Carbon dioxide-enhanced photosynthesis of methane and hydrogen from carbon dioxide and water over Pt-promoted polyaniline–TiO₂ nanocomposites

Guodong Liu,^{a‡} Shunji Xie,^{a‡} Qinghong Zhang,^{*a} Zhengfang Tian^b and Ye Wang^{*a}

^aState Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

^bHubei Key Laboratory for Processing and Application of Catalytic Materials, Huanggang Normal University, Huanggang 438000, China

Electronic Supplementary Information

1. Experimental details

(1) Material synthesis

TiO₂ (P25), which contained 20% of rutile and 80% of anatase, was purchased from Degussa. The PANI–TiO₂ composites were synthesized by an in situ oxidative polymerization method. Powdery TiO₂ was first ultrasonically dispersed in deionized water. Then, aniline aqueous solution with a concentration of 0.090 mol dm⁻³ and a fixed volume was added into the suspension and the suspension was stirred for 20 min. Then, HCl aqueous solution with a concentration of 1.0 mol dm⁻³ and a fixed volume was added into the suspension. The mixture was further stirred for 20 min. Subsequently, ammonium peroxydisulfate [(NH₄)₂S₂O₈] was added into the mixture. The resulting suspension was kept at room temperature under continuous stirring for 4 h and the polymerization occurred in this stage. After polymerization, the obtained solid product was recovered by centrifugation, washing, drying at 333 K and calcination at 473 K for 2 h. By changing the volume of aniline aqueous solution, we prepared PANI–TiO₂ composites with PANI contents varying from 0.17 to 4.12 wt%, and the samples were denoted as *x*% PANI–TiO₂, where *x* was the content of PANI in weight percentage.

Pt was loaded onto the PANI–TiO₂ composites or TiO₂ by a photodeposition technique. Typically, the powdery TiO₂ or PANI–TiO₂ was dispersed in an aqueous solution of hexachloroplatinic acid (H₂PtCl₆) containing 0.10 mol dm⁻³ methanol as a hole scavenger. The suspension was irradiated with a 200 W Xe lamp at UV-vis ($\lambda = 320-780$ nm) for 3 h. The obtained sample was recovered by filtration, followed by washing repeatedly with deionized water and drying at 333 K overnight in vacuum. The loading amount of Pt was fixed at 0.2 wt% in this work.

(2) Catalyst characterization

The contents of C and N elements in the catalyst were determined by Vario EL III elemental analyzer (Elementar Analysen System GmbH). Powder X-ray diffraction (XRD) patterns were recorded on a Panalytical X'pert Pro diffractometer using Cu K_{α} radiation (40 kV, 30mA). Specific surface areas were measured by N₂ physisorption with Micromeritics Tristar II 3020. Diffuse reflectance Ultraviolet-visible (UV-vis) spectroscopic measurements were performed on Varian-Cary 5000 spectrophotometer equipped with a diffuse reflectance accessory. The spectra were collected with BaSO₄ as a reference.

TEM measurements were performed on a Philips Analytical FEI Tecnai 20 electron microscopy and were operated at an acceleration voltage of 200 kV. Samples for TEM measurements were suspended in ethanol and dispersed ultrasonically. Drops of suspensions were applied on a copper grid coated with carbon.

Transmission Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet Avatar 330 FT-IR spectrometer. The spectra were collected from 4000-400 cm⁻¹ with a 4 cm⁻¹ resolution. FT-IR spectra of samples under N_2 and CO₂ atmospheres were recorded in an in-situ IR cell. The catalyst mounted in the IR cell was first pretreated at 423 K under vacuum for 1 h, and then cooled down to 298 K, followed by purging with N_2 or CO₂ saturated with water vapour for 15 min. The cell was evacuated to remove gaseous residue before IR measurement. For in situ IR spectroscopic measurements, the resolution was controlled at 1 cm⁻¹.

The photoluminescence spectroscopic measurements were performed with an Edinburgh Analytical Instrument FLS 920 spectrophotometer with an excitation wavelength of 355 nm. The sample was placed in an in-situ cell. The atmosphere of the cell was controlled under either N_2 or CO_2 saturated with water.

The amount of CO_2 chemisorption was measured with a Micromeritics ASAP2020C apparatus by adopting the procedure reported by Teramura et al.¹ In brief, the sample after pretreatment at 423 K was subjected to CO_2 adsorption at 298 K and a Langmuir-type adsorption isotherm was obtained. After evacuation at 298 K, the adsorption of CO_2 was performed again for the same sample. The amount of chemisorbed CO_2 was obtained by subtraction between the two adsorption amounts at saturated equilibrium pressures.

The photoelectrochemical measurements were carried out with an Ivium CompactStat (Holland) using a standard three-electrode cell with a working electrode, a Pt wire as the counter electrode, and an SCE electrode as the reference electrode.² The gaseous atmosphere in the cell could be controlled under either N₂ or CO₂. A 0.5 mol dm⁻³ Na₂SO₄ aqueous solution was used as the electrolyte. The working electrode was prepared with an F-doped SnO₂-coated FTO glass. The photocatalyst was mixed with dimethylformamide under sonication. The slurry was spread onto the FTO glass, and then the film was dried at 373 K for 1 h.

The electrochemical impedance spectroscopy and Mott-Sckotty measurements were carried out at open circuit potential. An electrochemical analyzer (CHI660C instruments, CHI, China) of a standard three-electrode system was used for measurements. The sample with a fixed amount of \sim 3 mg was coated onto a FTO glass electrode. Before each measurement, the FTO was sintered at 473 K for 1 h. The sample-coated FTO, Pt wire and Ag/AgCl were used as the working, counter and reference electrodes, respectively. Na₂SO₄ aqueous solution (0.5 mol dm⁻³) was used as the electrolyte. Although Ag/AgCl was used as the reference electrode, all the potentials mentioned in this work were described with respect to the reversible hydrogen electrode (RHE) by using the following equation:

 $E_{\rm RHE} = E_{\rm Ag/AgCl} + 0.197 + 0.059 \times \rm pH$

where $E_{Ag/AgCl}$ was the potential measured using the Ag/AgCl electrode.

(3) Photocatalytic reaction

Photocatalytic reactions were carried out in a stainless-steel reactor (volume, 100 cm³) with a quartz window on the top of the reactor. The reactor design was reported in our previous paper.³ A 200 W Xe lamp (PLS-SXE 300) at UV-vis ($\lambda = 320-780$ nm) was used as the light source. The photocatalytic reaction was performed in a gas-solid heterogeneous reaction mode. The powdery photocatalyst (10 mg) was placed on a Teflon catalyst holder in the upper region of the reactor. Distilled water with a volume of 4 cm³ was pre-charged in the bottom of the reactor. The pressure of CO₂ was typically regulated at 0.2 MPa. The temperature of the reactor was kept at 323 K, and the vapour pressure of H₂O was 12.3 kPa under such a circumstance.

The reaction system was connected to an on-line gas chromatograph (GC) through valves, and the gaseous products could be directly introduced to the GC for analysis. We adopted a flame ionization detector (FID) for quantifying the amounts of CO and CH₄ formed from CO₂ to ensure high sensitivities. After the effluents containing CO₂, CO and CH₄ were separated by a carbon molecular sieve (TDX-01) column, CO and CO₂ were further converted to CH₄ by a methanation reactor, and were then analyzed by the FID detector. The detection limits of our analytic method for CH₄ and CO were both 0.002 µmol. H₂ was analyzed by an Agilent Micro GC3000 (Micro GC) equipped with a Molecular Sieve 5A column and a high-sensitivity thermal conductivity detector (TCD). The Micro GC was connected directly to the reactor by a stainless-steel tube, and the gaseous products were introduced to the Micro GC by a self-suction type injection pump. The detection limit for H_2 was 0.004 µmol (~1 ppm). The experiments for each catalyst under each condition was performed at leat for 3 times and the relative error was typically within 5%. Liquid products such as CH₃OH, HCHO and HCOOH possibly formed and dissolved in water were also analyzed carefully by gas chromatography or high-performance liquid chromatography, but no such products were detected under our reaction conditions.

2. XRD patterns for PANI-TiO₂ composites as well as TiO₂ and PANI

Fig. S1 shows the XRD patterns of TiO₂, PANI and PANI–TiO₂ composites. PANI did not show distinct diffraction peaks, indicating the amorphous feature of PANI. TiO₂ exhibited diffraction peaks at 2 θ degrees of 25.3, 37.8, 48, 53.9, 55.1, 62.7, 68.8, 70.3 and 75, which could be ascribed to the anatase phase of TiO₂. Weak diffraction peaks at 2 θ degrees of 27.4, 36.1 and 41.2 were also observed and were assignable to the rutile phase of TiO₂, consistent with the fact that our TiO₂ (P25) was composed of both anatase and rutile. The PANI–TiO₂ composites with different PANI contents showed the same diffraction peaks with TiO₂. Thus, the presence of PANI did not exert influences on the lattice structure of TiO₂.



Fig. S1 XRD patterns of PANI-TiO₂ composites as well as TiO₂ and PANI.

3. FT-IR spectra for PANI-TiO₂ composites as well as TiO₂ and PANI

Fig. S2 shows the FT-IR spectra of TiO₂, PANI and PANI–TiO₂ composites. PANI prepared in our work showed distinct IR bands at 1599, 1510, 1400, 1293 and 1130 cm⁻¹. These bands are in consistent with those reported for PANI in literature.⁴ Generally, the bands at 1599 and 1510 cm⁻¹ can be assigned to the C=N and C=C stretching modes for quinone and benzene rings, respectively, while the bands at 1400 and 1293 cm⁻¹ are attributable to C–C and C–N stretching modes for the benzene and quinonoid units. The band at 1130 cm⁻¹ can be assigned to a plane bending vibration mode associated with the quinonoid unit. These bands have also been observed for our PANI–TiO₂ composites, although the positions of some bands shifted probably because of the interaction between PANI and TiO₂. These results suggest the formation of PANI with the structure in Scheme 1 (see the main text) on TiO₂.



Fig. S2 FT-IR spectra of PANI-TiO₂ composites as well as TiO₂ and PANI.

4. UV-vis spectra and the corresponding plots of modified Kubelka-Munk function versus the energy of exciting light for PANI–TiO₂ composites as well as TiO₂ and PANI

Fig. S3 show the diffuse-reflectance UV-vis spectra for PANI–TiO₂ composites as well as TiO₂ and PANI. TiO₂ exhibited absorption in UV region with a peak at 250-300 nm (Fig. S3A). PANI alone possessed absorption both in UV and in visible regions. The background in the visible region increased significantly with addition of PANI onto TiO₂ due to the strong absorption of PANI in the visible region, which could be attributed to the charge-transfer excitation-like transition from the highest occupied energy level (HOMO) to the lowest unoccupied energy level (LUMO).^{4a} From the plots of the modified Kubelka-Munk function, i.e., $[F(R_{\infty})hv]^{1/2}$, versus the energy of exciting light (*hv*), the band-gap energy for a semiconductor can be evaluated. The plots of $[F(R_{\infty})hv]^{1/2}$ against *hv* for the PANI–TiO₂ composites with different PANI contents are shown in Fig. S3B. The plot for TiO₂ alone afforded a band-gap energy of 3.2 eV. The increase in the content of PANI in the PANI–TiO₂ composites gradually decreased the band-gap energy, and the 4.1% PANI-TiO₂ possessed a bandgap energy of 2.8 eV.



Fig. S3 A) UV-vis spectra and B) the corresponding plots of modified Kubelka-Munk function versus the energy of exciting light for PANI–TiO₂ composites as well as TiO₂ and PANI.

5. TEM micrographs for PANI–TiO₂ composites as well as TiO₂

Fig. S4 shows the TEM micrographs for the PANI–TiO₂ composites. TiO₂ possessed particulate morphology with sizes of 20-50 nm. The images for the composites clearly reveal that a layer of amorphous PANI exists on TiO₂. The thickness of the PANI layer increased from ~2.5 nm to ~8 nm upon increasing the content of PANI in the composite from 0.17 to 4.1 wt%.



Fig. S4 TEM micrographs of PANI–TiO₂ composites. (a) TiO₂, (b) 0.17% PANI–TiO₂, (c) 0.85% PANI–TiO₂, (d) 4.1% PANI-TiO₂. The scale bar was 5 nm.

6. TEM micrographs and the corresponding Pt particle size distributions for Pt-PANI-TiO₂ composites

Fig. S5 shows the TEM micrographs for the Pt–PANI–TiO₂ composites with different PANI contents. It can be seen that Pt was deposited on TiO_2 or the PANI–TiO₂ composites with relatively homogeneous sizes. The mean sizes of Pt nanoparticles derived from the Pt particle size distributions were 2.5-3.5 nm over TiO_2 and PANI–TiO₂ composites.



Fig. S5 TEM micrographs and the corresponding Pt particle size distributions for Pt–PANI–TiO₂ composites. (a) Pt–TiO₂, (b) Pt–0.17% PANI–TiO₂, (c) Pt–0.85% PANI–TiO₂, (d) Pt–4.1% PANI–TiO₂. The scale bar was 10 nm.

7. Repeated uses of the Pt–0.85% PANI–TiO₂ catalyst under CO₂ and N₂ atmospheres

Fig. S6 shows the results obtained for the repeated uses of the Pt–0.85% PANI–TiO₂ catalyst under CO₂ and N₂ atmospheres. Under CO₂, the formations of CH₄ and H₂ declined gradually in the initial 5 cycles and then only changed slightly (Fig. S6A). The rates of CH₄ and H₂ formations were 30 and 255 μ mol g⁻¹ h⁻¹ after 10 reaction cycles. Under N₂, a small amount of CH₄ was observed, and the initial rate of CH₄ formation was ~5 μ mol g⁻¹ h⁻¹, one order of magnitude lower than that under CO₂. The rate of CH₄ formation decreased to ~1 μ mol g⁻¹ h⁻¹ after 10 reaction cycles under N₂, which was 1/30 of that formed under CO₂. These results clearly indicate that most of the CH₄ molecules formed under CO₂ atmosphere arise from the reduction of CO₂. In addition to the small amount of CH₄, as expected, H₂ was formed as the main product under N₂ atmosphere in the presence of H₂O vapour. The rate of H₂ formation was ~90 μ mol g⁻¹ h⁻¹ over the Pt–0.85% PANI–TiO₂ catalyst after 10 reaction cycles.



Fig. S6 Repeated uses of the Pt–0.85% PANI–TiO₂ catalyst. (A) Under CO₂ atmosphere. (B) Under N₂ atmosphere. Reaction conditions for each cycle: catalyst, 0.010 g; CO₂ or N₂ pressure, 0.20 MPa; light source, 320-780 nm; time, 4 h. After each cycle for 4 h, the reactor was degassed and re-pressurized again to start the next reaction cycle.

8. FT-IR spectrum for the Pt-0.85% PANI-TiO₂ catalyst after the repeated uses under CO₂ atmosphere

Fig. S7 shows the FT-IR spectrum for the Pt-0.85% PANI-TiO₂ catalyst after 10 cycles of the repeated uses for the photocatalytic reduction of CO₂ with H₂O vapor. The reaction conditions were displayed in Fig. S6. No significant changes in FT-IR spectra were observed after the repeated uses, thus indicating that PANI in the composite catalyst was sustained after the repeated uses.



Fig. S7 FT-IR spectrum for the Pt-0.85% PANI $-TiO_2$ catalyst after 10 cycles of the repeated uses as well as the fresh catalyst. The reaction conditions are displayed in Fig. S6.

9. Transient photocurrent responses for PANI–TiO₂ and Pt–PANI–TiO₂ with different PANI contents under CO₂ atmosphere

Fig. S8 shows the transient photocurrent response results for the PANI–TiO₂ and Pt–PANI–TiO₂ series of catalysts with different PANI contents under CO₂ atmosphere. For both series of catalysts, the current density increased with an increase in the PANI content from 0 to 0.85 wt%. This confirms the role of PANI in accelerating the separation of photogenerated electrons and holes under CO₂ atmosphere. However, a further increase in the PANI content to 4.1 wt% in both series of catalysts rather decreased the current density. Thus, the thicker PANI film on TiO₂ may be unfavourable for the migration of photogenerated electrons to catalyst surfaces to participate in the reduction of CO₂. This would result in lower rates of CH₄ and H₂ formations at PANI content of 4.1 wt% (Table 1).



Fig. S8 Transient photocurrent responses for PANI–TiO₂ and Pt–PANI–TiO₂ series of catalysts under CO₂ atmosphere. (A) TiO₂ and PANI–TiO₂: (a) TiO₂, (b) 0.17% PANI–TiO₂, (c) 0.85% PANI–TiO₂, (d) 4.1% PANI–TiO₂. (B) Pt–TiO₂ and Pt–PANI–TiO₂: (a) Pt–TiO₂, (b) Pt–0.17% PANI–TiO₂, (c) Pt–0.85% PANI–TiO₂, (d) Pt–4.1% PANI–TiO₂.

10. Electrochemical impedance spectra for samples under N_2 and CO_2 atmospheres

Fig. S9 displays the Nyquist plots of electrochemical impedance spectra for our catalysts measured under N_2 and CO_2 atmospheres. It is known that the electron-transfer resistance is reflected by the arc of the Nyquist plot; a larger arc corresponds to a larger electron-transfer resistance.⁵ As compared to those under N_2 , the arcs of the Nyquist plots under CO_2 atmosphere for TiO₂ and Pt–TiO₂ catalysts decreased slightly (Fig. S9A-a and b and Fig. S9B-a and b). This is probably because of the change of the electrolyte solution after the dissolution of CO_2 into the solution. In other words, the conductivity of the electrolyte solution may be increased by the dissolution of CO_2 , contributing to the decrease in the resistance of electron transfer under CO_2 atmosphere. For the 0.85% PANI–TiO₂ and Pt–0.85% PANI–TiO₂ catalysts, the decreases in the arcs of Nyquist plots under CO_2 atmosphere became more significant (Fig. S9A-c and d and Fig. S9B-c and d). This suggests a decreased electron-transfer resistance for the PANI-containing catalysts under CO_2 atmospheres compared to those obtained under N_2 atmosphere.



Fig. S9 Nyquist plots of electrochemical impedance spectra for samples under N_2 and CO_2 atmospheres. (A): (a) TiO₂ under N_2 , (b) TiO₂ under CO_2 , (c) 0.85% PANI–TiO₂ under N_2 , (d) 0.85% PANI-TiO₂ under CO₂. (B): (a) Pt–TiO₂ under N_2 , (b) Pt–TiO₂ under CO₂, (c) Pt–PANI–TiO₂ under N_2 , (d) Pt–PANI–TiO₂ under N_2 , (d) Pt–PANI–TiO₂ under CO_2 .

11. Photoluminescence spectra for TiO₂ and 0.85% PANI–TiO₂ samples under N₂ and CO₂ atmospheres

Fig. S10 shows the photoluminescence spectra for TiO_2 and 0.85% PANI–TiO_2 samples under different atmospheres. Generally, the photoluminescence is generated during the recombination of photogenerated electron-hole pairs on a semiconductor. We observed a visible luminescence band centered at ~440 nm for TiO_2 and 0.85% PANI–TiO_2 under both N_2 and CO_2 atmospheres (Fig. S10-a and b). This band could be ascribed to the recombination of photogenerated electron-hole pairs on TiO_2 .⁶ TiO_2 and 0.85% PANI–TiO_2 showed similar intensities of the luminescence band under N₂. The switch of N₂ to CO₂ significantly decreased the intensity of the luminescence band for the 0.85% PANI–TiO₂, whereas that for TiO₂ remained unchanged. This clearly suggests a reduced recombination of charge carriers over the 0.85% PANI–TiO₂ under CO₂ atmosphere.



Fig. S10 Photoluminescence spectra for TiO_2 and 0.85% PANI– TiO_2 under N_2 and CO_2 atmospheres. (a) TiO_2 under N_2 . (b) TiO_2 under CO_2 . (c) 0.85% PANI– TiO_2 under N_2 . (d) 0.85% PANI– TiO_2 under CO_2 .

12. FT-IR spectra for PANI under N₂ and CO₂ atmospheres

Fig. S11 shows the FT-IR spectra of PANI under N₂ and CO₂. For reference, the IR spectrum of PANI after HCl modification is also displayed in Fig. S11. As compared to that under N₂, the characteristic IR bands of PANI shifted to lower-wavelength positions after HCl modification (Fig. S11, curves a and b), indicating the charge delocalization due to proton-induced spin unpairing mechanism.⁷ The IR bands related to C=N and C-N stretching vibrations also underwent red shifts under CO₂ atmosphere, although the shifts were not as large as those for the sample pretreated by HCl (see Table S1for the shift in detail). Furthermore, an additional IR band at 1384 cm⁻¹, which corresponded to the chemical interaction of CO₂ with nitrogen containing groups of PANI,⁸ appeared. It should be pointed out that the IR bands could be restored after the evacuation of CO₂, indicating the reversible nature of the interaction of CO₂ with PANI.



Fig. S11 FT-IR spectra of PANI under N_2 and CO_2 atmospheres. (a) PANI under N_2 . (b) PANI under CO_2 . (c) PANI evacuated at 323K after exposure to CO_2 atmosphere. (d) PANI modified by aqueous HCl.

Table S1 IR bands of PANI under N_2 and CO_2 as well as after HCl modification

Samples	Position of IR band ^a				
PANI under N ₂	1599 cm ⁻¹	1510 cm ⁻¹	1400 cm ⁻¹	1293 cm ⁻¹	1130 cm ⁻¹
PANI under CO ₂	1594 cm ⁻¹	1510 cm ⁻¹	1400 cm ⁻¹	1289 cm ⁻¹	1128 cm ⁻¹
After evacuation of	1599 cm ⁻¹	1510 cm ⁻¹	1400 cm ⁻¹	1293 cm ⁻¹	1130 cm ⁻¹
CO ₂ at 323 K					
PANI modified by	1584 cm ⁻¹	1502 cm ⁻¹	1400 cm ⁻¹	1286 cm ⁻¹	1120 cm ⁻¹
HC1					
Assignment	C=N	C=C	C-C stretching	C-N stretching	A mode of
	stretching in	stretching in	in benzene ring	in Q=NH-B	Q=N ⁺ H-B or
	quinone (Q)	benzene (B)			B-NH-B
	ring	ring			

^a The resolution of IR band was controlled at 1 cm⁻¹.

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