

Supporting Information

Ultra-small C-TiO_{2-x} Nanoparticle/g-C₃N₄ Composite for Photo-induced CO₂-to-CO Conversion with H₂O

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Materials and methods

All reagents and solvents for the syntheses were purchased from commercial sources and used as received, unless otherwise indicated.

PXRD patterns were recorded on a Siemens D5005 diffractometer with Cu KR ($\lambda = 1.5418 \text{ \AA}$) radiation in the range of 3–80°. ICP spectroscopy was conducted on Agilent 7500a Inductively Coupled Plasma Mass Spectrometry (ICP-MS 7500). TEM images were recorded on a JEM-2010 transmission electron microscope at an accelerating voltage of 200 kV. SEM images were recorded on XL-30 ESEM-FEG Scanning Electron Microscope. The elemental mappings of the samples were determined by EDX equipped on SEM with the type of Genesis 2000. UV–Vis absorption spectroscopy was obtained on U-3010 spectrophotometer (Hitachi, Japan). Infrared spectra were obtained from KBr pellets in a wavelength ranging from 4000–400 cm⁻¹ on a Nicolet 380 FT-IR spectrophotometer. XPS was performed using an Escalab 250 instrument. Nitrogen gas porosimetry measurements were performed on an automatic volumetric adsorption equipment (ASIQM0G002-3) and porosity analyzer after the samples were outgassed under a vacuum at 70 °C for 6 h. Emission lifetime measurements were performed on photon technology international quanta master/time master TM 400 phosphorescence/fluorescence Spectrofluoromete. The gas product in photocatalytic reaction was measured by Shimadzu Gas Chromatography.

Synthesis procedure of some catalysts in Table 1

Preparation of TiO_{2-x} photocatalyst (Entry 3). At room temperature, 2 g of the P25 was mixed with 4 g of NaBH₄ and the mixture was ground for 30 min thoroughly. Then the mixture was placed in a porcelain boat and heated in a tubular furnace for 1 h at 350 °C with a heating rate of 5 °C·min⁻¹ under Ar atmosphere. After naturally cooling down to room temperature, the TiO_{2-x} was obtained. The obtained sample was washed with deionized water and absolute ethanol for several times and then vacuum drying with 60 °C.

Preparation of TiO₂@g-C₃N₄ photocatalyst (Entry 4). At room temperature, 200 mg g-C₃N₄ and 12 mg P25 was dispersed in a mixture of 100 mL deionized water and ethanol (v:v = 1:1) under stirring for 4 h. The suspension was transferred to a 250 mL Teflon-lined reactor heating in an oven at 180 °C for 12 h. After naturally cooling down to room temperature, the TiO₂@g-C₃N₄ was obtained. The obtained sample was washed with deionized water and absolute ethanol for several times and then vacuum dry with 60 °C.

Preparation of TiO₂@g-C₃N₄ photocatalyst by traditional hydrothermal method (Entry 5). At room temperature, 200 mg g-C₃N₄ and 3 ml titanium isopropoxide (0.01 mol) was dispersed in a mixture of 100 mL solution containing 50 mL of ethanol, 10ml acetic acid and 40 mL of deionized water, followed by stirring for 30 min until a suspension was formed. The suspension was transferred to a 250 mL Teflon-lined reactor heating in an oven at 180 °C for 72 h. After naturally cooling down to room temperature, the TiO₂@g-C₃N₄ was obtained. The obtained sample was washed with deionized water and absolute ethanol for several times and then vacuum drying with 60 °C. The content of TiO₂ was 4.9 % by ICP.

Preparation of TiO_{2-x}@g-C₃N₄ photocatalyst by Zhou et al (Entry 6). 0.5 g of P25 was mixed with 100 mL of 10 M NaOH aqueous solution. The suspension was transferred to a 250 mL Teflon-lined autoclave and maintained at 180 °C for 72 h. The obtained products were washed thoroughly with deionized water and immersed in 0.1 M HCl aqueous solution for 24 h. Then the samples were immersed in a 0.02 M H₂SO₄ aqueous solution and maintained at 100 °C for 10 h. Then, the products were washed with deionized water for several times and dried at 70 °C for 10 h. A given amount of melamine was ground with the TiO₂ (weight ratios of TiO₂ to melamine: 1:10). And then, the mixture was calcined in a muffle furnace for 2 h at 550 °C with a heating rate of 20 °C·min⁻¹ in air atmosphere. Afterwards 1 g of the prepared sample was mixed with 2 g of NaBH₄ and the mixture was ground for 30 min thoroughly. Finally the mixture was placed in a porcelain boat and heated in a tubular furnace for 1 h at 350 °C under Ar atmosphere. After naturally cooling down to room temperature, the TiO_{2-x}@g-C₃N₄ was obtained. The obtained sample was washed with deionized water and absolute ethanol for several times and then vacuum drying with 60 °C. The content of TiO₂ was 6.7 % by ICP.

The detailed operation of enlargement experiment:

The surface area of glass and volum of reaction vessels are enlarged equally. As-prepared C-TiO_{2-x}@g-C₃N₄ catalyst (5 mg) was dispersed in a mixture of 10 mL deionized water and ethanol (v:v = 1:1) under sonication. After heating to 70 °C, the suspension was drop-coated onto a glass of 5 × 2.5 cm². Then the glass was moved to a five times bigger quartz photoreactor and 0.5 mL deionized water was added to keep the glass surrounded by water vapor. After bubbled 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. For 10-fold and 30-fold enlargement experiment, the surface area of the glass is enlarged into 5 × 5 cm² and 7.5 × 10 cm² and the amount of catalyst and water is enlarged into the corresponding fold.

Table S1. Summary of the reported CO generation rate.

Light source	photocatalyst	Experimental condition	Generation rate ($\mu\text{mol}\cdot\text{g}^{-1}\text{h}^{-1}$)	Ref.
UV Xe lamp 500W	In-TiO ₂	He, CO ₂ and H ₂ O vapor, 100 °C	81.25	1
250 < λ < 400 nm	Cu-doped TiO ₂ -SiO ₂	CO ₂ and H ₂ O vapor	20.3	2
UV Xe lamp 300W	g-C ₃ N ₄ -N-TiO ₂	CO ₂ and H ₂ O vapor	14.73	3
400 nm < λ	I-doped TiO ₂ nanoparticles	CO ₂ and H ₂ O vapor	2.4	4
400 nm < λ	Cu, I co-doped TiO ₂ nanoparticles	CO ₂ and H ₂ O vapor	10.8	5
200 < λ < 1000 nm	MgO-TiO ₂ microspheres	CO ₂ and H ₂ O vapor 150 °C	30.0	6
Xe lamp 300W sun-like radiation	TiO ₂ /graphitic carbon	CO ₂ and H ₂ O vapor	10.05	7
Xe lamp 300W 420 nm \leq λ	C-TiO _{2-x} @g-C ₃ N ₄	CO ₂ and H ₂ O vapor	205.0	This work
Xe lamp 300W 200 \leq λ \leq 1000 nm	C-TiO _{2-x} @g-C ₃ N ₄	CO ₂ and H ₂ O vapor	375.0	This work

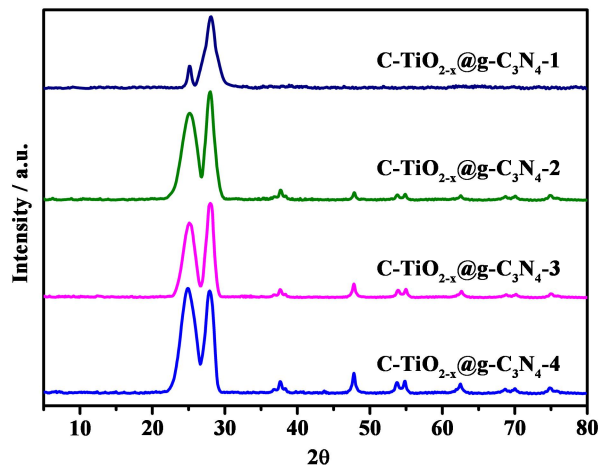


Figure S1. Powder X-ray diffraction (PXRD) of the C-TiO_{2-x}@g-C₃N₄ with the different of C-TiO_{2-x} content.

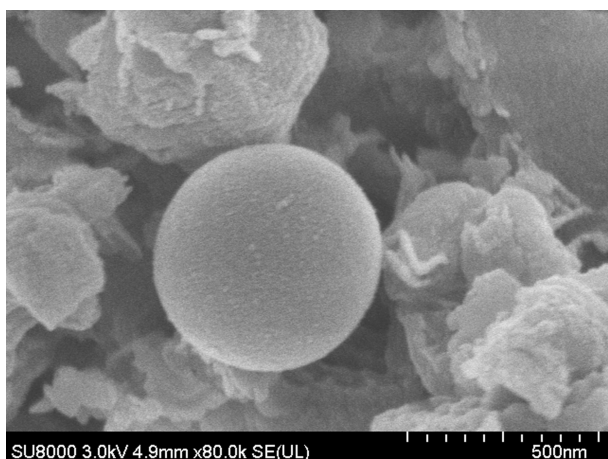


Figure S2. Scanning electron micrographic (SEM) by synthesizing in traditional hydrothermal method of TiO₂@g-C₃N₄.

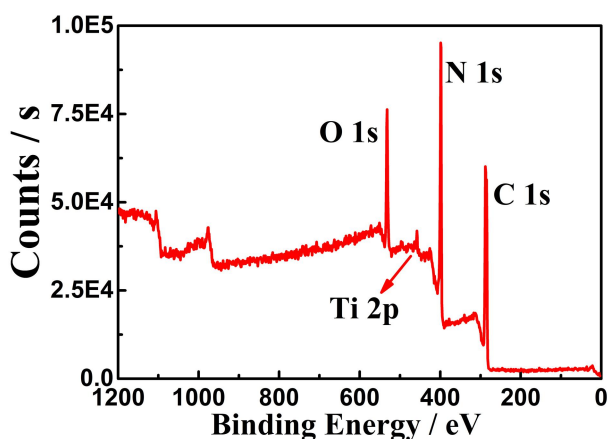


Figure S3. XPS spectrum of the composited of C-TiO_{2-x}@g-C₃N₄ hybrid.

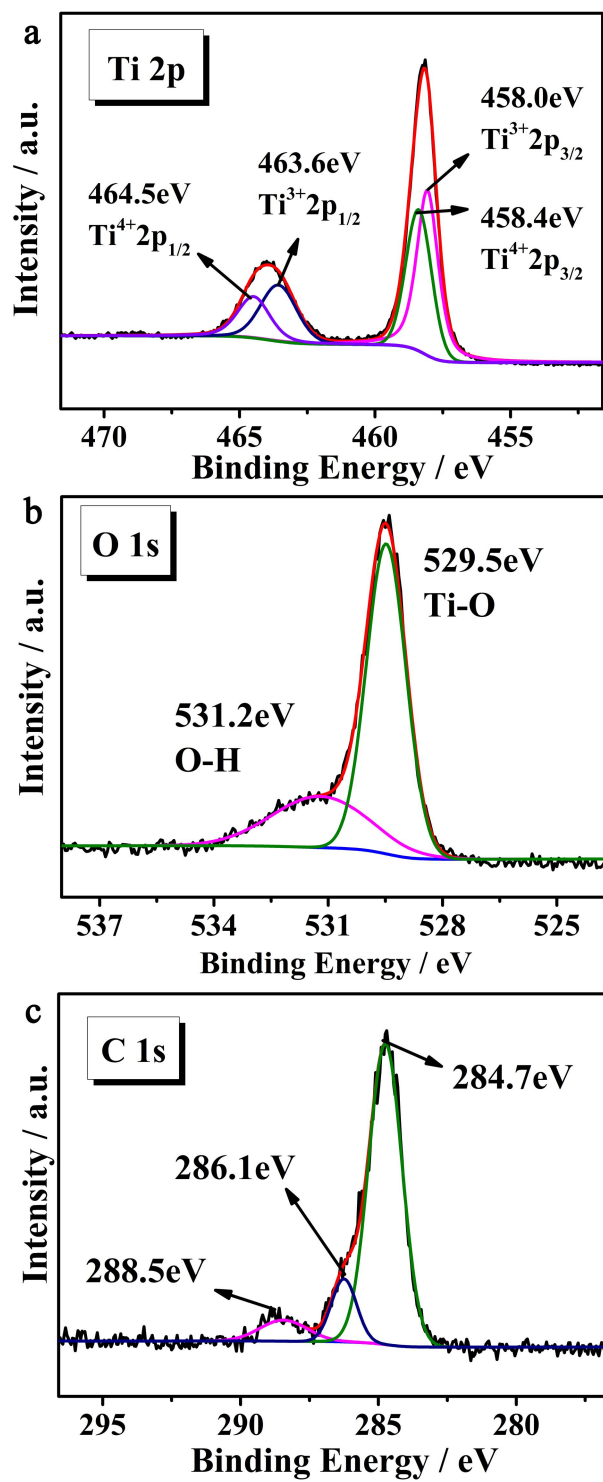


Figure S4. XPS spectrum of the composited of C-TiO_{2-x}.

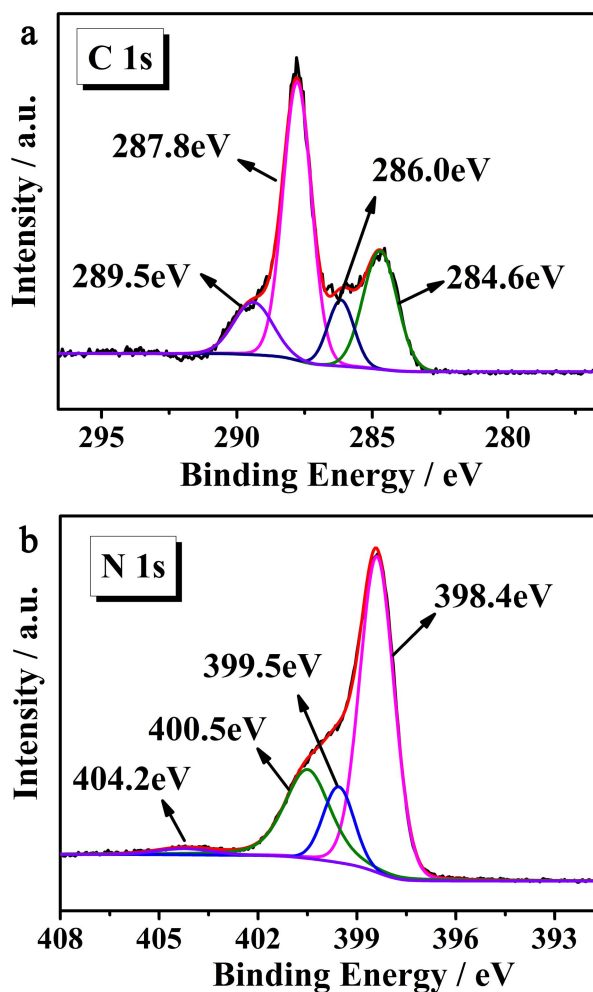


Figure S5. XPS spectrum of the composite of the $g\text{-C}_3\text{N}_4$.

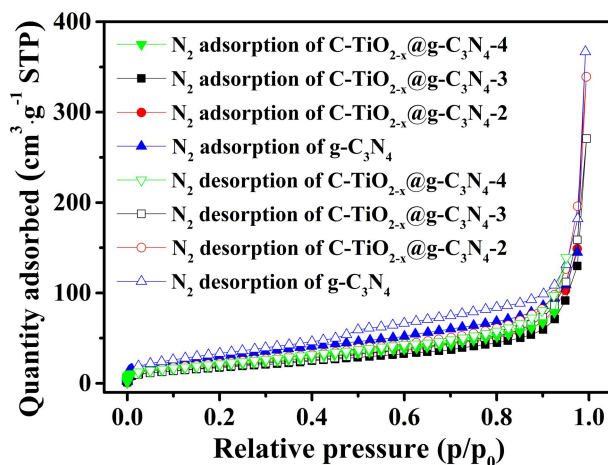


Figure S6. Gas isotherms adsorption. N_2 adsorption–desorption isotherms for pure $g\text{-C}_3\text{N}_4$ and composite sample with $\text{C-TiO}_{2-x}@g\text{-C}_3\text{N}_4\text{-2}$, 3, 4. The data are plotted based on the total weights of materials.

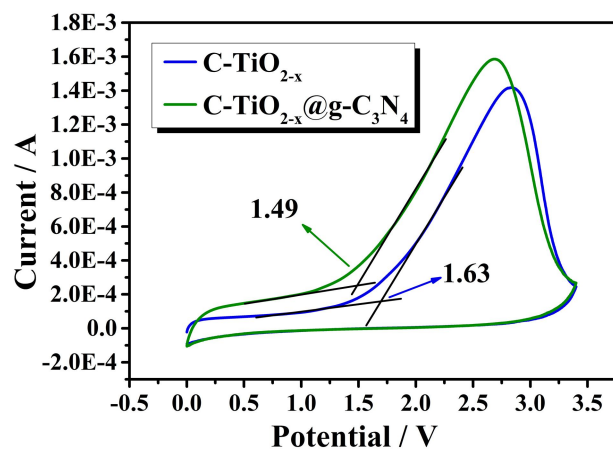


Figure S7. Cyclic voltammograms of C-TiO_{2-x} and C-TiO_{2-x}@g-C₃N₄ (solvent: acetonitrile, atmosphere: N₂).

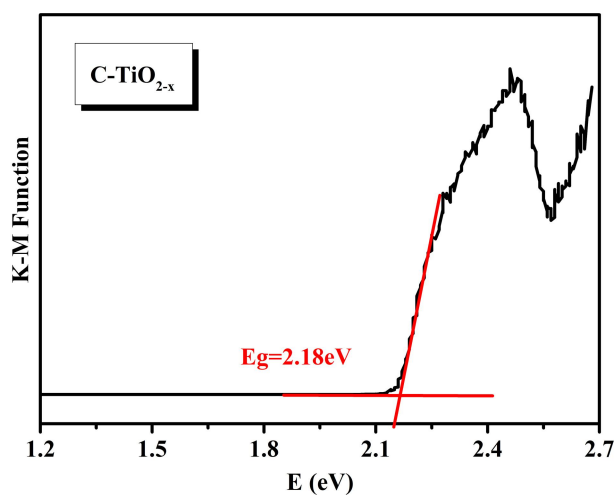


Figure S8. Band structure diagram for C-TiO_{2-x}.

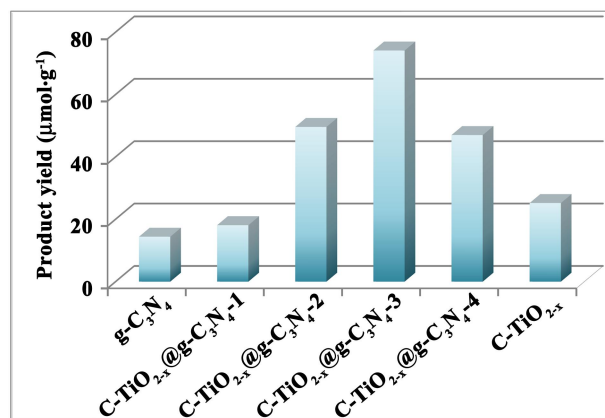


Figure S9. Photocatalytic performance for H₂ generation with different catalyst.

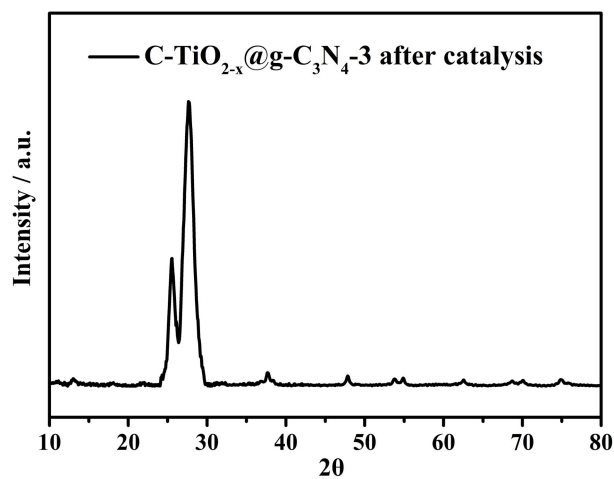


Figure S10. Powder X-ray diffraction (PXRD) of the after catalysis C-TiO_{2-x}@g-C₃N₄-3.

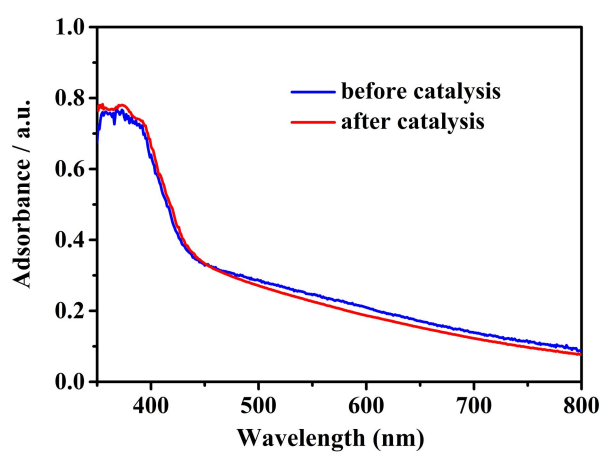


Figure S11. UV-visible adsorption spectra of the before and after catalysis C-TiO_{2-x}@g-C₃N₄-3.

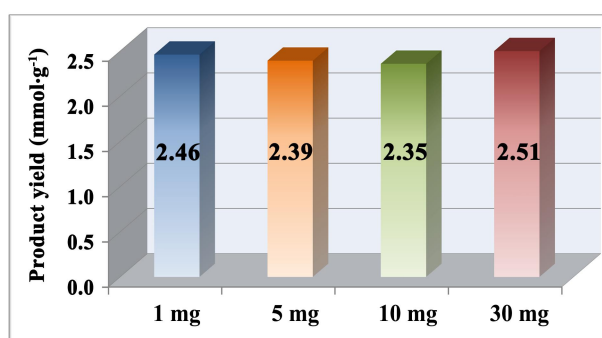


Figure S12. Photocatalytic performance for CO generation with different C-TiO_{2-x}@g-C₃N₄-3 amount.

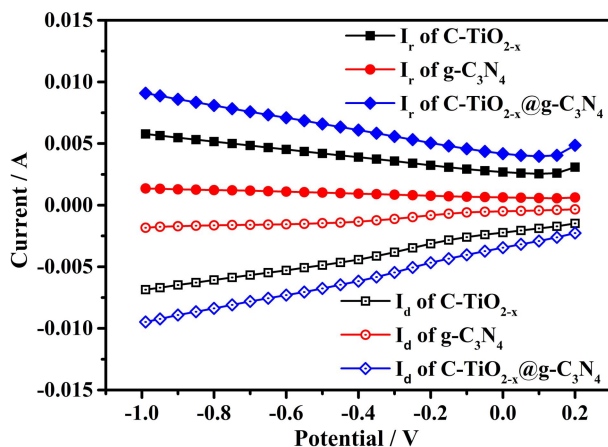


Figure S13. The Rotating ring-disk electrode (RRDE) experiments of using C-TiO_{2-x}@g-C₃N₄ as photocatalyst under rotation rates of 1600 rpm.

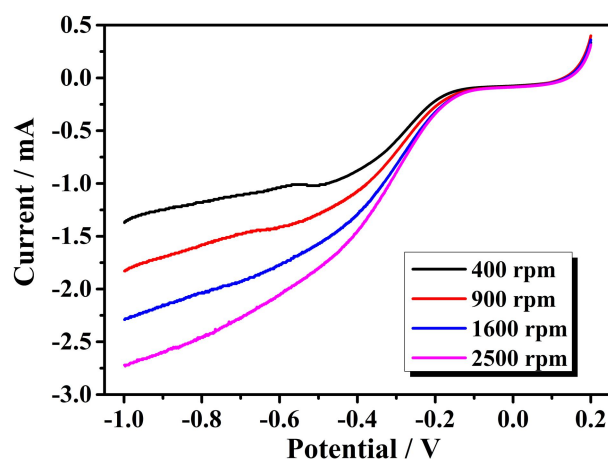


Figure S14. I-V curves of bare RRDE in 0.1 M KCl containing 0.01 M K₃Fe(CN)₆ under rotation rates of: 100, 400, 900 and 1600 rpm. These curves were used to determine the collection efficiency N .

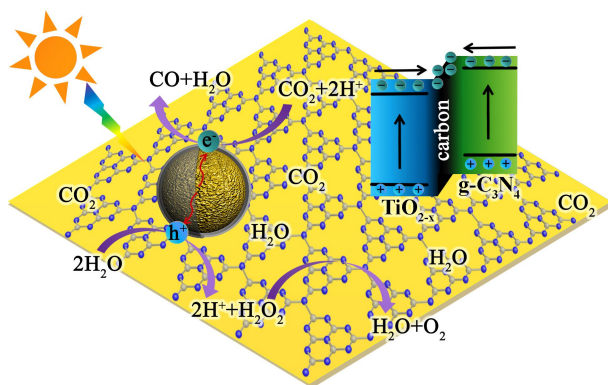


Figure S15. Schematic diagram of the reaction mechanism induced by C-TiO_{2-x}@g-C₃N₄-3. The thin carbon layer facilitates charges separation, C-TiO_{2-x} are the possible site for CO generation and the g-C₃N₄ may be the oxidative site for water.

Supplementary Reference

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