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Introduction

Increasing fossil fuel consumption in human activities has led to a global energy crisis and high emissions of carbon dioxide, which contribute more than 60% to global warming.1-3 Sustainable CO₂ reduction into useful chemicals with solar energy as a power source is regarded as an economic, safe, and clean avenue to combat these issues simultaneously.4-6 As one of the main products from CO₂ reduction, CO has aroused great attention because it is regarded as one of the most valuable raw materials of syngas.^{7,8} As we know, syngas is an important feedstock for the generation of synthetic fuels and industrial chemicals, potentially replacing traditional production technology that usually relies on the reformation of fossil fuels.8 Therefore, exploring a cheap, efficient, and durable photocatalytic system for converting CO2 into CO is crucial for a global new energy program in a clean and sustainable way. Coupling the CO₂ reductive process with a matched water

Ultrasmall C-TiO_{2-x} nanoparticle/g-C₃N₄ composite for CO₂ photoreduction with high efficiency and selectivity^{\dagger}

Jie Zhou,^a Han Wu,^a Chun-Yi Sun,^{*a} Cheng-Ying Hu,^a Xin-Long Wang, ^b*^a Zhen-Hui Kang ^b*^b and Zhong-Min Su ^b^a

The photoreduction of CO₂ to CO offers a promising sustainable and clean approach for a global new energy program. Coupling this reductive process with a matched water photo-oxidation pathway is an attractive avenue to accelerate the half-reaction of CO₂ reduction. Herein, we propose a three-component photocatalyst design strategy for reducing CO₂ to CO coupled with water oxidation *via* a two-electron/two-step pathway. Employing polyoxotitanium ($[Ti_{17}O_{24}(OPr^i)_{20}]$) as a titanium source, ultrasmall TiO_{2-x} nanoparticles coated with ultrathin carbon layers (C-TiO_{2-x}) were fabricated and loaded on to a g-C₃N₄ matrix through chemical bonding (C-TiO_{2-x}@g-C₃N₄) for the first time. The optimized C-TiO_{2-x}@g-C₃N₄ photocatalyst showed a very high activity of 12.30 mmol g⁻¹ (204.96 mmol g_{TiO₂}⁻¹) CO generation within 60 h visible-light irradiation, which represents the highest CO production rate to date among the reported TiO₂-based materials under similar conditions. The excellent adsorption capability of C-TiO_{2-x}@g-C₃N₄ for photons, H⁺ protons, and CO₂ molecules together with efficient charge separation and the two-electron/two-step oxidative pathway lead to the high reactivity.

oxidation pathway is a promising avenue to boost the reductive half-reaction activity.⁹ For water oxidation, the challenge mainly lie in O₂ release, which usually involves a four-proton coupled four-electron transfer process.¹⁰ Although the four-electron process is thermodynamically more favorable than the two-electron way, two electrons participating in the process is kinetically favored.¹¹ A stepwise two-electron/two-step pathway is proposed as an optimum approach between the thermodynamic and kinetic constraints for water oxidation.⁹ A significant issue toward achieving the stepwise pathway is to incorporate a co-catalyst to decompose H₂O₂ to O₂ and H₂O.

As a classical photocatalyst, titanium dioxide (TiO_2) has been widely used in photocatalysis.12-14 Benefiting from its excellent stability, cheap, and favorable band edges, TiO₂ is also a popular semiconductor photocatalyst in CO₂ reduction.¹⁵ It is worth noting that TiO₂ is one of the few photocatalysts able to reduce CO₂ into CO under H₂O conditions, albeit with a low efficiency (below several micromole).15-18 Significant efforts have been devoted to enhancing the performance of TiO₂, mainly focused on increasing the harvesting of visible light and charge separation.¹⁵ Unfortunately, the rate of reduction of CO₂ to CO is still limited to tens of micromoles per hour.¹⁹ For CO₂ photoreduction, the current TiO2-based catalysts still face several challenges: (i) a low proportion of active surface area (random aggregates of nanoparticles or crystals with a large size); (ii) poor stability of the doping and sensitization agents; (iii) negligible hydrogen proton adsorption, which is necessary to trigger CO2 reduction reactions via a proton-coupled

^aNational & Local United Engineering Laboratory for Power Batteries, Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun, 130024 Jilin, People's Republic of China. E-mail: suncy009@nenu.edu.cn; wangxl824@nenu.edu.cn

^bJiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, 199 Ren'ai Road, Suzhou 215123, Jiangsu, China. E-mail: zhkang@suda.edu.cn

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Paper

pathway; (iv) an insufficient oxidation pathway. Herein, we propose a design strategy involving a highly durable TiO₂-based three-component photocatalyst for the efficient and selective generation of CO with H₂O and visible-light irradiation, comprising coupling an active CO₂ reductive photocatalyst with an efficient water oxidation catalyst via a two-electron/two-step oxidative pathway. For water oxidation, we adopted a low-cost graphitic carbon nitride $(g-C_3N_4)$ coupled amorphous carbon layer as the catalyst. By cooperating with carbon dots, this material has exhibited excellent performance in water splitting via a two-electron pathway.¹¹ Furthermore, the stable mesoporous material of g-C₃N₄ is a good substrate for the dispersion of TiO₂ nanoparticles and as an adsorbent for CO₂ molecules²⁰ and H⁺ protons. An ultrasmall black TiO₂ (TiO_{2-x}) nanoparticlecoated carbon layer was designed for the photocatalyst for converting CO_2 to CO_2 based on the following consideration: (i) TiO_{2-x} possesses excellent visible-light adsorption ability and could be a rich electron source for the reduction reaction; (ii) its ultrasmall size guarantees a large reactive surface area; (iii) the carbon coating could serve as an electron reservoir to promote electron transfer and boost CO2 chemisorption.21 Further, the spatial separation of reductive and oxidative sites may exclude the possibility of re-oxidation of reduction products.

During this study, polyoxotitanium [Ti₁₇O₂₄(OPrⁱ)₂₀]²² was selected as a precursor of TiO₂ for its carbon-rich and smallsized-cluster structure. Through heating a mixture of [Ti₁₇- $O_{24}(OPr^{i})_{20}$] and g- $C_{3}N_{4}$, the targeted three-component composite C-TiO_{2-x}@g-C₃N₄ was obtained, in which TiO_{2-x} nanoparticles (5-8 nm) were coated by ultrathin carbon layers. The resultant C-TiO_{2-x}@g-C₃N₄ material exhibited significant adsorption capabilities for photons, CO₂, and H⁺ protons. CO₂ photoreduction experiments under visible-light irradiation in water vapor showed around 12.30 mmol g^{-1} (204.96 mmol $g_{TiO_2}^{-1}$) CO generation within 60 h reaction (Fig. 1). This generation rate is one order higher than most TiO₂-based catalyst and presents the highest amount of CO production to date among the reported TiO₂-based materials under similar conditions. Mechanism studies revealed that the reductive and oxidative sites were spatially separated on C-TiO_{2-x} and g-C₃N₄.



Fig. 1 Schematic illustration on the photocatalytic process in the system of $C-TiO_{2-x}@g-C_3N_4$.

In addition, its excellent proton-accumulation capability (300 μ mol g⁻¹ min⁻¹) provided a reliable guarantee for CO₂ reduction through a low-energy proton-coupled pathway. Under the assistance of the carbon layer, water oxidation was performed *via* an efficient two-electron/two-step pathway. The thin carbon layer served as an electron reservoir and played a crucial role in facilitating the generated electron–hole (e–h⁺) pairs separation.

Experimental section

Synthesis procedure of the photocatalysts

All the reagents and solvents used in the synthesis and photocatalysis were purchased from commercial sources and used without pretreatment.

Synthesis of C-TiO_{2-x}

To prepare C-TiO_{2-x}, $[Ti_{17}O_{24}(OPr^i)_{20}]$ was synthesized first. Titanium isopropoxide (8.4 mL, 0.0285 mol) was added to acetic acid (2.1 mL, 0.037 mol). Then, the mixture was transferred and sealed in a Teflon reactor with 23 mL capacity at 150 °C over 5 days. After cooling to room temperature, a white powder of $[Ti_{17}O_{24}(OPr^i)_{20}]$ was obtained with a yield of 38.6%.²⁴ C-TiO_{2-x} was prepared by adding $[Ti_{17}O_{24}(OPr^i)_{20}]$ (200 mg) into diacetone (10 mL) and then heating to 80 °C until the solution became clear. Then the temperature was kept at 60 °C to evaporate most diacetone to form a slurry. The slurry was heated to 350 °C with a heating rate of 10 °C min⁻¹ in a muffle furnace with a cap for 2 h. After cooling to room temperature, black powder was obtained.

Fabrication of the C-TiO_{2-x}@g-C₃N₄ composites

The used g-C₃N₄ was obtained using a thermal polycondensation method, which was prepared by heating urea in an alumina crucible with a cover to 550 °C with a heating rate of 10 °C min⁻¹ in a muffle furnace for 2 h. After allowing to naturally cool to room temperature, g-C₃N₄ with a faint yellow color was obtained and then ground into powder. The C-TiO_{2-x}@g-C₃N₄ composite photocatalyst was prepared as follows: first, an appropriate amount of [Ti₁₇O₂₄(OPrⁱ)₂₀] was added into diacetone solution and heated to 80 °C until the solution became clear. Then, the right amount of g-C₃N₄ in acetonitrile solution was added. After ultrasonication for 60 min, the above mixture was transferred into an alumina crucible with a cover under stirring. A water bath of 60 °C was used to evaporate the solvent to form a slurry. Finally, the mixture was heated to 350 °C with a heating rate of 10 °C min⁻¹ in a muffle furnace for 2 h. A brown or grey solid was obtained and then ground into powder.

Photocurrent measurements

Photocurrent measurements were performed on an electrochemical workstation (CHI660e, CH Instruments, Inc., USA) with a three-electrode configuration. Our sample, Ag/AgCl electrode, and Pt-wire electrode were employed as the working, reference, and counter electrodes, respectively. Irradiation was carried out using a 300 W xenon lamp. The Na₂SO₄ solution (0.1 M) was used as the electrolyte. The working electrodes (1 cm \times 1 cm) were prepared by spreading aqueous slurries of the various samples on an ITO glass substrate.

Electrochemical impedance measurements

Electrochemical impedance spectroscopy was performed on g-C₃N₄, C-TiO_{2-x}, and C-TiO_{2-x}@g-C₃N₄-3. To obtain anodes materials, the above samples were mixed with conductive carbon black (CB) and poly(vinylidene fluoride) (PVDF), respectively, with a mass ratio of 7:2:1. Then, the obtained anodes materials were dispersed uniformly into N-methyl-2pyrrolidinone (NMP). After that, a paste with appropriate viscosity was formed. Then, the paste was coated on copper flakes mildly and vacuum-dried at 50 °C for 24 h. A button cell was assembled with the sample anode, Li cathode, and approximately 50 μ L typical electrolyte, here 1 M LiPF₆ in diethyl carbonate (DEC) and ethylene carbonate (EC) with a ratio of 50:50 (w/w). The electrochemical workstation produced by Princeton Applied Research (Germany) was employed to record the electrochemical impedance spectroscopy of the batteries at constant ambient temperature. The frequency limits were set at 10^5 to 10^{-2} Hz with an amplitude of 5 mV.

Cyclic voltammetry

Cyclic voltammetry tests of g- C_3N_4 , C-TiO_{2-x}@g- C_3N_4 -3, and C-TiO_{2-x} were performed using an electrochemical workstation (CHI 760e, China) with a three-electrode system. The working electrode was a GC electrode (d = 3 mm), with platinum wire as the auxiliary electrode and an Ag/AgCl electrode as the reference electrode. First, 5 mg of the samples and 5 mg of carbon black (Vulcan XC-72R) were dispersed in 0.6 mL of solution containing 300 µL of 0.5 wt% Nafion solution, 150 µL of water and 150 µL of ethanol, followed by sonication for 60 min until a suspension was formed. After sonication, 5 µL of the asprepared suspension was drop-cast onto the GC electrode. Then, the working electrode was dried spontaneously under ambient temperature. The final mass loading of the catalysts was about 0.59 mg cm⁻². The electrochemical measurements were tested in methyl cyanide solution.

Photocatalytic activity measurements

The as-prepared C-TiO_{2-x}@g-C₃N₄ catalyst (1 mg) was dispersed in a mixture of 2 mL deionized water and ethanol (v/v = 1 : 1) under sonication. After heating to 70 °C, the suspension was dropcoated onto a glass of 1 cm × 2.5 cm. Then, the glass was moved to a quartz photoreactor and 0.1 mL deionized water was added to keep the glass surrounded by water vapor. After bubbling through with water-vapor-saturated CO₂ for 30 min, the quartz photoreactor was put into a water-cooled reactor and irradiated under visible light using a PLS-SXE300 Xe lamp with a 420 nm cutoff filter. To detect the gas product of CO, 500 μ L gas in the middle of the test tube was taken out by syringe and injected into FID detector, using argon as carrier gas. The volume of the CO produced was calculated by comparing the integrated area of the signals of CO with a calibration curve. The injector and detector temperatures were set to 60 °C. The retention time of hydrogen was 1.9 min. To detect the formation of hydrogen from the reaction mixture, 1000 μ L of the headspace of the test tube was taken out by syringe and injected into a TCD detector, using a 5 Å molecular sieve column and argon as the carrier gas and reference gas. The volume of the hydrogen produced was calculated by comparing the integrated area of the signals of hydrogen with a calibration curve. The injector and detector temperatures were set to 60 °C. The retention time of hydrogen was 0.7 min.

Electron-transfer number (n) calculation

The electron-transfer number (n) was calculated as follows:

$$n = 4I_{\rm disk}/(I_{\rm disk} + I_{\rm ring}/N)$$

where *N* is the RRDE collection efficiency, measured to be 0.4 using the system by Liu *et al.*⁹ In detail, the RRDE electrode was dipped into 0.01 mol L⁻¹ K₃[Fe(CN)₆] in 0.1 mol L⁻¹ KCl solution and rotated under different rotation rates ($\omega = 400$, 900, 1600 2500 rpm). The disk potential E_{disk} was scanned from 0.2 V to -1.0 V *vs.* Ag/AgCl at a scan rate of 10 mV s⁻¹, with the ring potential E_{ring} fixed to 0.454 V *vs.* Ag/AgCl (the reduced product [Fe(CN)₆]⁴⁻ can be oxidized at this potential), and the current-potential voltammograms were then recorded during the electrode rotation. The RRDE measurement is shown in Fig. S13 and S14.[†] The ratio of $I_{\text{ring}}/I_{\text{disk}}$ was almost constant under various ω . The calculation method of the electron-transfer number (*n*) was also considered by Liu *et al.*⁹ The result of the calculation was that *n* equals 2.

Results and discussion

Synthesis and structural analysis of the C-TiO $_{2-x}$ @g-C $_3N_4$ composite

For the synthesis of the targeted three-component photocatalyst, g-C₃N₄ (ref. 23) and $[Ti_{17}O_{24}(OPr^{i})_{20}]^{22,24}$ were first prepared following the reported literature. Through one-pot pyrolyzing the mixtures of [Ti₁₇O₂₄(OPrⁱ)₂₀] and g-C₃N₄ with different weight ratios under 350 °C and an air atmosphere, the three-component composites of C-TiO_{2-x}@g-C₃N₄ with different contents of C- TiO_{2-x} were fabricated (Fig. 2). Bare C-TiO_{2-x} was obtained by directly heating [Ti₁₇O₂₄(OPrⁱ)₂₀] under similar conditions. Their photographs are shown in Fig. 3g. As determined by inductively coupled plasma mass spectrometry (ICP-MS), the corresponding TiO_{2-x} content in the resultant C-TiO_{2-x}@g-C₃N₄ composites was respectively 1 wt%, 4.5 wt%, 6 wt%, and 10 wt% based on the Ti content and the samples were labeled as C-TiO_{2-x}@g-C₃N₄-1, C- $TiO_{2-x}@g-C_3N_4-2$, C-T $IO_{2-x}@g-C_3N_4-3$, and C-T $IO_{2-x}@g-C_3N_4-4$. The powder X-ray diffraction (PXRD) patterns of the as-prepared g-C₃N₄, C-TiO_{2-x}, and C-TiO_{2-x}@g-C₃N₄ composites (Fig. 3f) showed that the pure $C-TiO_{2-x}$ possessed similar patterns with anatase TiO₂. C-TiO_{2-x}@g-C₃N₄ composites exhibited the characteristic PXRD peaks of both g-C₃N₄ and C-TiO_{2-x}, with the intensity of the characteristic peaks of $C-TiO_{2-x}$ increasing with the enhancement of C-TiO_{2-x} content (Fig. S1[†]).

SEM and TEM images of C-TiO_{2-x}@g-C₃N₄ composite were taken to directly analyze its structure (Fig. 3a–d). As shown in the SEM image (Fig. 3a), the layered structure of g-C₃N₄ was



Fig. 2 Schematic illustration of the fabrication of C-TiO_{2-x}@g-C₃N₄ composites. The cluster in green represents $[Ti_{17}O_{24}(OPr^{i})_{20}]$, the layer structure is representative of $g-C_3N_4$, the ball in yellow is on behalf of TiO_{2-x} and the fullerene-like structure with grey shell is presented for the carbon layer.

maintained in C-TiO_{2-x}@g-C₃N₄. Energy dispersive X-ray (EDX) elemental mappings and the spectrum (Fig. 3b) of the selected area showed that the Ti and O elements were highly dispersed on the g-C₃N₄ surface. TEM images of C-TiO_{2-x}@g-C₃N₄ in Fig. 3c reveal the size of TiO_{2-x} nanoparticles were mainly distributed between 6 and 9 nm. Compared with the 590 nm particle size of TiO₂ in TiO₂@g-C₃N₄ (Fig. S2[†]), which was synthesized by a traditional hydrothermal method,¹³ the size of TiO_{2-x} in C-TiO_{2-x}@g-C₃N₄ was reduced by two orders of magnitude. Therefore, employing polyoxotitanate as a Ti source

could be an efficient and effective method to obtain ultrasmall TiO_{2-x} nanoparticle-based composite materials. Highresolution TEM (HRTEM) was employed to identify the phase of the TiO_{2-x} nanoparticles in the C- TiO_{2-x} @g-C₃N₄ composite. As shown in Fig. 3d, the distance between the adjacent lattice planes was 0.35 nm along [101] direction, which is a typical lattice plane distance for anatase TiO2.20 The structure of the TiO_{2-r}-coated amorphous carbon layer can be clearly observed from Fig. 3e. Furthermore, the carbon layer was the link connecting $g-C_3N_4$ and TiO_{2-x} nanoparticles. For the electron pool character of the carbon layer, such a structure will facilitate photoinduced electron transfer. In order to illuminate the source of amorphous carbon, an HRTEM image of bare C- TiO_{2-x} was collected. A clear carbon coating around TiO_{2-x} nanoparticles was found, which strongly excluded the possibility of the carbon source being from g-C₃N₄.

X-ray photoelectron spectroscopy (XPS) was further employed to determine the atomic valence states and bonding environment in C-TiO_{2-x} and C-TiO_{2-x}@g-C₃N₄. Fig. 3 shows the XPS of C-TiO_{2-x}, in which the high-resolution spectra of Ti 2p located at 465.0, 464.2, 459.2, and 458.7 eV could be assigned to $Ti^{4+} 2p_{1/2}$, $Ti^{3+} 2p_{1/2}$, $Ti^{4+} 2p_{3/2}$, and $Ti^{3+} 2p_{3/2}$, respectively.²⁵ The C 1s had three peaks at 284.7, 286.1, and 288.5 eV, corresponding to C-C, C-O, and C-O-Ti,26 respectively, which provided strong evidence for TiO_{2-x} connecting to the carbon layer with chemical bonds. The O 1s had two peaks located at 531.2 eV and 529.5 eV, attributing to the O-H and Ti-O bonds,²⁷ respectively. The formation of Ti³⁺ and C might originate from the reduction effect of H₂ and CO²⁸ gas, which may come from the hydrolysis and decomposition of diacetone under high temperature. Control experiments were carried out to illuminate these issues. Without diacetone, only white TiO2 was obtained, implying the indispensable role of diacetone during the formation of C-TiO_{2-x}. When using titanium isoproposide to replace $[Ti_{17}O_{24}(OPr^{i})_{20}]$, yellow TiO_{2} emerged, revealing



Fig. 3 Morphology, microstructure, and optical property. (a–d) SEM, EDX elemental mappings, TEM with the size distribution of C-TiO_{2-x} and HRTEM images of C-TiO_{2-x}@g-C₃N₄-3. (e) HRTEM images of C-TiO_{2-x}. (f) PXRD of g-C₃N₄, C-TiO_{2-x}@g-C₃N₄-3, C-TiO_{2-x}, and anatase TiO₂. (g) UV-visible adsorption spectra and photographs of C-TiO_{2-x}@g-C₃N₄ composites, C-TiO_{2-x} and g-C₃N₄.

 $[Ti_{17}O_{24}(OPr^{i})_{20}]$ clusters may be the main source of amorphous carbon.

The XPS of C-TiO_{2-x}@g-C₃N₄ is presented in Fig. S3,† and the high-resolution XPS results of C 1s, N 1s, O 1s, and Ti 2p are exhibited in Fig. 4a-d. Compared to the peaks of Ti 2p in pure C- TiO_{2-r} (Fig. S4[†]), the corresponding peaks in C-TiO_{2-r}@g-C₃N₄ are a little shifted, centering around 464.2, 463.3, 458.3, and 457.8 eV. The O 1s of C-TiO_{2-x}(a)g-C₃N₄ has two peaks at 532.3 and 529.5 eV, ascribed to the O-H group and Ti-O bond. Compared with C-TiO_{2-x}, the peak of O-H group is shifted a little, which should be attributed to the chemical environment change.29 The C 1s XPS spectrum exhibits anisomerous peaks with an obvious shoulder. After fitting, five peaks could be observed with the binding energies of 289.9, 288.6, 287.6, 286.0, and 284.6 eV. The peaks located at 287.6 and 286.0 eV are attributed to hybridized carbon atoms containing the C-(N)₃ and N-C-N group of g-C₃N₄, while the one at 284.6 eV is assigned to the C-C coordination, originating from adventitious carbon of the XPS instrument itself.30 The peak emerging at 288.6 eV is matched with the Ti-O-C. The left peak at 289.9 eV is

N 1s

O 1s

537

a.u.

402 399 396 Binding Energy / eV

534 531 528 Binding Energy / eV

529.5eV Ti-O

C-TIO, @g-C.N.

2.0 Time (h-1)

TiO.

75 100 Z'(ohm) 125 150

- g-C,N

393

52

Fig. 4 XPS, adsorption, and photoelectrical properties. (a–d) XPS of C-TiO_{2-x}@g-C₃N₄. (e) CO₂ adsorption of C-TiO_{2-x}@g-C₃N₄ composites and g-C₃N₄. (f) H⁺ adsorption of C-TiO_{2-x}@g-C₃N₄-3, and g-C₃N₄. (g and h), transient photocurrent responses and electrochemical impedance spectroscopy of C-TiO_{2-x}@g-C₃N₄, g-C₃N₄, C-TiO_{2-x}, and TiO₂.

25 50

1.0



Adsorption study

The N₂ adsorption behavior was measured to reveal the change in surface of the C-TiO_{2-x}@g-C₃N₄ composites. The adsorptiondesorption isotherms at 77 K (Fig. S6[†]) of C-TiO_{2-x}@g-C₃N₄-2, 3, 4 showed a gradual decrease in BET surface areas (S_{BET}) with values of 94.1, 87.2, and 77.8 m² g⁻¹, respectively, while the S_{BET} of bare $g-C_3N_4$ was relatively high (99.4, m² g⁻¹). Compared with the S_{BET} of bare g-C₃N₄, the decrease in composite materials accounted for the loading of C-TiO_{2-x}, whereby with the increase in loading content, the decrement enhances. The CO2 adsorption ability of C-TiO_{2-x}@g-C₃N₄ was also measured. As shown in Fig. 4e, the maximum CO2 uptake at 273 K for C-TiO2-x@g-C3N4-2, 3, 4 was 17.7, 15.9, and 9.2 cm³ g⁻¹, respectively, which are different to that of pure g- C_3N_4 (11.5 cm³ g⁻¹). In contrast to N₂ adsorption, the improvement in CO₂ adsorption of C-TiO_{2-x}@g-C₃N₄-2 and 3 probably comes from the increased interaction of $C-TiO_{2-x}$ with CO_2 molecules, while the decrease in C-TiO_{2-x}@g-C₃N₄-4 may be due to the sharply decreased surface area.

As H⁺ protons have a significant influence on the CO₂ reduction activity, the H⁺ proton adsorption capability of C-TiO_{2-x}@g-C₃N₄ was studied with HCl as the H⁺ source. The H⁺ adsorption curve of C-TiO_{2-x}@g-C₃N₄ is presented in Fig. 4f. It was found that at the initial 5 min, 1.5 mmol g⁻¹ H⁺ was adsorbed by C-TiO_{2-x}@g-C₃N₄, corresponding to 300 µmol g⁻¹ min⁻¹. After 3 h, it reached saturated adsorption and the amount was 4.46 mmol g⁻¹, which is 2.8-fold higher than bare g-C₃N₄ (1.55 mmol g⁻¹). Such a high protons accumulation capability of C-TiO_{2-x}@g-C₃N₄ may significantly boost the reductive performance of C-TiO_{2-x}@g-C₃N₄ *via* the low-energy proton-coupled pathway.

Optical property

UV-Visible adsorption spectra can provide insightful information into the interactions of photocatalytic materials with photons of different energy. Fig. 3g shows the optical absorption spectra of g-C₃N₄, C-TiO_{2-x} and their composite materials. Pure C-TiO_{2-x} has strong absorption within the whole visible light, while bare g-C₃N₄ was only able to absorb light with $\lambda_m \leq$ 450 nm. All C-TiO_{2-x}@g-C₃N₄ composites showed an obvious light absorption from 300 to 800 nm, and with increase in doping concentration of TiO_{2-x}, the absorption intensity region from 460 to 800 nm was improved. Therefore, we could expect that the C-TiO_{2-x}@g-C₃N₄ may exhibit an outstanding performance in visible-light photocatalysis.

Electrochemical property

As for heterojunction semiconductor, the energy level of each component has a significant influence on the catalytic

C 1s

Ti 2p

290 285 Binding Energy / eV

465 Binding En

C-TiO, @g-C,N,-4

C-TIO, @g-C,N,-3

C-TIO, @g-C,N_-

C-TiO₂₄

40

ergy / eV

TTTER BERGER

0.4 0.6 live pressure (p/p_e)

— C-TIO₂₋₁@g-C₃N

80 100

g-C,N

280

457.8eV

a.u.

ntensity

uptake (cm³.g.⁴ STP)

co'

reactivity. The energy level of the synthesized g-C₃N₄ was well studied in our former work³³ and the band gap was 2.73 eV, with the conduction band energy (E_{CB}) and the valence band energy (E_{VB}) at -0.75 eV and +1.98 eV, respectively, *vs.* a normal hydrogen electrode (NHE). For our materials, E_{VB} was determined from cyclic voltammograms (CV, Fig. S7†) and E_{CB} was calculated based on the optical band gap (E_g).⁹ Using analyses and calculations based on Fig. S8,† the E_{VB} energy of C-TiO_{2-x} was 1.63 eV. E_g was estimated from the Tauc plot (Fig. S8†), which was determined to be 2.18 eV. According to the formula $E_{CB} = E_{VB} - E_g$, the E_{CB} of C-TiO_{2-x} was estimated to be -0.55 V. The energy levels of both g-C₃N₄ and C-TiO_{2-x} were appropriate for reducing CO₂ to CO and water oxidation.

Given that charge separation has a significant effect on the redox reaction occurring at a photocatalyst surface, the transient photocurrent responses and electrochemical impedance spectroscopy (EIS) of C-TiO_{2-x}@g-C₃N₄-3, g-C₃N₄, and C-TiO_{2-x} were collected.34,35 In Fig. 4g, the photocurrent value of C- TiO_{2-x} (a)g-C₃N₄-3 can be seen to be rapidly elevated with the light turned on and then it gradually climbs up to the highest current level (up to 0.83 μ A cm⁻²) during irradiation. When the irradiation was turned off, a sharp decrease emerged. This switch loop could be implemented repeatedly multiple times. A similar phenomenon occurred with pure $C-TiO_{2-x}$ and bare g-C₃N₄ materials during on-off irradiation; however, the photocurrent densities of them were 4-fold and 2.5-fold lower than C- TiO_{2-x} @g-C₃N₄-3. Additionally, the photocurrent value of pure TiO_2 was 2-fold lower than that of C-TiO_{2-x}, illuminating that the C doping plays a crucial role in facilitating the charge separation generated by TiO_{2-x} .

Under visible light irradiation, the EIS of C-TiO_{2-x}@g-C₃N₄-3 heterjunction, bare g-C₃N₄, and C-TiO_{2-x} and TiO₂ were measured. As shown in Fig. 4h, the charge-transfer resistance (R_{ct}) of C-TiO_{2-x}@g-C₃N₄-3 was 47 Ω cm⁻², which was considerably lower than those of bare C-TiO_{2-x} (108 Ω cm⁻²) and g-C₃N₄ (82 Ω cm⁻²). These results indicate that the C-TiO_{2-x}@g-C₃N₄-3 composite performed a higher separation efficiency of the photogenerated charge carriers and a relatively lower recombination rate of electron–hole pairs under visible light. Simultaneously, R_{ct} of pure TiO₂ was 172 Ω cm⁻², which was 1.6-fold higher than C-TiO_{2-x}. This further revealed that the carbon layer plays a positive role in promoting photoinduced charge separation.

Photocatalytic CO₂ reduction study

The CO₂ reduction experiment was performed following the photocatalytic condition using (Au, Cu)/TiO₂ as the catalyst reported by Neatu and co-worker, in which only light, CO₂, and H₂O were used in the system.³⁶ Our experiment was carried out employing C-TiO_{2-x}@g-C₃N₄ as a photocatalyst under a visible-light-driven system ($\lambda \ge 420$ nm) with CO₂ atmosphere and water vapor. As a control, the photocatalytic performances of bare g-C₃N₄ and C-TiO_{2-x} were investigated. Fig. 5a shows that CO gas was generated as the main reductive reaction products after 12 h irradiation. Clearly, pure C-TiO_{2-x} showed around 0.575 mmol g⁻¹ CO and 0.0252 mmol g⁻¹ H₂ while bare g-C₃N₄ presented 0.164 mmol g⁻¹ CO and 0.0144 mmol g⁻¹ H₂

(hydrogen production is shown in Fig. S9[†]). Compared with pure $g-C_3N_4$ and $C-TiO_{2-x}$, a higher photocatalytic activity was achieved by C-TiO2_x@g-C3N4 composites and the content of C- TiO_{2-x} showed a considerable influence on the photocatalytic activity: (I) the catalyst with 1% content of Ti (C-TiO_{2-x}@g-C₃N₄-1) showed an obvious improvement in CO generation (up to 0.412 mmol g^{-1}), while H₂ evolution was almost unchanged $(0.0181 \text{ mmol g}^{-1})$, (II) enhancing the amount of C-TiO_{2-r} to 6 wt% of Ti (C-TiO_{2-x}@g-C₃N₄-3) resulted in an evident enhancement in both yield and selectivity. CO generation was around 5 and 15 times higher than that of bare C-TiO_{2-x} and g- C_3N_4 , respectively, keeping in 2.460 mmol g^{-1} , while the yield of H₂ was scarcely increased to about 0.0741 mmol g⁻¹, corresponding to 97% selectivity of CO. When normalizing the quality of TiO₂, the generation of CO in C-TiO_{2-x}@g-C₃N₄-3 remained at 40.995 mmol $g_{TiO_2}^{-1}$, (III) further enhancement of the C-TiO_{2-x} content (C-TiO_{2-x}@g-C₃N₄-4) led to a decrease in CO generation, which might result from the decreased CO_2 adsorption capacity. These results reveal that the combination of C-TiO_{2-x} with g-C₃N₄ led to a superior enhancement in both production and selectivity toward CO and showed that the optimal catalyst was C-TiO_{2-x}@g-C₃N₄-3.

To illuminate the source of generated CO, isotopic experiments were carried out using ${}^{13}\text{CO}_2$ as the gas atmosphere 33 under similar photocatalytic conditions. As exhibited in Fig. 5g, peaks at 1.88 min and 13.08 min with m/z 29 and 45 were assigned to ${}^{13}\text{CO}$ and ${}^{13}\text{CO}_2$, respectively. No signal at m/z 28



Fig. 5 Photocatalytic performance for CO generation. (a) Different catalysts under 12 h visible-light irradiation. (b) Different catalysts under 12 h visible light or whole light irradiation. (c) The generation in (b) after normalizing the quality of TiO_{2-x} . (d) Recycling experiments using C-TiO_{2-x}@g-C₃N₄-3 as catalyst. (e) Time course of the CO and H₂ with the C-TiO_{2-x}@g-C₃N₄-3 as catalyst under 12 h irradiation. (f) GC-Mass result of isotopic experiment under ¹³CO₂ atmosphere. (g) The corresponding GC spectrum of (f).

was found (Fig. 5f). This information provided unambiguous evidence that the produced CO originated from the photoreduction of CO_2 rather than from the decomposition of any other organic species in the system.

In order to further reveal the importance of the composite structure of C-TiO_{2-r}@g-C₃N₄ in CO₂ photoreduction, control experiments employing different TiO2-based composites as photocatalysts were carried out under similar conditions (Table 1). When using commercial P25 TiO_2 (entry 2) as the photocatalyst, around 0.0301 mmol g^{-1} CO was generated, which was about 20fold lower than that of C-TiO_{2-x}. When reducing TiO₂ to TiO_{2-x}, the generation of CO was enhanced to 0.255 mmol g^{-1} (entry 3); however, this was still 2.3-fold lower than that of $C-TiO_{2-x}$. These results implied the carbon layer played a positive part in TiO₂ in CO_2 reduction. With TiO₂@g-C₃N₄ (entry 4) as the catalyst, made from P25 and g-C₃N₄, the yield was higher than bare P25 but was 68 times lower than that from C-TiO_{2-x}@g-C₃N₄-3. Replacing P25 with titanium isopropoxide as the starting material, the resultant TiO₂(ag-C₃N₄ (entry 5) exhibited a sharply increased reactivity, with up to 0.274 mmol g^{-1} CO generation. However, this reactivity was one order of magnitude lower than that of C-TiO_{2-x}@g-C₃N₄-3. These results illuminated that the carbon layer and excellent light adsorption of TiO_{2-x} play a pivotal role in the photocatalysis. Using black TiO₂ nanobelts-doped g-C₃N₄ (ref. 25) as the catalyst (entry 6), 0.535 mmol g^{-1} CO was produced, which was 4.6-fold lower than that from C-TiO_{2-x}@g-C₃N₄-3, revealing a small size of nanoparticles was indispensable. Besides these TiO2-based catalysts, the CO generation rate of $C-TiO_{2-r}$ (a)g-C₃N₄ was one order higher than most the reported TiO2-based catalysts and it outperformed any other reported TiO2-based material under similar conditions (Table S1[†]).^{25,37}

 Table 1
 Variation of the reference experiments conditions^a

Entry	$CO (mmol g^{-1})$	$H_2 \ (mmol \ g^{-1})$	Sel. (%) ^{<i>k</i>}	
1 ^C	2,4560	0.0741	07.0	
2^d	0.0301	0.0056	97.0 84.3	
3 ^e	0.2550	0.0813	75.8	
4^{f}	0.0365	0.0141	72.1	
5^g	0.2740	0.0556	82.9	
6^h	0.5350	0.0685	88.6	
7 ^{<i>i</i>}	0.1670	0.0394	80.9	
8 ^j	0.0997	< 0.0001	_	
9^k	< 0.0001	< 0.0001	_	
10^l	< 0.0001	< 0.0001	_	
11^m	< 0.0001	< 0.0001	_	

^{*a*} Reaction conditions: H₂O (0.20 mL), CO₂ (1 bar), photocatalyst (1 mg), 25 °C, 12 h, and $\lambda > 420$ nm. ^{*b*} Selectivity = $n_{\rm CO}/n_{\rm (CO+H_2)} \times 100$. ^{*c*} Using C-TiO_{2-x}@g-C₃N₄-3 as catalyst. ^{*d*} Employing commercial P25 as catalyst. ^{*f*} Applying TiO_{2-x} (made from reduced P25 by NaBH₄) as catalyst. ^{*f*} Employing TiO₂@g-C₃N₄ as photocatalyst, prepared by mixing g-C₃N₄ and P25 in Teflon reactor, heating in an oven at 180 °C for 12 h. ^{*g*} Using TiO₂@g-C₃N₄ as photocatalyst, which was prepared with a similar procedure to that in (f), except P25 was replaced by with titanium isopropoxide. ^{*h*} Black TiO₂ nanobelts@g-C₃N₄ acted as photocatalyst, which was prepared following the procedure reported by Zhou *et al.* ^{*i*} Using directly mixed C-TiO_{2-x} and g-C₃N₄ to replace C-TiO_{2-x}@g-C₃N₄. ^{*j*} Without H₂O vapour. ^{*k*} Without C-TiO_{2-x}@g-C₃N₄. ^{*i*} In dark. ^{*m*} Using Ar to replace CO₂. Detailed synthesis procedure of these catalysts please see the ESI. To further expose the photocatalytic ability of C-TiO_{2-x}(@g-C₃N₄, the CO₂ reduction reaction was performed under the irradiation of whole light (Fig. 5b). Under irradiation of 12 h, around 4.500 mmol g⁻¹ CO was produced by C-TiO_{2-x}(@g-C₃N₄-3. The yields of C-TiO_{2-x} and g-C₃N₄ were 2.900 and 0.600 mmol g⁻¹, respectively. These results suggest that in C-TiO_{2-x}(@g-C₃N₄, C-TiO_{2-x}, commercial P25, and TiO₂@g-C₃N₄, the yields were 0.800, 0.050, and 0.180 mmol g⁻¹, respectively. When normalizing the quality of TiO₂, the generation of CO in C-TiO_{2-x}(@g-C₃N₄-3 stayed at 78.98 mmol g_{TiO₂}⁻¹ (Fig. 5c), which was around 70 times higher than that of bare TiO_{2-x}.

The reactivity of the C-TiO_{2-x}@g-C₃N₄-3 catalyst in different time periods was revealed through detecting the amount of CO every other hour (Fig. 5e). No apparent CO was detected in the first hour, illustrating this photocatalytic system needed an activation process for light excitation and adsorption equilibrium of the starting materials on the catalyst. After that, the yield of CO per hour almost increased at a constant speed in a linear fashion.

The stability of a photocatalyst is vital to its practical and industrial application. The stability of C-TiO_{2-x}@g-C₃N₄-3 was studied through five-run cycling photocatalytic experiments (Fig. 5d). After 60 h visible-light irradiation, almost no obvious decrease was observed in CO generation, and the total production amount reached 12.30 mmol g^{-1} , corresponding to 204.96 mmol g_{TiO₂}⁻¹. After catalysis, PXRD spectroscopies (Fig. S10[†]) and UVvisible adsorption spectra (Fig. S11[†]) of the sample were collected, which revealed there was little change in the structure of the catalyst and thus is demonstrated a reliable photostability. Furthermore, we also investigated the influence of the amount of C-TiO_{2-x}@g-C₃N₄-3 catalyst on the photocatalytic reactivity. When increasing the catalyst amount to 5, 10, or 30 mg, nearly the same catalytic activity to 1 mg was observed and their CO yields were close at 2.39, 2.35, 2.51 mmol g^{-1} . These results demonstrate that with the increase in C-TiO_{2-x}@g-C₃N₄-3 amount, the high reactivity rate can still be maintained (Fig. S12[†]).

Control experiments were performed to elucidate the importance of the components in the photoreduction system. Through mechanically mixing C-TiO_{2-x} (6 wt%) with g-C₃N₄ (entry 7), the yield was similar to bare g-C₃N₄. The significant decreases implied that a loose contact is insufficient for the reduction of CO₂. Without either C-TiO_{2-x}@g-C₃N₄-3 (entry 8) or light (entry 9), no gas was detected, which indicated that the other components cannot arouse CO₂ reduction, and thus again proved that the photogenerated charge pairs originated from C-TiO_{2-x}@g-C₃N₄-3. Once CO₂ gas was changed to Ar (entry 10), the generation of CO also stopped, therefore further excluding the source being from the degradation effects of organic species. In the absence of vapor (entry 7), the yield of CO dramatically decreased to 0.0997 mmol g⁻¹, implying vapor might be essential as an electron/proton donor.

Possible photocatalytic mechanism

The performance of a photocatalytic system in CO_2 reduction is dictated by a balance between the thermodynamics and kinetics. A famous mechanism path is to first convert CO_2 into

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 CO_2 ., which needs a high negative equilibrium potential of 1.9 V versus NHE.^{38,39} However, the photoinduced electrons in the conduction band edge of all semiconductors cannot provide enough driving force to carry out the one-electron reduction of CO₂ to CO₂^{•-}.^{40,41} Another mechanistic route is through protoncoupled electron transfer processes, which could bypass the formation of CO_2 . Through transferring the protons with electrons, the large activation barriers can be readily avoided.42 However, the proton-participating route has a significant kinetic dependence on the electron density on the surface of semiconductors catalysts. As discussed above, the initial H⁺ protons capture-speed of C-TiO2-x@g-C3N4-3 is 300 µmol g^{-1} min⁻¹, which is two orders of magnitude higher than the generation speed of CO (3.41 μ mol g⁻¹ min⁻¹). The affluent protons accumulated on the surfaces of photocatalyst provide a guarantee for the successful reduction of CO₂ through the proton-coupled pathway.

As for the other half reaction, the reactivity of water oxidation triggered by photogenerated holes has a considerable influence on the efficiency of CO₂ reduction in H₂O system. For water oxidation, the challenge lies mainly in the release of diatomic O₂. The stepwise two-electron/two-step pathway is proposed as an optimum approach between thermodynamic and kinetic constraints for water oxidation.^{9,16} In our photocatalytic system, g-C₃N₄ incorporated with amorphous carbon layers was designed to fulfil the two-electron/two-step oxidation pathway. The oxidation product of O₂ around 1.22 mmol g⁻¹ and negligible H₂O₂ was detected in the catalytic system using C-TiO_{2-x}@g-C₃N₄-3 as the photocatalyst. Rotating ring-disk electrode (RRDE) experiments (Fig. S13 and S14†) directly confirmed that the oxidation reaction undergoes a two-electron process.

In photocatalysis, three universally accepted steps are involved: light harvesting, charge separation, and transportation to surface sites, thus triggering redox reactions.^{43,44} As for CO_2 reduction, two more steps should be taken into account, they are CO_2 and proton adsorption. CO_2 adsorption through interactions with surface atoms facilitates the formation of a partially charged species, which could lower the energy barrier and lead to increased reactivity. Proton participation could also conduct the reduction in a low-energy way.⁴⁵

In CO2 reduction with C-TiO2-x@g-C3N4-3 as the photocatalyst, C-TiO_{2-x} contributes most of the adsorbed photons, while g-C₃N₄ could absorb the light before 450 nm. The ultrathin carbon layer serving as an electron reservoir takes an important role in accumulating the photoinduced electrons, therefore efficiently suppressing the recombination of the generated electronhole $(e-h^+)$ pairs. The ultrasmall size of C-TiO_{2-x} supplies sufficient reductive sites. Owing to the slower recombination speed of electron-hole pairs of g-C₃N₄ than that of C-TiO_{2-x}, g-C₃N₄ could supply photoexcited electrons to C-TiO_{2-x}. The mesoporous structure of g-C₃N₄ provides an appropriate accumulation space for CO_2 and H⁺ protons. Under the assistance of the carbon layer, g-C₃N₄ becomes an active photocatalyst for water oxidation through an efficient two-electron/two-step pathway. The spatially separated reductive and oxidative sites could exclude the possibility of re-oxidation of the reduction products.

Based on the above discussion, a possible catalytic mechanism for CO₂ reduction over C-TiO_{2-x}@g-C₃N₄ is proposed (Fig. S15†). First, CO₂ is adsorbed on the surface of TiO_{2-x} spheres and unoccupied g-C₃N₄. After irradiation, charge separation occurs in g-C₃N₄ and TiO_{2-x}, producing the electron-hole pairs. The generated electrons transfer to the amorphous carbon and trigger the reductive reaction under the assistance of a H⁺ proton from water to produce CO, while the remaining holes on g-C₃N₄ with the assistance of the carbon layers perform the oxidative reaction and generate O₂ *via* a twoelectron/two-step pathway.

Conclusions

In conclusion, we propose a design strategy of a low-cost, highly durable, and efficient TiO2-based three-component photocatalyst C-TiO_{2-x}@g-C₃N₄ for the generation of CO coupled with water oxidation. In this strategy, polyoxotitanium, $[Ti_{17}O_{24}]$ $(OPr^{i})_{20}$], is ingeniously employed as the precursor of TiO₂. In the composite photocatalyst, an ultrasmall TiO_{2-x} nanoparticle (5-8 nm) coated ultra-thin carbon layer was fabricated as the catalyst for converting CO2 toward CO, and a g-C3N4 coupled amorphous carbon layer was adopted as a catalyst for water oxidation via a two-electron/two-step pathway. Such a delicate structure widens the light adsorption into the whole visible light, meanwhile it was shown to possess a good adsorption capability for CO_2 (17.7 cm³ g⁻¹). Under visible-light irradiation, C-TiO_{2-x}(a)g-C₃N₄ showed around 12.30 mmol g^{-1} (204.96 mmol $g_{TiO_2}^{-1}$) CO generation within 60 h reaction, corresponding to 0.205 mmol g^{-1} h⁻¹. When switching the condition of visible light into whole light, the photocatalytic activity displayed a 1-fold enhancement. This CO generation rate is one order higher than the reported TiO₂-based catalyst under similar conditions. The experiments for H⁺ protons adsorption showed the capture speed of C-TiO_{2-x}@g-C₃N₄ was 300 μ mol g⁻¹ min⁻¹, which was two orders of magnitude higher than the generation speed of CO (3.41 µmol g^{-1} min⁻¹). Such rich protons accumulation provides a guarantee for CO2 reduction through the low-energy protoncoupled pathway. Coupling the reductive process with a matched water oxidation route is an attractive avenue to boost the reductive half-reaction. Rotating ring-disk electrode (RRDE) experiments indicated that the oxidative reaction in the C-TiO_{2-x}@g-C₃N₄ system was carried out *via* the efficient two-electron/two-step pathway with O2 as the final oxidative product. Photocurrent studies revealed the thin carbon layer serving as electron reservoir played an important role in facilitating the generated electron-hole $(e-h^+)$ pairs separation. Because of the slower recombination speed of electronhole pairs of $g-C_3N_4$ than that of $C-TiO_{2-x}$, the photoexcited electrons on the conduction band of g-C₃N₄ could transfer to that of $C-TiO_{2-x}$, therefore enhancing the change separation and further increasing the photocatalytic activity. This work might open up an alternative method to produce ultrasmall black TiO₂ nanoparticles based materials and provides novel insights for the design of high-performance and low-cost photocatalysts for converting CO₂ to CO.

Conflicts of interest

There are no conflicts to declare.

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