field of energy conversion and environmental applications.²¹,²₅⁻₆⁶ We recently reported the preparation of robust G-TiO₂ hollow spheres consisting of molecular-scale alternating titania nanosheets and graphene nanosheets as building blocks, which exhibit nine times increase of photocatalytic reduction of CO₂ into renewable fuels (CO and CH₄) relative to commercial P25.²⁸ The large enhancement of the photocatalytic activity benefits from: 1) the ultrathin nature of TiO₂ nanosheets allows charge carriers to move rapidly onto the surface to participate in the photoreduction reaction; 2) the sufficiently compact stacking of ultrathin TiO₂ nanosheets with G nanosheets allows the photogenerated electron to fast transfer from TiO₂ nanosheets to G to enhance lifetime of the charge carriers; and 3) the hollow structure potentially acts as a photon trap well to allow the multisattering of incidence light for the enhancement of light absorption. Production of higher-level hydrocarbon fuel through CO₂ conversion will make such artificial photosynthesis more significant.

In this paper, we demonstrate a novel in situ simultaneous reduction-hydrolysis technique (SRH) for fabrication of 2D sandwich-like graphene-TiO₂ hybrid nanosheets in a binary ethylenediamine (En)/H₂O solvent. The so-called SRH technique is based on the mechanism of the simultaneous reduction of graphene oxide (GO) into graphene by En and the formation of TiO₂ nanoparticles through hydrolysis of titanium (IV) (ammonium lactato) dihydroxysub, subsequently in situ loading onto graphene through chemical bonds (Ti–O–C bond) to form 2D sandwich-like nanostructure. The dispersion of TiO₂ hinders the collapse and restacking of exfoliated sheets of graphene during reduction process. In contrast with preexistent G-TiO₂ nanocomposites, abundant Ti³⁺ was detected on the surface of TiO₂ of the present hybrid, caused by reducing agent En. The Ti³⁺ sites on the surface can serve as sites for trapping photogenerated electrons to prevent recombination of electron-hole pairs. The high photocatalytic activity of the G-TiO₂ hybrid was evaluated by photocatalytic conversion of CO₂ to valuable hydrocarbons (CH₄ and C₂H₄) in the presence of water vapor. The synergistic effect of the surface-Ti³⁺ sites and graphene favors the generation of C₂H₆, and the yield of the C₂H₆ increases with the content of incorporated graphene. Our work may open a new doorway for new significant application of graphene for selectively catalytic C–C coupling reaction.

2. Results and Discussion

G-TiO₂ composites with different weight percent of graphene were synthesized. The weight contents of graphene designated as x (wt%) in G-TiO₂ nanocomposites were 0, 1%, 2%, and 5%, and the corresponding samples were labeled as G₀-TiO₂ (pure TiO₂), G₁-TiO₂, G₂-TiO₂, and G₅-TiO₂ respectively. FE-SEM images (Figure 1) show that the typical G₂-TiO₂ nanohybrid well maintains the 2D sheet-like structure of graphene with several-micrometer lateral size (Figure 1a) and exhibits remarkable structural flexibility (Figure 1b), which is in sharp contrast with irregular aggregation of the pure G₀-TiO₂ nanoparticle formed in the absence of graphene (Supporting Information Figure S1). The TiO₂ nanoparticles with size of 10 to 20 nm of the hybrid are in intimate contact with graphene and uniformly distributed on the graphene nanosheets to form a sandwich-like structure (Figure 1c,d). A crack part of the hybrid clearly reveals the existence of graphene and TiO₂ nanoparticles, as indicated with arrowheads in the Figure 1d. It indicates that in situ loading of TiO₂ nanoparticles can not only be an effective way to prevent graphene nanosheets from being restacked during the reduction process, but also prevents the aggregation of TiO₂ nanoparticles.

TEM images (Figure 2) further reveal that a large number of TiO₂ nanoparticles spread uniformly and densely on the graphene. And the edge of the graphene can be clearly visible as indicated by the arrow (Figure 2b). No apparent aggregation of TiO₂ nanoparticles on the graphene further demonstrates that

![Figure 1. FE-SEM images of G₂-TiO₂ at different magnifications.](image)
graphene scaffold is able to spread the nanoparticles to hinder the aggregation. The high-resolution TEM image (the inset of Figure 2b) reveals well-defined lattice fringes of TiO₂ nanoparticles, corresponding to the (101) plane of anatase TiO₂.

Powder X-ray diffraction (XRD) patterns (Supporting Information Figure S2) show that all the identified peaks of Gₓ-TiO₂ nanocomposites can be perfectly indexed to anatase TiO₂ (JCPDS card no. 21-1272).[29] With increasing graphene content, the diffraction peaks become weaker and the widths of the peaks become slightly wider, implying a slight decrease in the average crystallite size. The average crystallite size of TiO₂ determined by the (101) diffraction peak using the Scherrer equation slightly decrease from 15.3 nm to 12.8 nm (Supporting Information Table S1). It indicates that the graphene serve as a 2D “mat” well to anchor the forming TiO₂ nanoparticles to restrain from growing into large particles. No diffraction peak at about 25° assigned to the characteristic peak of restacked graphene appears, indicating that the regular stack was destroyed by the intercalation of TiO₂ particles.

As shown in Figure S3a (Supporting Information), the C1s XPS spectrum of as-used GO (solid line) clearly indicates a high degree of oxidation with three main components, corresponding to carbon atoms in different functional groups (dashed lines): C–C bond (284.6 eV), C=O/C=O bond (epoxy, hydroxyl and carboxyl) (286.7 eV), and O–C=O bond (carboxyl) (288.5 eV).[43,44] In the C1s XPS spectrum of the G₂-TiO₂, the peak for C–O/C=O bond almost vanishes and the intensity of the peak for O–C=O band (dashed line) is much lower than that in GO, demonstrating the removal of most oxygen-containing functional groups. The C–C bond carbon content of G₂-TiO₂ resumes drastically relative to GO (81% versus 46%), further confirming excellent restoration of the sp²-hybridized carbon by the En-assisted solvothermal reduction process. The peak ascribed to Ti–C bond at around 281 eV is not detected in the spectrum of the G₂-TiO₂, suggesting that Ti was not connected with carbon, and carbon was also not doped into the lattice of the TiO₂. In addition, appearance of a peak at 286.20 eV corresponding to C–N bond in the C1s XPS spectrum of G₂-TiO₂ indicates that the reduction of GO is accompanied by nitrogen incorporation from the reducing agent En. A peak of amine group is also visible in the Ni₅ XPS spectrum of G reduced by the solvothermal reduction process (Supporting Information Figure S4). The chemical state variations of Ti atoms on TiO₂ surface were studied through Ti2p XPS spectra of G-TiO₂ samples (Supporting Information Figure S3b). Two main peaks of pure TiO₂ located at 463.3 eV and 457.6 eV are assigned to Ti 2p₁/₂ and Ti 2p₃/₂, respectively. Compared to the Ti2p peak for Ti⁴⁺ (464.6 eV for Ti 2p₁/₂ and 458.9 eV for Ti 2p₃/₂), a shift of 1.3 eV toward the lower binding energy is visibly observed, indicating the formation of Ti³⁺.[46] The Ti2p XPS spectrum of G₂-TiO₂ also shows a shift of 1.1 eV. As the crystalline phase of the formed TiO₂ has no discernable change proved by XRD result, it is confirmed that Ti³⁺ was only formed on the surface of TiO₂. The reduction of Ti⁴⁺ to Ti³⁺ is possibly caused by reducing agent En. The Ti³⁺ sites on the surface can serve as sites for trapping photogenerated electrons to prevent recombination of electron-hole pairs.[47]

Fourier-transform infrared (FTIR) spectroscopic study shows the spectrum of GO and G₂-TiO₂ (Supporting Information Figure S5). The characteristic absorption bands of GO (1734 cm⁻¹ for C=O stretching, 1240 cm⁻¹ and 1370 cm⁻¹ for C–OH stretching, 1077 cm⁻¹ for C–O stretching) are absent, and in contrast the skeletal vibration at 1631 cm⁻¹ attributed to the aromatic C=C group in G₂-TiO₂ spectrum appears, suggesting that GO was primely reduced to graphene (Supporting Information Figure S5). The characteristic peak of En is not observed in the spectrum of G₂-TiO₂, demonstrating that En is absent in the product.[49] Moreover, an obvious shoulder peak at around 798 cm⁻¹ in the spectrum of G₂-TiO₂ assigned to the Ti–O–C vibration was observed.[50] The results suggest that Ti atoms of TiO₂ can interact with the graphene to form chemisorption interfaces via Ti–O–C bonding. The presence of Ti–O–C band indicates that this method ensures good TiO₂–graphene contact through chemical bonds, favoring the charge transfer between TiO₂ and graphene upon light excitation. The Raman spectrum of G₂-TiO₂ reveals the existence of two peaks of D band and G band of carbon species, indicating the existence of graphene, relative to G₀-TiO₂ (Supporting Information Figure S6). The intensity ratio of the D band to G band, I(D)/I(G), changes from 0.91 to 0.89, due to the removal of hydroxyl and epoxy groups, and the restoring of sp²-hybridized carbon.

UV-visible (UV-vis) diffuse reflectance spectroscopy shows that G₀-TiO₂ with an absorption edge at about 400 nm displays a bandgap of 3.1 eV (Supporting Information Figure S7). The absorption in the visible range is significantly enhanced as compared with pure TiO₂, which is attributed to the electronic interactions between the graphene and TiO₂.[26,31] and increases with increasing graphene ratio in G-TiO₂, as evidence with the film color of the nanocomposites becoming darker (Figure 3).

To prove the favored impact of incorporated graphene on separation and transportation of photogenerated electron-hole...
pairs under light irradiation, photocurrent measurements were carried out on Gx-TiO2 after deposition on FTO electrodes. Figure 4 shows that the fast and reproducible photocurrent responses for each switch-on and switch-off light cycles for all Gx-TiO2 electrodes under UV light irradiation. With stopping of the illumination, the photocurrent decreases back to zero immediately. Gx-TiO2 photoanodes show significant enhancement in photocurrent response over TiO2-only films. The enhancement of photocurrent demonstrates that photogenerated electrons in TiO2 nanoparticles are transferred onto graphene and percolate to the collecting electrode, which is expected to minimize charge recombination losses. The photocurrents increase along with the increase of the mass ratio of GO from 1 to 2 wt%, reflecting the higher separation efficiency of photogenerated electron-hole pairs through electronic interaction between graphene and TiO2. However, further increase of the mass ratio of GO (5 wt%) leads to a decrease of photocurrent intensity, probably due to intense light scattering and absorbance of the G.

The G0-TiO2 exhibits a broad emission peak around 512 nm under bandgap excitation, arising from surface oxygen vacancies and surface defects of TiO2 (Figure 5a). The PL of these nanocrystals was suppressed after the hybridization with G, showing diminished PL intensity, which indicates reduced charge recombination in comparison to bare TiO2. Under UV illumination, graphene accepts photogenerated electrons from TiO2, resulting in the decrease of electron-hole recombination within TiO2 and the PL quenching. This reduction increases with increasing graphene ratio in the G-TiO2. Figure 5b compares TiO2 emission decay traces as a function of increasing G concentration. The radiative lifetime of TiO2 nanoparticles was obviously reduced when the graphene layers were incorporated. This also implies that an additional nonradiative decay channel through the transfer of electrons from TiO2 to graphene is opened for the charge carriers created in the TiO2 nanoparticles, consistent with PL quenching results.

The effect of graphene on the BET surface area and porous structure for G-TiO2 samples was investigated using nitrogen adsorption-desorption measurements (Supporting Information Figure S8). The nitrogen adsorption-desorption isotherms of all samples are type IV, indicating the presence of mesopores. For G0-TiO2, a H1 hysteresis loops indicates agglomerates of uniform particles with high pore size uniformity and facile pore connectivity, proven by Figure S1 and the inset in Figure S8 (Supporting Information). After hybridization of with graphene, the shape of the hysteresis loops of G2-TiO2 and G5-TiO2 is of type H3, totally distinctly different from that of G0-TiO2, which is associated with slit-like pores originating from stacking of the G-TiO2 nanohybrid sheet. The pore size of mesopores ranges from 2 nm to 30 nm (inset in Supporting Information Figure S8). The porous structure of the G-TiO2 facilitates the transportation of reactants and products through the interior space. The BET surface area \( S_{\text{BET}} \) of the nanohybrids gradually increases with increasing graphene content, from 95.8 to 114.9 m² g⁻¹, which is 1.8–2.1 times larger than that of P25. The amount of CO2 absorbed on the Gx-TiO2 (x = 1, 2, 5) under ambient pressure at 0°C is 2–2.8 time larger than that of P25 and increases with increasing graphene content (Supporting Information Table S1).

To evaluate the photocatalytic activity of G-TiO2 samples, the photocatalytic CO2 conversion in the presence of water vapor was investigated. Figure 6 shows that CO2 can be photoreduced to CH4 and C2H6 by using G-TiO2 samples as photocatalysts
to react with CO$_2$, as schematically illustrated in Figure 7. The longer lifetime and mean free path for electrons on graphene implies that energetic electrons will cover a larger area of the graphene surface, thereby increasing the likelihood of interaction with adsorbed reactants. The total production rate reaches the highest value ($8 \mu$mol g$^{-1}$ h$^{-1}$ CH$_4$ and $16.8 \mu$mol g$^{-1}$ h$^{-1}$ C$_2$H$_6$) with the graphene content of 2.0 wt%. However, a further increase of graphene content leads to a deterioration of photocatalytic performance, which may probably be attributed to increased scattering and absorbance of photons through excess graphene in the photocatalytic system, shielding the light from reaching the surface of TiO$_2$ photocatalysts. As a result, a suitable content of graphene is important for optimizing the photocatalytic activity of G-TiO$_2$ nanocomposites. With cooperation of graphene, an interesting phenomenon rises that the production rate of CH$_4$ slowly decreases but the production rate of C$_2$H$_6$ noticeably increases, i.e., the molar ratio of C$_2$H$_6$ to CH$_4$ increases from 0.71 (for G$_0$-TiO$_2$), 2.09 (G$_1$-TiO$_2$), 2.10 (G$_2$-TiO$_2$), to 3.04 (G$_5$-TiO$_2$), implying that C$_2$H$_6$ is easily produced with introduction of graphene. It is obvious that graphene has a right for selecting the products obtained by photocatalytic CO$_2$ conversion. Methoxyl (•OCH$_3$) and methyl (•CH$_3$) radicals were proved as reaction intermediates during the process of photocatalytic CO$_2$ conversion.[18, 54–56] CH$_4$ can be produced by •CH$_3$ radical reacting with proton and electron (•CH$_3$+H$^+$+e$^-$+H$^+$→CH$_4$) and coupling of two •CH$_3$ leads to C$_2$H$_6$ (•CH$_3$+•CH$_3$→C$_2$H$_6$).[57] Paul and Hoffmann[58] suggested that the dimerization of •CH$_3$ preferably occurs via a radical–substrate reaction mechanism in a hydrogen deficient system. The low coordinated oxygen species caused by abundant Ti$^{3+}$ sites on the surface of TiO$_2$ generate relatively stronger active sites due to the suppression of acidic sites, thus the C$_2$ selectivity is more specific than that of the without any noble-metal co-catalysts such as Pt and Au and oxides RuO$_2$. It is obvious that G$0$-TiO$_2$ (10.1 μmol g$^{-1}$ h$^{-1}$ CH$_4$ and 7.2 μmol g$^{-1}$ h$^{-1}$ C$_2$H$_6$) exhibits much higher activity than commercial P25 (0.69 μmol g$^{-1}$ h$^{-1}$ CH$_4$ and minor CO 0.16 μmol g$^{-1}$ h$^{-1}$, C$_2$H$_6$ is absent).[28] The higher conversion is attributed to two factors: 1) the specific surface area of G$0$-TiO$_2$ is 2.73-time larger than that of commercial P25, offering more active adsorption sites and photocatalytic reaction centers; and 2) the surface of G$0$-TiO$_2$ has abundant Ti$^{3+}$ sites which serves as energetically favorable sites for electron transfer to CO$_2$.[4,20] trapping electrons to prevent the recombination of electron-hole pairs. A CO$_2$ reduction experiment performed in the dark or in the absence of the photocatalysts showed no appearance of productions (CH$_4$ and C$_2$H$_6$), proving that the CO$_2$ reduction reaction is driven by light with the photocatalysts. With increasing graphene content, the total production rate increases. The enhanced conversion rate is attributed from that the d-orbital of TiO$_2$ and π-orbital of graphene match well in energy levels, and the G-TiO$_2$ have chemical bond interactions and form d–π electron orbital overlap. The excited-state electrons transporting from the TiO$_2$ upon UV illumination into the graphene can be shuttled freely along the conducting network of graphene, and subsequently transfer to the surface.

Figure 6. a) Comparison of photocatalytic activity of samples G$_x$-TiO$_2$ (x = 0, 1, 2, 5) and P25. The molar ratio of C$_2$H$_6$ to CH$_4$ increases from 0.71 (for G$_0$-TiO$_2$), 2.09 (G$_1$-TiO$_2$), 2.10 (G$_2$-TiO$_2$), to 3.04 (G$_5$-TiO$_2$). b,c) Photocatalytic CH$_4$ and C$_2$H$_6$ evolution amounts for samples G$_x$-TiO$_2$ (x = 0, 1, 2, 5).

Figure 7. Schematic illustration of the charge separation and transfer in the G-TiO$_2$ system and photoreduction of CO$_2$ into CH$_4$ and C$_2$H$_6$. 

higher acidic-based systems.\textsuperscript{[37]} In the presence case, existence of abundance of Ti\textsuperscript{4+} ion sites on the surface through reduction of Ti\textsuperscript{4+} caused by reducing agent En plays vital role the coupling of photoformed •CH\textsubscript{3} radicals into C\textsubscript{2}H\textsubscript{6} compared with commercial P25 and G-P25, which only produce CH\textsubscript{4}.

For the G-x-TiO\textsubscript{2} systems, •CH\textsubscript{3} radicals may be absorbed on the surface of graphene via π-conjugation between the unpaired electron of the radical and aromatic regions of the graphene.\textsuperscript{[26,27]} The electron-rich graphene may help to stabilize the •CH\textsubscript{3} species, which restrains combination of •CH\textsubscript{3} with H\textsuperscript{+} and e\textsuperscript{−} into CH\textsubscript{4}. Meanwhile, subsequent increasing accumulation of •CH\textsubscript{3} on the graphene raises the opportunity of formation of C\textsubscript{2}H\textsubscript{6} by the coupling of •CH\textsubscript{3}.

3. Conclusions

The so-called SRH technique was explored to fabricate 2D sandwich-like graphene-TiO\textsubscript{2} hybrid sheets. The dispersion of TiO\textsubscript{2} hinders the collapse and restacking of exfoliated sheets of graphene during reduction process. The photogenerated electrons in TiO\textsubscript{2} nanoparticles are transferred onto graphene under light irradiation, which minimizes charge recombination losses to improve the conversion efficiency of the photoreduction of CO\textsubscript{2} into hydrocarbon fuel. The synergistic effect of the surface-Ti\textsuperscript{4+} abundant TiO\textsubscript{2} and graphene favors the generation of C\textsubscript{2}H\textsubscript{6}, and the yield of the C\textsubscript{2}H\textsubscript{6} increases with the content of incorporated graphene. Our work may open a new doorway for new significant application of graphene for selectively catalytic C–C coupling reaction.

4. Experimental Section

Materials: Titanium (IV) (ammonium lactato)dihydroxybis (50 wt% in aqueous solution) was purchased from Alfa Aesar. GO nanosheets were prepared using a modified Hummer’s method from graphite powders.\textsuperscript{[42]} Distilled water was used in all experiments.

Synthesis of G-TiO\textsubscript{2} Nanocomposites: G-TiO\textsubscript{2} nanocomposites with a varying amount of graphene were prepared by one-step hydrothermal method using GO nanosheets, En, and titanium (IV) (ammonium lactato)dihydroxybis as the starting materials. The synthesis procedure was as follows: a varying amount of GO, 1 g of titanium (IV) (ammonium lactato)dihydroxybis and 5 mL of En were dispersed into 10 mL of water and then stirred for 30 min at room temperature. The weight contents of graphene designated as x (wt%) in G-TiO\textsubscript{2} nanocomposites were 0%, 1%, 2%, and 5%, and the corresponding samples were labeled as pure TiO\textsubscript{2} (G0-TiO\textsubscript{2}), G1-TiO\textsubscript{2}, G2-TiO\textsubscript{2}, and G5-TiO\textsubscript{2}, respectively. Next, the mixtures were transferred into the stainless Teflon-lined autoclave of 25 mL inner volume, and then heated to 200 °C for 24 h under autogenous pressure, followed by cooling naturally to room temperature. The precipitates were collected by centrifugation, washed thoroughly with alcohol and water for three times respectively. Finally, the resulting products were dispersed in water by sonication and fully dried by lyophilization. For comparison, the bare graphene sample without any TiO\textsubscript{2} was prepared under the same experimental conditions and was labeled as G.

Characterization: The morphology of the samples was observed by the field emission scanning electron microscopy (FE-SEM) (FEI NOVA NanoSEM230, USA) and transmission electron microscopy (TEM) (JEOL 3010, Japan). The crystallographic phase of the as-prepared products was determined by powder X-ray diffraction (XRD) (Rigaku Ultima III, Japan) using Cu-Kα radiation (λ = 0.154178 nm) with scan rate of 10° min\textsuperscript{−1} at 40 kV and 40 mA. The crystallite size was calculated using Scherrer formula (d = 0.9λ/βCosθ, where d, λ, β and θ are crystallite size, Cu Kα wave length, full width at half maximum intensity (FWHM) in radians and Bragg’s diffraction angle, respectively). The samples were analyzed with X-ray photoelectron spectroscopy (XPS) (K-Alpha, THERMO FISHERSCIENTIFIC). The XPS spectrum was calibrated with respect to the binding energy of the adventitious C1s peak at 284.8 eV. The specific surface area of the samples was measured by nitrogen sorption at 77 K on surface area and porosity analyzer (Micromeritics TriStar, USA) and calculated by the BET method. The CO\textsubscript{2} sorption on surface of the samples was evaluated by the above-mentioned adsorption apparatus under ambient pressure and 0 °C. Fourier transform infrared (FTIR) spectroscopy was conducted using a Nicolet NEXUS870 (USA) spectrometer. Raman spectra were measured on a JY HR800 laser Raman spectrometer (JOBIN YVON, France) with 488 nm argon laser excitation. The UV-visible (UV-vis) diffuse reflectance spectra were recorded with a UV-vis spectrophotometer (UV-2550, Shimadzu) at room temperature and transformed to the absorption spectra according to the Kubelka–Munk relationship. Photocurrent Measurements: the photocatalysts were deposited on FTO electrode used as working electrodes by electrophoresis deposition method in the same condition. To attach photocatalysts to ITO glass, working electrodes were heated at 600 °C for 1 h in argon atmosphere. Photoelectrochemical measurements were carried out in three-electrode configuration system: a FTO working electrode, Hg/Hg\textsubscript{2}Cl\textsubscript{2} as the reference electrode, and a Pt foil as the counter electrode. Na\textsubscript{2}SO\textsubscript{4} (1 M) aqueous solution was used as the electrolyte. The photocurrent was observed for each switch-on/off event by using a 500 W xenon lamp. The area of the samples exposed to light was 0.28 cm\textsuperscript{2}. An applied potential of working electrode against the counter electrode was set to 0 V.

Photocatalytic Experiments: In the photocatalytic reduction of CO\textsubscript{2}, 0.1 g of samples was uniformly dispersed on the glass reactor with an area of 4.2 cm\textsuperscript{2}. A 300W Xenon arc lamp was used as the light source of photocatalytic reaction. The volume of reaction system was about 230 mL. The reaction setup was vacuum-treated several times, and then the high purity of CO\textsubscript{2} gas was followed into the reaction setup for reaching ambient pressure. 0.4 mL of deionized water was injected into the reaction system as reducer. The as-prepared photocatalysts were allowed to equilibrate in the CO\textsubscript{2}/H\textsubscript{2}O atmosphere for several hours to ensure that the absorption of gas molecules was complete. During the irradiation, about 1 mL of gas was continually taken from the reaction cell at given time intervals for subsequent CH\textsubscript{4} or C\textsubscript{2}H\textsubscript{6} concentration analysis by using a gas chromatograph (GC-2014, Shimadzu Corp., Japan). All samples were treated at 300 °C in nitrogen atmosphere for 2 h for removal of organic adsorbates before the photocatalysis reaction.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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