A Heterogeneous Carbon Nitride-Nickel Photocatalyst for Efficient Low-Temperature CO₂ Methanation

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The Sabatier reaction, i.e. the hydrogenation of CO₂ to methane (CH₄) using hydrogen (H₂), constitutes a potentially scalable method to store energy in a product with a high energy density. However, up to today, this reaction has been mainly thermally driven and conducted at high temperatures (typically 400 – 600 °C). Using light as a renewable energy source would allow for a more sustainable process by lowering the reaction temperature. Here, we demonstrate that Ni nanoparticles supported on graphitic carbon nitride (g-CN) are a highly efficient and stable photocatalyst for the gas-phase CO₂ methanation at low temperature (150 °C). Detailed mechanistic studies reveal a very low activation energy for the reaction and high activity under visible light, leading to a remarkable and continuous CH₄ production of 28 μmol g⁻¹ h⁻¹ of CH₄ for 24 hours.

1. Introduction

Growing energy demand together with increasing environmental concerns have led to the recent development of clean, abundant, and renewable energy sources. Solar-to-chemical conversion via photocatalytic water splitting or CO₂ reduction, which mimics the natural photosynthetic process, has specifically attracted considerable attention.^[1] This photocatalytic CO₂ conversion with H₂O can give rise to various products, such as carbon monoxide, formic acid or methane,

depending on the operating mechanism of the photocatalytic system (Scheme S1).^[2] Nevertheless, the product formation rate and energy conversion efficiency remain extremely low due to the limited utilization of the solar spectrum by existing photocatalysts and the harsh thermodynamic conditions.^[3]

One energetically favorable case of CO₂ reduction in particular, which is attracting widespread attention of late, is the CO₂ methanation reaction with H₂, i.e. the Sabatier reaction (Scheme S1, Equation 6).^[4] However, this reaction typically takes place at high temperatures (ranging 400 - 600 °C) using metal-based catalysts (Ni, Ru, Rh, Co, etc) supported on inorganic porous metal oxides (e.g., TiO₂, SiO₂, MgO, Al₂O₃),^[5] or graphenes.^[6] Therefore, decreasing the required temperature by using light as an energy source to photocatalyze CO₂ methanation will make the process more benign, simple and sustainable. Unfortunately, most of the photocatalysts currently reported for this reaction are still not fully suitable because of their instability in the reaction media, poor light-harvesting properties, and the use of precious or toxic elements, thereby limiting their potential application.

Graphitic carbon nitride (g-CN) materials, have emerged as metal-free semiconductors for environmental and energy-related applications,^[7] such as water splitting,^[8] solar cells,^[9] LEDs,^[10] water treatment,^[11] and others.^[12] Despite the well-established application of g-CN as a photocatalyst for water splitting, CO₂ reduction and organic reactions, CO₂ reduction experiments are typically carried out in solution with relatively low production rates.^[13] Yet, to the best of our knowledge, g-CN has never been utilized as a (photo)catalyst for CO₂ methanation, a process that may occur through different mechanisms and requires different conditions, particularly heating of the system.^[14] Here, we report the preparation of Ni nanoparticles (NPs) supported on g-CN (Ni/g-CN) as the photocatalyst for the gas-phase CO₂ methanation at low temperature. The Ni NPs were deposited on g-CN and submitted to UV-Vis irradiation at 150 °C, a very low reaction temperature compared to the state of the art and to the

temperatures usually seen at the industrial scale.^[4a] Under these conditions, 28 $\mu\text{mol g}^{-1} \text{h}^{-1}$ of CH_4 were produced continuously over a 24-h period, which is among the highest values reported for noble metal-free carbon nitride-based photocatalysts. Moreover, detailed studies give insights into the reaction mechanism and that approximately one third of the CH_4 production is a consequence of photon absorption in the visible region.

2. Results and discussion

2.1. Photocatalyst characterization

$\text{Ni}(x)/\text{g-CN}$ photocatalysts were prepared by wet impregnation with different amounts of Ni(II) salt on g-CN, followed by a thermal reduction under H_2 flux (**Figure 1a**, see Experimental Section for further details). The XRD pattern of bare g-CN shows the typical diffraction peaks at 13.0 and 27.5 ° corresponding to its (100) and (002) crystal planes (**Figure S1** in supplementary Information). The XRD patterns of the as-prepared $\text{Ni}(x)/\text{g-CN}$ samples confirm the presence of Ni metal and g-CN (**Figure 1b**); the formation of Ni^0 is evidenced by the appearance of the peaks at 44.5, 51.6 and 76.5 °, which correspond to the (111), (200) and (220) crystal planes of metallic Ni. As can be observed in Figure 1b, the high crystallinity of the Ni NPs largely overshadows the contribution of g-CN at Ni(II) wt.% of 10 (Ni(10)/g-CN) already.

The diffuse reflectance UV-Vis spectra of the samples (**Figure 1c**) show an enhancement of the optical absorption according to the Ni NPs loading which suggests a strong modification of the band structure of g-CN.

XPS measurements were performed in order to evaluate the chemical and electronic structure of the Ni nanoparticles in the g-CN material (**Figure 2a-c**, the analysis was performed for Ni(25)/g-CN as it showed the highest photocatalytic activity, as indicated later in the paper). The C 1s spectrum shows the typical components of g-CN materials, the C=N-C coordination at 288.2 eV as the main component as well as the adventitious C at 284.8 eV and a small

component related to C-O bond probably coming from adsorbed water from the environment. The N 1s spectrum presents three different components corresponding to C=N-C coordination at 398.6 eV, tertiary amines (N-(C)₃) at 399.9 eV and remaining amino groups (-NH) at 401.1 eV. The Ni 2p_{3/2} spectrum shows three different chemical states that correspond to metallic Ni, NiO and Ni(OH)₂. The formation of oxide on the Ni surface is due to the spontaneous oxidation at an ambient atmosphere of some of the outermost Ni atoms, as shown previously for different Ni-based catalysts.^[15] HRTEM images (**Figure 2d-f**) of Ni(25)/g-CN confirm the presence of Ni NPs supported on g-CN and a typical laminar morphology of g-CN containing homogeneously distributed Ni NPs. The g-CN exhibited 2D structure with lateral sizes < 1 μm containing holes and wrinkles. The supported Ni NPs have a round morphology as can be seen in Figure 2d-2e. The size distribution of Ni NPs (Figure 2e) in Ni(25)/g-CN reveals an average particle size of 16.±7 nm. The particle lattice fringe is 0.19 nm as determined from the HRTEM image, corresponding to the interplanar distance of the 200 facets of FCC Ni metal particles.^[16] A STEM image acquired in dark field mode and the corresponding elemental mapping obtained from EDS elemental analysis confirm that the large particle is mainly composed of C and N, corresponding to g-CN, while the smaller bright NPs correspond to Ni (**Figure S2**).

2.2. Photocatalytic activity

The photocatalytic activity of the bare g-CN and 5 Ni(x)/g-CN samples were tested by performing the CO₂ methanation reaction in the gas phase under UV-Vis irradiation and at 150 °C (**Figure 3, Figure S3 and Table 1**). The samples were placed in a cylindrical quartz photoreactor equipped with an electrical heating ribbon and loaded with H₂ and CO₂ at stoichiometric amounts (4:1) at a total pressure of 1.3 bar. Unless otherwise indicated, the photocatalytic tests were carried out at 150 °C under 1080 W/m² irradiation with a 300 W Xe lamp. All samples promoted CH₄ formation at these conditions. Note that the presence of CO or C₂⁺ hydrocarbons was not detected or below the detection limit of the MicroGC equipment. The bare g-CN at 150 °C under illumination produced very small quantity of CH₄ (0.39 μmol)

after a 8-h reaction. The introduction of low amounts of Ni NPs (Ni(2)/g-CN and Ni(5)/g-CN) on the g-CN did not lead to a significant change in the photocatalytic activity at these conditions. However, further increase of the Ni content promoted an enhancement of the CH₄ production, reaching a maximum value of 5.51 μmol of CH₄ for Ni(25)/g-CN after 8 h which corresponds to an AQY of 0.01 %. We note that given the experimental difficulty of using monochromatic lights with the reported setup, the number of incident photons was estimated as an average of the total Xe lamp spectrum. Further increase of the Ni relative content (Ni(40)/g-CN) resulted in a decrease of the CH₄ evolution. The maximum performance at a certain Ni amount implies that there should be at least two opposite factors contributing to the observed photocatalytic activity. Knowing its hydrogenating ability, it is proposed that Ni NPs serve as catalytic sites for the reaction and therefore, the higher the Ni loading, the higher the expected activity. However, for a Ni loading of 40 %, the average size of Ni NPs increases, leading to lower exposed surface for the reaction. To confirm it, the Ni average particle size of Ni(10)/g-CN and Ni(40)/g-CN was measured (**Figure S4**). Ni average particle sizes of 16 ± 8 nm and 27 ± 15 nm for Ni(10)/g-CN and Ni(40)/g-CN, respectively, were calculated based on the measurement of a statistically relevant number of Ni NPs. Therefore, it can be concluded that while the increase of Ni loading from Ni(10)/g-CN to Ni(25)/g-CN does not produce a notable change in the particle size, further increase from Ni(25)/g-CN to Ni(40)/g-CN promotes a significant enlargement of the particle size. As a consequence, a compromise between these two opposite effects, loading and particle size, is reached for the Ni(25)/g-CN sample, achieving a maximum photocatalytic activity of $220 \mu\text{mol CH}_4 \text{ g}^{-1} \text{ 8h}^{-1}$ ($28 \mu\text{mol CH}_4 \text{ g}^{-1} \text{ h}^{-1}$). To our knowledge, this is the highest value reported in the literature for noble metal-free carbon nitride-based photocatalysts (**Table S1**).

In order to confirm the origin of the C source in the CH₄ production, isotopically labelled ¹³CO₂ was used as substrate in the photocatalytic CO₂ methanation and the obtained products were analyzed after reacting for 8 h under optimal conditions by GC-MS (**Figure S5** in

supplementary Information). The analysis shows a main peak at $m/z = 17$ and its fragmentation at $m/z=16, 15, 14$, etc., which corresponds to $^{13}\text{CH}_4$. The latter confirms that the produced CH_4 arises completely from the reduction of the $^{13}\text{CO}_2$. Moreover, the lack of observation of volatile molecules from g-CN indicates its good stability as photocatalyst in the reaction conditions. Control experiments in the absence of CO_2 , H_2 (gases substituted with Ar in order to achieve the same total pressure), light or photocatalyst were carried out, and only a negligible CH_4 production was measured in all these control experiments (**Table 1**), indicating that the reduction of CO_2 by H_2 is photocatalytic. The influence of temperature was studied by measuring the catalytic activity at 50, 100, 150 and 200 °C (**Table 1**). The CH_4 production rate grew exponentially with temperature following an Arrhenius dependence. The estimated apparent activation energy was 5.06 KJ mol⁻¹ (**Figure S6**) which to our knowledge is the lowest value ever reported for the CO_2 methanation reaction.^[4a, 5c, 17]

No CH_4 production was detected at 50 °C: a threshold temperature of 100 °C was found necessary to promote the CO_2 methanation reaction. It has been previously reported that a minimum temperature is needed in this reaction in order to desorb the H_2O molecules formed as byproduct in the catalysts. Mateo et al. also observed this behavior in analogous systems.^[17a, 18] Thus, we attribute the requirement of temperatures higher than 100 °C to the desorption of H_2O molecules from the photocatalyst sites during the reaction.

2.3. Mechanism

With the aim of elucidating whether the photocatalytic activity of Ni(25)/g-CN arises from a photothermal or photo-induced charge transfer process, CO_2 methanation was carried out by replacing H_2 with a sacrificial electron donor (dimethylaniline (DMA), **Table 1**). A temperature of 200 °C was used in this reaction in order to be above the high boiling point of DMA (194 °C). Under these conditions, the Ni(25)/g-CN produced 107.7 $\mu\text{mol g}^{-1}\text{h}^{-1}$ of CH_4 , suggesting

the photogeneration of electron-holes pairs as the main reaction mechanism.

Photoluminescence experiments (**Figure 4d**) unveil a significant quenching of the g-CN emission upon Ni deposition, owing to the operation of non-radiative paths through Ni-N covalent bonds.^[19] This fact, along with the enhanced optical absorption observed in the UV-vis spectra confirms the strong modification of the band structure of g-CN upon formation of Ni NPs in the surface. The resulting electron-rich Ni NPs in the surface of g-CN serve as reactive sites that increase the affinity of the catalyst towards CO₂ and H₂ molecules, reducing the activation energy of the photo-catalytic reaction.^[20]

Photocurrent measurements further confirmed the generation of photoexcited electron-hole pairs (**Figure 4a**). The photoelectrodes were fabricated by depositing identical amounts of g-CN and Ni(25)/g-CN on FTO substrates (see experimental section). The Ni(25)/g-CN sample exhibits enhanced photocurrent density compared to the pristine g-CN, owing to the improved charge separation, which in turn explains the observed higher photocatalytic activity. The light response was further confirmed by photocurrent measurements and incident photon-to-current (IPCE) measurements, revealing the photoactivity of Ni(25)/g-CN photocatalyst upon monochromatic light irradiation at 400, 420, 450, 480 and 510 nm (**Figure 4b and Figure S7**). This indicates that the catalyst is photoactive even in the visible region, which corresponds to the absorption of the material. The photocatalytic CO₂ methanation reaction using Ni(25)/g-CN photocatalysts was carried out at 150 °C upon irradiation of visible light using a 400 nm cut-off filter in the Xe lamp. The CH₄ production rate is shown in Table 1, obtaining 8 μmol of CH₄ g⁻¹ h⁻¹ under these conditions, indicating that approximately 30 % of the total CH₄ production is obtained from photons absorbed in the visible region. Electrochemical impedance spectroscopy measurements disclose an enhancement in the charge transfer resistance for Ni(25)/g-CN, speaking for the improved charge transfer processes between Ni NPs and g-CN (**Figure 4c**).

With all data in hand we can confirm that following the generation of electron-hole pairs, the electron travels rapidly through the g-CN-Ni interface towards the surface of the catalyst creating an electron rich reactive spots with enhanced affinity for CO₂ and H₂. Furthermore, enhancing the reaction temperature rises the pressure in the reactor and therefore the reactant molecules mobility, which results in a higher reactivity and higher methane production values.

2.4. Photocatalyst stability

The stability of Ni(25)/g-CN in the methanation reaction was investigated by performing recycling experiments, wherein the photocatalysts were exposed to the methanation reaction for multiple 8-h cycles. During each cycle, the gases evolved were continuously measured. Each new cycle starts with thorough Ar purging of the system to remove the products of the previous run, prior to a subsequent CO₂ and H₂ loading and an 8-h irradiation test. This procedure was repeated again and the temporal gas evolution in the three consecutive cycles are presented in Figure 5 (a). Despite the long photocatalytic experiments and the high temperature of the photocatalytic methanation, the catalyst preserved up to ~70 % of its initial activity, a value which is high considering the state of art. We believe that this decrease in the production is related to the increase of the Ni NPs size during long reaction time (Figure 5b), which results in less amount of active sites and therefore lower catalytic performance.

3. Conclusion

In summary, we showed an efficient CO₂ methanation at relatively low temperature using g-CN decorated with Earth-abundant Ni as photocatalyst for a gas-phase Sabatier reaction. The Ni(x)/g-CN photocatalysts were prepared by impregnating a g-CN substrate with various amounts of Ni precursor, reaching a homogeneous dispersion. Our results reveal a low activation energy for the reaction and high response in the visible region, leading to a remarkable CH₄ production for a non-noble metal catalyst. We believe that this work constitutes a substantial step toward the utilization of g-CN and nanoparticles for CO₂ reduction and other important catalytic reactions.

4. Experimental Section

4.1. g-CN synthesis

g-CN was synthesized following a previously described method.^[21] In brief, a supramolecular assembly was prepared by mixing cyanuric acid and melamine (1:1 molar ratio) in water for 4 h. The assembly was isolated by centrifugation and removal of the supernatant, and dried overnight in vacuum at 60 °C. The resulting powders were calcined at 500 °C for 4 h (heating rate of 2.3 °C min⁻¹) under an inert atmosphere of nitrogen.

4.2. Ni/g-CN synthesis

Ni/g-CN composites were obtained by a wet-impregnation method.^[18, 22] Here, aqueous solutions of Ni(NO₃)₂·6H₂O of different concentrations were added dropwise to a g-CN dispersion in water. The resulting material was filtered, washed with acetone and dried overnight at 60 °C. The Ni(II)/g-CN powders were reduced under H₂ flow (100 mL min⁻¹) at 400 °C for 2 h with a heating rate of 10 °C min⁻¹. The resulting solid was washed with water and acetone, dried overnight and labelled as Ni(x)/g-CN (Where x corresponds to the weight percentage of Ni(II) added in the wet impregnation, namely 2, 5, 10, 25 and 40).

4.3. Photocatalytic CO₂ methanation

Ni(x)/g-CN photocatalysts were loaded in quartz photoreactors (51 mL) equipped with a heating mantle, a nickel alloy thermocouple and temperature controller in the presence of H₂ and CO₂ in stoichiometric amounts (4:1). The photoreactor was heated at the required temperature, and after temperature stabilization it was irradiated with a UV-Vis light from a 300 W Xe lamp. The CH₄ formation was followed by direct measurement of the gases evolved during reaction with an Agilent 490 MicroGC. Gas quantification was based on prior calibration of the system injecting mixtures with known percentage of gases. The average quantum yield

(AQY) was calculated utilizing an incident photon number obtained by the average of the total Xe lamp spectrum. AQY value was obtained following the next equation:

$$AQY (\%) = \frac{8 * \text{number of produced } CH_4 \text{ molecules}}{\text{number of incident photons}} * 100$$

4.4. Characterization

High resolution Transmission Electron Microscopy (HRTEM) images and Energy Dispersive X-ray (EDX) spectroscopy and elemental mapping were obtained using a JEOL JSM-7400F system operated at 3 KV equipped with Thermo Scientific NORAN System SIX. High Resolution Transmission electron microscopy (HRTEM) images were recorded using a FEI Tecnai T-12 G² TWIN transmission electron microscope operated at 120 kV. X-ray diffraction patterns (XRD) of the synthesized powders were obtained using an Empyrean powder diffractometer (Panalytical). Ultraviolet-visible spectroscopy (UV-Vis) spectra were collected using a Cary 100 spectrophotometer. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher Scientific ESCALAB 250 using monochromated Al K α X-Rays (1486.6 eV). Electrochemical measurements were recorded using a three-electrode system on an Autolab potentiostat (Metrohm, PGSTAT 101). A Pt foil and an Ag/AgCl (sat. KCl) electrodes were used as the counter and reference electrodes, respectively. Photocurrent measurements were obtained under 1000 W m⁻² illumination in basic electrolyte (0.1 M KOH), and the electrodes were prepared by drop casting a dispersion (2 mg ml⁻¹) of the materials in water over pre-cleaned FTO substrates.

Supporting Information

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

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Figure 1. Preparation procedure for the Ni(x)/g-CN samples (a), and their XRD patterns (b) and diffuse reflectance UV-Vis spectra (c).

Figure 2. Experimental XPS C1s (a), N 1s (b) and Ni 2p3 (c) peaks measured for Ni(25)/g-CN sample. It should be noted that, for the Ni spectra, the 2p1 and satellite contributions have been excluded for simplicity and a more accurate fitting of the 2p3 chemical state. HRTEM images of Ni(25)/g-CN photocatalyst at different magnifications. Inset in (e) shows the histogram of

particle size distribution and (f) shows one of the Ni NP with the interplanar distance highlighted in yellow.

Figure 3. CH₄ evolution using the Ni(x)/g-CN photocatalyst at 150 °C and 1080 W m⁻² illumination after a reaction time of 2 h. 25 mg of each photocatalysts and partial pressures of 1.05 and 0.25 bar for H₂ and CO₂, respectively, were used.

Table 1. Reaction conditions and initial CH₄ production rates (2 h) obtained upon 1080 W m⁻² irradiation at a total pressure of 1.3 bar. The amount of photocatalyst in all experiments was 25 mg.

Sample	Conditions	CH ₄ (μmol g ⁻¹ h ⁻¹)
g-CN	150 °C	2.7
Ni(2)/g-CN	150 °C	2.9
Ni(5)/g-CN	150 °C	6.2
Ni(10)/g-CN	150 °C	14.9
Ni(40)/g-CN	150 °C	5.9
Ni(25)/g-CN	150 °C, 400 nm cut-off filter	8
Ni(25)/g-CN	50 °C	-
Ni(25)/g-CN	100 °C	4.8
Ni(25)/g-CN	150 °C	28
Ni(25)/g-CN	200 °C	103.5
Without cat.	150 °C	-
Ni(25)/g-CN	150 °C, Ar + H ₂	-

Ni(25)/g-CN	200 °C, DMA + CO ₂	107.7
Ni(25)/g-CN	150 °C, darkness	-
Ni(25)/g-CN	150 °C, only Ar	-
Ni(25)/g-CN	150 °C, Ar + CO ₂	-
NiO	200 °C	31.1

Figure 4. (a) Photocurrent measurements using full light illumination in electrodes prepared by depositing g-CN (black) and Ni(25)/g-CN (red) photocatalysts on FTO. (b) IPCE measurement (red) of Ni(25)/g-CN-based photoelectrode and the Ni(25)/g-CN diffuse reflectance UV-Vis spectrum (black). (c) Nyquist plot of g-CN (black) and Ni(25)/g-CN (red) photocatalysts. (d) Emission spectra of g-CN (black) and Ni(25)/g-CN photocatalysts dispersions in water at 2 mg ml^{-1} under excitation at 370 nm.

Figure 5. (a) CH_4 evolution using Ni(25)/g-CN photocatalyst upon 1080 W m^{-2} at 150°C and several reuses. (b) HRTEM image of Ni(25)/g-CN photocatalyst after reusing. Inset shows the particle size histogram. Total photocatalyst amount 25 mg.

A new, highly efficient and stable photocatalyst comprises of Ni nanoparticles supported on graphitic carbon nitride (g-CN) for the gas-phase CO₂ methanation at very low temperature (150 °C) is reported. Detailed mechanistic studies reveal a very low activation energy for the reaction due to the interaction of g-CN and the Ni nanoparticles, leading to very high activity under visible light.

Keywords: Sabatier reaction, CO₂ reduction, carbon nitride, Ni nanoparticles, photocatalysis

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A Heterogeneous Carbon Nitride-Nickel Photocatalyst for Efficient Low-Temperature CO₂ Methanation

Supporting Information

Supporting information for:

A Heterogeneous Carbon Nitride-Nickel Photocatalyst for Efficient Low-Temperature CO₂ MethanationJesús Barrio,¹ Diego Mateo,² Josep Albero,² Hermenegildo García^{2*} and Menny Shalom^{1*}

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E-mail: hgarcia@qim.upv.es **Scheme 1.** Typical CO₂ reduction reactions and their corresponding potentials.

Figure S1. XRD pattern of bare g-CN

Figure S2. STEM image of Ni(25)/g-CN and elemental analysis for the individual elements by EDS.

Figure S3. CH₄ evolution using the Ni(x)/g-CN photocatalyst at 150 °C and 1080 W m⁻² illumination. 25 mg of each photocatalysts and partial pressures of 1.05 and 0.25 bar for H₂ and CO₂, respectively, were used.

Figure S4. HRTEM images of Ni(10)/g-CN (a) and Ni(40)/g-CN (b) photocatalyst. Insets show the histogram of particle size distribution.

Table S1. Performance of carbon nitride materials for methane production.

Material	CH ₄ production	Reaction conditions	Reference
S-CN	0.27 $\mu\text{mol g}^{-1}$	10 mg catalyst, CO ₂ - Vapor H ₂ O	[1]
rGO/CN	13.93 $\mu\text{mol g}^{-1}$	100 mg catalyst, CO ₂ - Vapor H ₂ O	[2]
CN-ns	1.39 $\mu\text{mol g}^{-1} \text{ h}^{-1}$	100 mg catalyst, NaHCO ₃ , H ₂ SO ₄	[3]
CN-Pt	0.12 $\mu\text{mol 4h}^{-1}$	100 mg catalyst, NaHCO ₃ , HCl	[4]
CN/SnS ₂	0.64 $\mu\text{mol g}^{-1}$	50 mg catalyst, NaHCO ₃ , H ₂ SO ₄	[5]
MCF-CN	0.78 $\mu\text{mol g}^{-1}$	10 mg catalyst, CO ₂ - Vapor H ₂ O	[6]
LDH/CN	3.7 $\mu\text{mol 24h}^{-1}$	0.5 wt% Pd, CO ₂ - H ₂ O	[7]
Mo-CN	123 $\mu\text{mol g}^{-1} \text{ 8h}^{-1}$	100 mg catalyst, CO ₂ - Vapor H ₂ O	[8]
NaNbO ₃ /CN	6.4 $\mu\text{mol g}^{-1} \text{ h}^{-1}$	50 mg catalyst, CO ₂ - Vapor H ₂ O	[9]
Defective CN	1.91 $\mu\text{mol h}^{-1} \text{ g}^{-1}$	41% humidity, 100 mg catalyst, NaHCO ₃ , H ₂ SO ₄	[10]

CNDs/TiO ₂	5.21 $\mu\text{mol h}^{-1} \text{g}^{-1}$	60 mg catalyst, NaHCO ₃ , H ₂ SO ₄	[11]
CeO ₂ /g-C ₃ N ₄	0.694 $\mu\text{mol h}^{-1}$	50 mg catalyst, CO ₂ - Vapor H ₂ O	[12]
MPCN	15.6 $\mu\text{mol h}^{-1}$	20 mg catalyst, NaHCO ₃ , H ₂ SO ₄	[13]

Figure S5. Mass spectra of the reaction product from $^{13}\text{CO}_2$ and H_2 on Ni(25)/g-CN showing that $^{13}\text{CH}_4$ is the main reaction product, as revealed by the peak at $m/z=17$ (further fragmentation results in peaks at 16 and 15).

Figure S6. CH_4 production rate at different temperatures (a), and Arrhenius $\ln K$ vs $1/T$ plot.

Figure S7. Photocurrent measurements in Ni(25)/g-CN-based photoelectrodes using different monochromatic illumination sources.

Figure S8. XRD patterns of Ni(25)/g-CN after (red) and before (black) reuses.

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