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Surface nonpolarization on g-C₃N₄ for improved CO₂ photoreduction by decoration of sensitized quantum dots

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Abstract: The concept of photocatalytic CO₂ conversion provides simultaneous solutions for global warming mitigation and fuels generation, which, however, is limited by the unsatisfactory photoconversion efficiency. Despite light harvesting and charge separation, enhancing adsorption of CO2 via surface modification could be an efficient way to improve CO₂ photoconversion efficiency. Herein, we doped nonpolar carbon quantum dots (denoted as CQDs) on g-C₃N₄ to construct a metal-free heterojunction photocatalyst (denoted as CQDs/g-C₃N₄). Besides the narrow bandgap and electron-withdrawing of CQDs to improve the visible-light absorption and photocarrier separation efficiency, we first discovered that nonpolar CQDs could simultaneously improve adsorption of nonpolar CO₂, photoinduced H₂, enhancing the reaction kinetics and altering CO₂ photoreduction pathways to generate CH₄. Consequently, in contrast to g-C₃N₄ that only generated CO and H₂, CQDs/g-C₃N₄ could generate 6-times CO and comparable CH₄ without detectable H₂ under the same condition. Therefore, this study first demonstrated the promising nonpolar surface modification strategy for efficient CO₂ adsorption, activation, and subsequent photoreduction.

Introduction

With the current rapid industrialization, the excessive burning of fossil fuels results in a large amount of anthropogenic CO2 emissions, leading to adverse global warming and environmental changes.^[1] Meanwhile, CO₂ as the main carbon source could be transformed into a variety of C1 and C2 products, including CO, CH₄, and other hydrocarbon fuels.^[2] Recently, photocatalytic reduction of CO₂ into renewable hydrocarbon fuels has attracted worldwide attention, which could provide potential simultaneous solutions for renewable fuels generation and global warming mitigation.^[3] However, due to unsatisfactory CO₂ photoconversion efficiency, photocatalytic reduction of CO₂ for fuel production remains a grand challenge.^[4] It is attributed to the limited light absorption and the rapid combination of photogenerated carriers. In addition, it is kinetically difficult to photoreduce CO2 into CO and CH₄, because of the chemically inert property and the highest oxidation state of carbon.^[5] Therefore, apart from increasing

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visible-light absorption and charge separation efficiency, appropriate surface modification ways to enhance CO₂ adsorption, activation, and lower the reaction barriers for the subsequent CO2 reduction could effectively improve the photocatalytic CO2 reduction performance.[6]

Different surface modification strategies, such as constructing oxygen vacancies, the introduction of functional groups and loading co-catalyst, have been developed to enhance CO2 adsorption and activation [17]. Theoretically, considering the nonpolar property of CO2, altering the polarity of the photocatalysts surface could potentially favour the adsorption of CO₂, enhancing the surface reaction kinetics of CO₂ photoreduction. However, few studies reported thus far have been focused on the surface polarity modification strategy to enhance the CO₂ photoreduction performance.

Carbon quantum dots, composed of sp² hybridized carbon, exhibit a unique electron reservoir, photo-induced electron transfer properties, and tunable optical absorption.^[8] Recent studies have demonstrated the enhanced visible light absorption, photoexcited charge carriers separation and photocatalytic activities for CQDsbased composites.^[9] Moreover, considering the nonpolar property of CQDs and CO₂, doping CQDs on photocatalyst could modify the surface polarity of photocatalyst potentially enhancing CO₂ adsorption to improve the surface reaction kinetics.^[10] Herein, we designed and demonstrated a series of CQDs modified graphitic carbon nitride nanocomposite (denoted as CQDs/g-C₃N₄) for CO₂ photoreduction. The photocatalytic properties of the CQDs/g-C₃N₄ composites were systematically explored under visible light irradiation. Due to the photo-sensitized effects, charge transfer property of CQDs, CQDs/g-C₃N₄ exhibits efficiently enhanced visible-light absorption and photocarrier separation efficiency. Furthermore, we first discovered that nonpolar CQDs dopant could simultaneously decrease the surface polarity of the photocatalyst, which could efficiently enhance the adsorption of nonpolar CO₂ molecules and alter the CO₂ photoreduction pathways to generate a considerable amount of CH₄ (20.78 µmol·h⁻¹·g⁻¹) and CO (23.38 µmol^{-h-1}·g⁻¹) with the presence of H₂O. In contrast, pristine g-C₃N₄ only generated one-sixth CO (4.14 μ mol·h⁻¹·g⁻¹) and H₂ (4.57 μ mol·h⁻¹·g⁻¹) without detectable CH₄ under the same condition. Therefore, this study first demonstrated the promising nonpolar surface modification strategy for efficient CO₂ adsorption, activation, and subsequent photoreduction into hydrocarbons.

Results and Discussion

Carbon quantum dots (CQDs) were synthesized according to a reported method, loaded on g-C₃N₄ with different amounts (1-4 wt%).^[11] As shown in the transmission electron microscopy (TEM) image, the synthesized CQDs are uniform with the average size of 2.5 nm, which is well-crystallized (Fig. S1, Fig. 1c). TEM image

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of pure g-C₃N₄ infers the mesoporous structure with the high surface area (Fig. 1a). Judged from TEM images of CQDs/g-C₃N₄, the doped CQDs could be well dispersed on the surface of g-C₃N₄ without observable aggregation (Fig. 1b-d). Furthermore, the CQDs doping showed negligible influence on the surface area and the porous structure of g-C₃N₄ (Fig. S2, Fig. S3, Table S1).



Figure 1. (a) TEM image of $g-C_3N_4$, (b) TEM image of 1 wt% CQDs/ $g-C_3N_4$; (c) TEM image of 2 wt% CQDs/ $g-C_3N_4$. Inset is the HRTEM image of a CQD particle on the $g-C_3N_4$ sheet. (d) TEM image of 4 wt% CQDs/ $g-C_3N_4$. (The white cycles indicate the CQDs).

The X-ray diffraction peaks of pure g-C₃N₄ and CQDs/g-C₃N₄ at 13.1° and 27.4° corresponding to (100) and (002) crystal planes of the layered g-C₃N₄ confirm the well-maintained crystal structure of g-C₃N₄ during the attachment procedures of CQDs (Fig. 2a).^[12] Judged from the Raman spectroscopy, compared with pure g-C₃N₄, the appearance of two Raman peaks at 1354 and 1600 cm⁻ ¹ of a series of CQDs/g-C₃N₄ should be ascribed to the D band and G band of carbon (Fig. 2b).^[13] Subsequently, the surface chemical compositions of g-C₃N₄ and the CQDs/g-C₃N₄ were analyzed by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 2c, the peaks at 284.9 eV and 288.25 eV of all these samples should be attributed to surface adventitious carbon and C-N-C, respectively.^[14] Additionally, compared with pure g-C₃N₄, the appearance peak at 286.5eV should be assigned to the sp²hybridized carbon, further confirming the successful incorporation of CQDs.^[15] The optical properties of prepared CQDs/g-C₃N₄ samples were investigated by diffuse reflectance ultravioletvisible (UV-Vis) spectroscopy (Fig. 2d). Noticeably, CQDs modified g-C₃N₄ exhibits substantially enhanced visible and even infrared light absorptions compared with pure g-C₃N₄. It should be ascribed to the narrow band-gap of the embedded carbon quantum dots (Fig. S4), implying a photo-sensitized effect of CQDs to enhance the visible light absorption.[16]



Figure 2. (a) XRD patterns, (b) Raman spectra, (c) C1s XPS spectra, (d) UV-vis absorption spectra of the g-C₃N₄, and 1 wt%, 2 wt%, 4 wt% CQDs/g-C₃N₄ samples.

Judged from the valence band XPS spectrum (Fig. 3a), the valence band maximum (VBM) energy of CQDs/g-C₃N₄ samples are similar with that of g-C₃N₄. From Mott-Schottky plots, the onset potential of CQDs/g-C₃N₄ samples (-0.75 Vs. RHE) is higher than that of g-C₃N₄ (-1.25 Vs. RHE), indicating a shift of flat band with CQDs incorporation. Also, the CQDs/g-C₃N₄ samples exhibit flatter Mott-Schottky plots (Fig. 3b) compared to that of g-C₃N₄, indicating higher carrier density. Therefore, the narrower band-gap of CQDs/g-C₃N₄ (2.5 eV) compared with that of g-C₃N₄ (2.8 eV) result from the redshift of conduction band minimum (Fig. S5), which should be ascribed to the transitions of π - π * and n- π * of C=C.^[17] Accordingly, the photoexcited electrons could transfer from $g-C_3N_4$ to the incorporated CQDs, enhancing the separation efficiency of photo-generated electrons and holes. Photoluminescence spectroscopy was further conducted to investigate the separation efficiency of photo-excited e⁻/h⁺.^[18] As shown in Fig. 3c, all of the CQDs/g-C₃N₄ composites displayed significantly decreased PL emission intensity compared with that of g-C₃N₄, indicating the improved charge-carrier separation efficiency with the incorporation of CQDs. This could be attributed to the effective shuttling of electrons from $g-C_3N_4$ to the sp^2 hybridized carbon of CQDs, where the CQDs act as electron reservoirs to trap the photoexcited electrons and suppress the recombination with photogenerated holes at VB.^[19] However, overloading amount of CQDs (4 wt%) demonstrated higher PL intensity than that of 2 wt% CQDs/g-C₃N₄, indicating the excessive doped CQDs acting as recombination centers to increase the recombination of photoexcited carriers, which may potentially decrease the photocatalytic activity. Fig. 3d shows the transient photocurrent responses of the g-C₃N₄ and CQDs/g-C₃N₄. Apparently, 2 wt% CQDs/g-C₃N₄ shows the highest current density, which is 3-times higher than that of pure g-C₃N₄. These confirmed the enhanced separation and transportation of photogenerated carriers by CQDs incorporation. EIS Nyquist plots (Fig. S6) were further conducted for a better understanding of the charge carrier migration.^[20] Compared with g-C₃N₄, the

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smaller arc sizes of CQDs/g-C₃N₄ indicate the more efficient charge transfer process for enhanced photocurrent density. Therefore, benefiting from the narrow bandgap, matched band potential and electron withdrawing effects of carbon quantum dots, CQDs/g-C₃N₄ exhibits remarkably extended visible-light absorption and substantially improved photocarriers separation efficiency.^[21]



Figure 3. (a) Valence band XPS spectra, (b) Mott-Schottky plots, (c) PL spectra, (d) Transient photocurrent density of g-C₃N₄, 1 wt%, 2 wt%, 4 wt% CQDs/g-C₃N₄.

The photoreduced CO₂ products of the prepared samples were evaluated under visible light irradiation. As displayed in Fig. 4a-b, all of the CQDs/g-C₃N₄ exhibited much higher photocatalytic CO generation rate than that of pristine g-C₃N₄ nanosheets, which should be ascribed to the significantly enhanced visible-light absorption and photocarriers separation efficiency by CQDs incorporation. Meanwhile, 2 wt% of CQDs on g-C₃N₄ was found to be an optimum loading which demonstrated the highest CO generation (Fig. 4a-b). The excessive CQDs might act as recombination centers for the photoexcited charge carriers, underlying the photocatalytic activity. Additionally, the photoexcited holes reacted with H₂O to generate O₂. (Fig. 4c-d).



Figure 4. (a) Time-dependent CO photoevolution, (b) CH₄ photoevolution, (c) O_2 photoevolution, and (d) H₂ photoevolution of different samples (20 mg each sample) under visible-light irradiation (λ >400 nm).

Interestingly, all of the CQDs/g-C₃N₄ could generate comparable CH₄ and CO, while, pure $g-C_3N_4$ only produced CO and H₂ (Fig. 5a) without detected generation of CH₄ under the same condition. Then, CO₂ was replaced by Ar as the negative control and measured under the same condition. As shown in Fig. S7, compared with g-C₃N₄, CQDs/g-C₃N₄ could photocatalytically generate two-times H₂ and O₂ in a ratio of 2:1 without detectable CO or CH₄, excluding the potential reaction between doped CQDs and H₂O. These result indicated the CO₂ photoreduction pathways could be changed by doping CQDs on g-C₃N₄. Judged from water contact angle measurements (Fig. 5b), the contact angle increased with the increasing amount of doped CQDs, indicating the decreased surface polarity via nonpolar CQDs dopant. Through the CO₂ adsorption experiment, the CO₂ adsorption capacity significantly increased with increasing CQDs dopant (Fig. 5c). Considering decreased surface polarity and negligible influence on surface area and the porous structure via CQDs doping. The remarkably enhanced CO₂ adsorption on CQDs/g-C₃N₄ should be ascribed to the attraction of CO₂ molecules on the nonpolar CQDs dopant (Fig. 5d).



Figure 5. (a) CH₄, CO, O₂ and H₂ photogeneration rates of different samples (20 mg for each sample) under visible-light irradiation (λ >400 nm). (b) Contact angle (black) and hydrogen generation rates (blue) of g-C₃N₄, 1 wt%, 2 wt%, 4 wt% CQDs/g-C₃N₄. The inserts are the contact angle images for droplets water on different samples. (c) CQDs doping content dependent CO₂ adsorption at room temperature for g-C₃N₄. (d) And corresponding schematic diagrams of their surface attraction for the nonpolar CO₂ molecules.

When replacing CO_2 by Ar and measured under the same condition, $CQDs/g-C_3N_4$ could photocatalytically generate more than one-fold amount of H_2 and O_2 than that of pure $g-C_3N_4$, further confirming the narrow band gap, electron-withdrawing properties of CQDs could efficiently enhance the photocatalytic activity (Fig. S7). Moreover, due to the nonpolar property of CQDs, CQDs dopant could efficiently enhance the adsorption of CO_2 and photoinduced H_2 on the photocatalyst, which could improve the photocatalytic reduction kinetics and alter CO_2 photoreduction pathways, leading to the remarkably enhanced generation of CO and CH_4 under visible light irradiation (Fig. 6).

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Figure 6. Schematic comparison of CO₂ photocatalytic reduction pathways between (a) g-C₃N₄, and (b) CQDs doped g-C₃N₄ in the presence of H₂O, respectively. The chemicals written in the circle represent the adsorbed species on the surfaces of the catalyst.

The stability of CQDs/g-C₃N₄ (2 wt%) nanocomposite was further evaluated by performing the recycle experiments of the photocatalyst under the same condition (Fig. 7a). After five recycles, no detectable performance deterioration could be observed, and the structure is well-maintained (Fig. S8), indicating the well-sustained long-term stability of CQDs/g-C₃N₄. Furthermore, compared with the other reported hetero-structured photocatalysts, CQDs/g-C₃N₄ exhibits much higher photoreduction of CO₂ performance under visible light irradiation (Table 1), which should be ascribed to the narrow bandgap, electron-withdrawing effects and non-polar property of carbon quantum dots to efficiently photoreduce CO₂ under visible light irradiation (Fig. 7b).



Figure 7. (a) Cycling measurements of CO (black) and CH₄ (red) photoevolution of 2% CQDs/g-C₃N₄ (20 mg) under visible-light irradiation (λ >400 nm); (b) Schematic illustration of the photocatalytic process for CO₂ reduction on the CQDs/g-C₃N₄ composite.

Conclusions

In summary, through doping nonpolar carbon quantum dots on g-C₃N₄ to decrease the surface polarity of the photocatalyst, CQDs/g-C₃N₄ exhibits significantly enhanced adsorption of nonpolar CO₂ and photoinduced H₂, increasing the reaction kinetics and altering CO₂ photoreduction pathways for hydrocarbon generation. Additionally, due to the photosensitization and electron withdrawing effects of CQDs, CQDs/g-C₃N₄ demonstrates enhanced visible light absorption and separation efficiency of photogenerated carriers, resulting in excellent CO₂ photoreduction performance. We believe that the present nonpolar surface modification strategy may open up a

new	dimension	for	the	design	and	construction	of	efficient		
photocatalyst for benign CO ₂ utilization.										

 $\label{eq:Table 1. Comparison of photocatalytic activity of the CQDs/g-C_3N_4 \\ nanocomposite with other reported nanocomposite photocatalysts.^{[22]}$

Catalysts	Cocatalysts /Reaction condition	Light source	CO ₂ Reduction product evolution rates	Refs.
CQDs/ g-C ₃ N ₄	water vapor; room temperature	300W Xe-lamp with a 400nm cut-off filter	CO: 23.38 µmol·g ⁻¹ ·h ⁻¹ CH₄: 20.78 µmol·g ⁻¹ ·h ⁻¹	This study
Ag ₂ CrO ₄ / g-C ₃ N ₄ / graphene oxide	water vapor; room temperature	300W Xe-lamp With a 420nm cut-off filter	CH₄ and CH₃OH: 1.03 µmol⋅g⁻¹⋅h⁻¹	[22a]
g-C ₃ N ₄ / Bi ₂ O ₂ CO ₃ / CoFe ₂ O ₄	water vapor; room temperature	880W Xe-lamp With a 400nm cut-off filter	СО: 14.88 µmol·g ⁻¹ ·h ⁻¹ СН₄: 16.38 µmol·g ⁻¹ ·h ⁻¹	[22b]
Mg∕ g-C₃N₄	water vapor; room temperature	300W Xe-lamp	CO: 2.85 µmol·g ⁻¹ ·h ⁻¹ CH ₄ : 0.69 µmol·g ⁻¹ ·h ⁻¹	[22c]
Cu/ g-C₃N₄	water vapor; room temperature	350W Xe-lamp	CO: 9.89 µmol·g ⁻¹ ·h ⁻¹	[22d]
g-C₃N₄/ NiAI-LDH	water vapor; room temperature	300W Xe-lamp With a 420nm cut-off filter	CO: 2.84 µmol·g ⁻¹ ·h ⁻¹	[22e]
Au/ g-C₃N₄	water vapor; room temperature	300W Xe-lamp	CO: 6.59 µmol·g ⁻¹ ·h ⁻¹ CH₄: 1.55 µmol·g ⁻¹ ·h ⁻¹	[22f]
(-CN)/ g-C ₃ N ₄	water vapor; room temperature	300W Xe-lamp With a 420nm cut-off filter	CO: 0.39 µmol·g ⁻¹ ·h ⁻¹	[22g]

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Experimental Section

Materials

Urea (\geq 99%) and glucose (\geq 99%) were purchased from Aladdin Reagent Co. Ltd. Shanghai. Citric acid and ethylenediamine were purchased from Lingfeng Chemical Reagent Co. Ltd. (Shanghai, China). Deionized water used throughout the experiments was prepared using ELGA water purification system (PURELAB Classic).

Preparation of photocatalysts

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Preparation of g-C₃N₄: The g-C₃N₄ was synthesized via thermal polymerization of urea according to a reported method. Typically, 20 g urea was placed in an alumina crucible, and calcined at 550 °C for 2 hours, with a heating rate of 4 °C/min. Then, the pure g-C₃N₄ with light yellow was obtained.

Preparation of CQDs/g-C₃N₄: A series of CQDs/g-C₃N₄ composites were prepared with different doping amount of CQDs. Firstly, the CQDs nanoparticles were prepared by a hydrothermal method. Generally, 0.02g, 0.04g, 0.08 g of citric acid were dissolved in 10 ml of ethylenediamine. After stirring at room temperature for 10 min, the solution was transferred to a 25 ml Teflon-lined autoclave, heated to 200 °C, and kept at that temperature for 12 h. Then, 2 g g-C₃N₄ powder was dispersed in the solution and stirred at 60 °C for 12 h. Finally, the products (named CQDs/g-C₃N₄-1, CQDs/g-C₃N₄-2, CQDs/g-C₃N₄-3) was collected by centrifuging, washed with water and ethanol for several times, and vacuum-dried at 80 °C for 12 h.

Characterization

Transmission electron microscope (TEM), high-resolution TEM (HRTEM) images were recorded by a JEM-2100F electron microscope operated at 200 kV. Nitrogen adsorption and desorption isotherms were measured at Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). All samples were degassed at 250°C for 3 h prior to the nitrogen-adsorption measurements. The BET surface area was determined by a multipoint Brunauer-Emmett-Teller (BET) method to analyze the adsorption data in the relative pressure (P/P_0) range from 0.5 to 1. The pore size was obtained from the adsorption branch of the nitrogen isotherms using the Barrett-Joyner-Halenda method. X-ray diffraction (XRD) of two samples were tested on a Bruker D8 ADVANCE powder diffract meter at Cu K α (λ = 0.154056 nm) in the 2θ range of 10-70°. The scanning rate is 4°/min. UV-vis diffuse reflectance spectroscopy was recorded on a spectrophotometer (Hitachi UV-310, Shimadzu) using a BaSO4 as a reflectance reference material in the range of 300-1000 nm. Photoluminescence (PL) spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer (excitation wavelength of 380 nm). The Raman measurements were performed using a LABRAM HR micro-Raman spectrometer (Kaiser Optical Systems Inc., Arbor, MI, USA), in which the Raman spectra are excited by an Invictus 785 nm NIR laser (Kaiser Optical Systems Inc., Ann Arbor, MI, USA). X-ray photoelectron spectroscopy (XPS) tests were implemented on a Thermo Scientific ESCALAB 250 spectrometer with a monochromatic AI Kg source (hv= 1486.6 eV). The hydrophobicity of all the samples was measured using a contact angle meter (SL200B, Solon, China). The CO2 adsorption isotherms of all the samples were carried out on a Micromeritics ASAP 2020 static volumetric analyzer at room temperature. Prior to adsorption analysis, each sample was dried in an oven at 150°C for 6 h and degassed for 4 h below 26.7 Pa at 150 °C.

Photo-electrochemical Measurements

Photo-electrochemical measurements were conducted bv an electrochemical workstation (Shanghai ChenHua Instrument, Inc.) in a standard three-electrode system. The platinum electrode and the saturated Ag/AgCl electrode were respectively used as the counter electrode and reference electrode. The working electrode was prepared by coating the sample solution on a 1.5 cm × 1.5 cm fluorine-doped tin oxide (FTO) glass substrate purged with N2. 0.2M Na2SO4 (pH = 7) was used as the electrolyte. A 300 W Xe lamp with a 400 nm cut-off filter was used as a light source. The measured potentials vs. Ag/AgCl were converted to reversible hydrogen electrode (RHE) scale via the Nernst equation $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059 pH$. Transient photocurrent measurements were conducted at a constant bias (10mV vs. RHE) with chopped AM 1.5 G illumination. Mott-Schottky plots were carried out at a fixed frequency of 5 kHz in dark. Electrochemical impedance spectra (EIS)

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were measured in the frequency range of 10 to 10^6 Hz with an AC voltage amplitude of 5 mV.

Photocatalytic Activity Evaluation

The carbon dioxide photocatalytic reduction is typically carried out in a gastight circulation system of a reactor (volume: 160 ml) topped with optical quartz glass available from Perfect Light Company (China, Beijing). In a typical procedure, 20 mg of sample was homogeneously dispersed on the bottom of the quartz reactor, fixed at 3.5 cm × 3.5 cm glass substrate. Then, high purity CO₂ (99.99%) gas monitored by a mass flow controller was passed through a water bubbler to produce a mixture of CO2 and water vapor. A 300 W Xenon-arc lamp (Zolix, Beijing) with a 400 nm cut-off filter was used as the light source. The temperature of the reactor was controlled at 25 °C by cooling water circulation. The gas products were analyzed by a gas chromatograph (GC-7900, Techcomp Corp. China) with a flame ionization detector (FID) equipped with an OV-101 reference column and a TDX-01 packed column. The product is quantified using external calibration standards with a calibration curve. During each measurement, 1 ml of gas product was periodically withdrawn from the reactor and analyzed by the gas chromatography (GC-7900, Techcomp Corp. China). The cycling test of CQDs/g-C₃N₄ was conducted for 5 consecutive days with 5-hour irradiation each day. After each cycle, the photocatalyst was heated at 100 °C for 2 hours to remove the potential surface adsorption of CO and CH₄.

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Besides light harvesting and charge separation, nonpolar carbon quantum dots dopant could efficiently increase CO_2 adsorption, enhancing reaction kinetics and changing CO_2 photoreduction pathways for hydrocarbon generation.



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Surface nonpolarization on g-C₃N₄ for improved CO₂ photoreduction by decoration of sensitized quantum dots