



Article Photocatalytic Reduction of CO₂ over Iron-Modified g-C₃N₄ Photocatalysts

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Abstract: Pure g-C₃N₄ sample was prepared by thermal treatment of melamine at 520 °C, and iron-modified samples (0.1, 0.3 and 1.1 wt.%) were prepared by mixing g-C₃N₄ with iron nitrate and calcination at 520 °C. The photocatalytic activity of the prepared materials was investigated based on the photocatalytic reduction of CO₂, which was conducted in a homemade batch reactor that had been irradiated from the top using a 365 nm Hg lamp. The photocatalyst with the lowest amount of iron ions exhibited an extraordinary methane and hydrogen evolution in comparison with the pure g-C₃N₄ and g-C₃N₄ with higher iron amounts. A higher amount of iron ions was not a beneficial for CO₂ photoreduction because the iron ions consumed too many photogenerated electrons and generated hydroxyl radicals, which oxidized organic products from the CO₂ reduction. It is clear that there are numerous reactions that occur simultaneously during the photocatalytic process, with several of them competing with CO₂ reduction.

Keywords: g-C₃N₄; iron; CO₂ reduction; photocatalysis

1. Introduction

The most pressing problems of the present time are undoubtedly the increasing energy requirements that are closely connected to fossil fuel combustion and the increasing concentration of greenhouse gases in the atmosphere. These problems are related, and finding a new clean source of energy is becoming increasingly important. Developed countries are trying to regulate greenhouse gas emissions; for example, the European Union has a long-term goal to reduce its carbon footprint. The first step towards this goal was to reduce greenhouse gas emissions by 20% (from 1990 levels) by 2020. This goal was successfully achieved, and emissions were reduced by 23% in 2018. However, a new legislation was put in place and added to the Paris Agreement. This legislation aims to reduce greenhouse gas emissions by 40% (from 1990 levels) by 2030. According to Energy in figures—Statistical Pocket Book 2019 issued by European Union, world energy production is increasing every year, and it is predicted that it will continue to rise in the years to come [1]. The highest annual increase of world energy production still comes from solid fossil fuels and natural gas compared to renewable or nuclear sources. Fossil fuel reserves are not infinite, and when considering the rate at which the world's energy consumption is increasing, it is clear that more focus has to be placed on finding new sources of energy. The photocatalytic reduction of carbon dioxide (CO_2) is currently one of the hottest candidates



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). for this purpose. Not only can the products (CO, CH₄) of this reaction be used as an energy source, but the reaction utilizes CO_2 , which is the most abundant source of carbon and is also considered to be a waste; therefore, it is not utilized [2]. The photocatalytic community has been studying the photocatalytic reduction of CO_2 for years. While the exact mechanism is not known, many important advances have been made [3,4].

There have been many photocatalysts that have been discovered, and different combinations of these photocatalysts have been tested to determine which combination produces the best photocatalytic reduction of CO₂ over the years [5,6]; however, most attention has focused on TiO₂ [7–9]. TiO₂ has quite large band gap energy, and more importantly, the conduction band potential is not in a convenient position located at around -0.5 V (vs. NHE at pH = 7), which is very close to the required redox potentials of essential reactions such as CO₂/HCOOH (-0.61 V) CO₂/HCHO (-0.48 V), 2H⁺/H₂ (-0.41 V), and CO₂/CH₄ (-0.24 V) [7]. Finding a new photocatalyst is an immediate goal that most of the photocatalytic community is focused on.

Graphitic carbon nitride (g-C₃N₄) has attracted increasing attention from the photocatalytic community, and research groups dealing with the photocatalytic reduction of CO₂ have already noticed its potential [10–12]. Its indirect band gap energy (around 2.7 eV) is especially narrow, and it has a conduction band potential (around -1.4 V) that makes it promising [13,14]. g-C₃N₄ has also high chemical stability, and more importantly, it has much more suitable potential of valence and conduction bands than TiO₂ [15]. The photocatalytic community is trying to shift the reaction into the visible light region, and the band gap energy of 2.7 eV can allow that. This corresponds approximately to a wavelength of 460 nm, which is somewhere on the edge between the blue and green region of visible light.

Even though $g-C_3N_4$ is a promising photocatalyst, it has a lot of drawbacks, such as low specific surface area, the fast recombination rate of generated charge carriers, and the particle boundary effects that interrupt the delocalization of electrons [16]. The advantages and disadvantages of $g-C_3N_4$ are summarized and discussed in the following reviews [16,17].

Many research teams have focused their attention to overcome the disadvantages of $g-C_3N_4$. Various modifications of $g-C_3N_4$ have been investigated in order to increase photocatalytic activity. For example, the specific surface area of $g-C_3N_4$ can be significantly enhanced by exfoliation [18,19]. There are several possibilities and techniques that can be used to achieve the exfoliation [20,21]. Another method for enhancing the photocatalytic activity of $g-C_3N_4$ is metal modification, which is mainly used as an effective approach to tune the electrical and optical properties [22]. Noble metals are the first and obvious choice [10,23]. However, noble metals are expensive, and therefore, other metal modification possibilities have been investigated. One such possibility is zero-valent iron, which is a cost-effective alternative, and $g-C_3N_4$ with incorporated iron particles has shown the improved absorption of visible light and as well as the lower recombination of charge carriers [24]. Modification caused by iron can also create a synergetic system that combines the Fenton and photocatalytic processes. When iron is present in a trivalent form, Fenton process can proceed [25]. Since there are a lot of lone electron pairs in the $g-C_3N_4$ heptazine structure, bonding with a foreign metal cation is relatively easy [26].

Although g-C₃N₄ only attracted the attention of the photocatalytic community just a few years ago, numerous papers about various modifications of g-C₃N₄ for the photocatalytic reduction of CO₂ can be found [11,27]. However, to the best of our knowledge, there is only a very limited number of works describing the utilization of g-C₃N₄/Fe for this application. In the present work, iron-modified g-C₃N₄ photocatalysts were synthesized by a simple in situ method. The photocatalysts were characterized and tested for photocatalytic CO₂ reduction where selectivity towards certain products was revealed and discussed.

2. Materials and Methods

2.1. Preparation

Melamine powder 99% was purchased from Alfa Aesar, and iron nitrate 98% was purchased from Chem-Lab.

Bulk g-C₃N₄ was synthesized by thermal polycondensation of melamine. The conditions were chosen by taking the relevant literature into account [28–31], and the results of our previous work were also considered [32,33]. Typically, 5 g of melamine was put into a covered alumina crucible and was heated in a muffle furnace in air to 520 °C with a rate of 5 °C/min, where it remained for 2 h. The yellow product (yield~2.4 g) was collected and was ground into fine powder. The sample was called CN.

A similar procedure was used for the preparation of the iron-modified g-C₃N₄ photocatalysts. In detail, 5 g of melamine was mixed with specific amounts of iron nitrate resulting in iron concentrations of 0.1, 0.3, and 1.1 wt.%. The mixture was stirred in 100 mL H₂O for 1 h to achieve a homogeneous suspension. After drying at 80 °C in an oven, the powder was put into a covered alumina crucible and was heated in a muffle furnace in air to 520 °C at a rate of 5 °C/min, where it remained for 2 h. The product (yield~2.5 g) was collected and ground into fine powder. The samples were called CN-Fe*x*, where *x* is the amount (wt.%) of iron.

2.2. Characterization

The crystalline structure, surface area, porosity, chemical composition, and optical characteristics of the samples were thoroughly examined, and the nature of the iron ions was also investigated. Details about the characterization techniques and the equipment that was used are presented in the Supplementary Materials.

2.3. Photocatalytic Test

The photocatalytic reduction of CO_2 was performed in a homemade batch-stirred stainless steel reactor (volume 348 mL) with a quartz glass window on the top (Figure S1). A UV 8 W Hg lamp (peak intensity at 365 nm; Ultra-Violet Products Inc., Cambridge, UK) was used as a light source, and it was located over the quartz glass window of the reactor at a specific height so that the intensity on the level of the suspension was 0.833 mW/cm².

The reactor was filled with 0.09 g of each photocatalyst and 100 mL of 0.2 M NaOH. The NaOH was added in order to increase the solubility of CO_2 in water, thus facilitating the photocatalytic reaction. The suspension was stirred with a magnetic stirrer the entire time to prevent the sedimentation of the photocatalyst. Before the photocatalytic reaction began, the reactor was tightly closed and purged with (He or) CO_2 . The pH of the suspension decreased during the purging from ~12.5 to ~6.9. A detailed description of the experimental procedure is available in the Supplementary Materials.

The gaseous samples were analyzed in 2 h intervals between the duration 0–8 h, where 0 corresponded to the moment prior to UV irradiation. Samples were collected using a gastight syringe (Hamilton Co., Reno, NV, USA) and were analyzed on a gas chromatograph (Shimadzu Tracera GC-2010 Plus) equipped with a BID detector. Each sample was measured at least three times using the same batch (same photocatalyst, same NaOH) in order to confirm the durability of the photocatalyst and the reproducibility of the experiments (within 5% error). The photon flux and apparent quantum yields (AQY) for individual products in the presence of each photocatalyst were calculated. The photocatalysts were first examined in an inert atmosphere to confirm that no products were formed, and after that the photocatalytic reduction of CO_2 was conducted.

3. Results and Discussion

3.1. Crystalline Structure

The XRD patterns of the g- C_3N_4 photocatalysts are presented in Figure 1. For all of the samples, the two characteristic diffraction peaks of g- C_3N_4 are observed (JCPDS, PDF #87-1526). The weak peak at 13.1° corresponds to the (100) plane, which is related to the

in-plane structural packing motif of the tri-s-triazine units with an interplanar distance of d = 0.675 nm [34,35]. The strong peak at 27.5° corresponds to the (002) plane, which is attributed to the interlayer stacking of aromatic rings with a distance of d = 0.324 nm [36,37]. After the modification, no additional peaks corresponding to iron are observed, which was probably due to the low initial amount of iron nitrate. Furthermore, there are no significant changes to the position or the intensity of the peaks, indicating that the crystalline structure of the materials is preserved [38].



Figure 1. XRD patterns of the g-C₃N₄ photocatalysts.

3.2. Surface Area and Porosity

The N₂ adsorption–desorption isotherms and pore-size distributions of the $g-C_3N_4$ photocatalysts are displayed in Figure S2, with the characteristic values given in Table 1. All of the samples showed characteristic hysteresis loops of type IV isotherms, which is typical for mesoporous materials [39]. After the modification, the specific surface area of the photocatalysts decreased, which can be attributed to the partial blocking of the $g-C_3N_4$ pores by the iron. On the other hand, the pore size distribution remained practically unchanged across all of the samples.

Table 1. BET surface area, average pore size, and total pore volume of the g-C₃N₄ photocatalysts.

Sample	BET Surface Area (m ² /g)	Average Pore Size (nm)	Total Pore Volume (cm ³ /g)
CN	16	13.7	0.11
CN-Fe0.1	13	19	0.12
CN-Fe0.3	11	18.7	0.11
CN-Fe1.1	7	38.5	0.12

3.3. Chemical Composition

The FT-IR analysis results are shown in Figure 2. For all of the samples, the known characteristic peaks of $g-C_3N_4$ can be observed. The broad peak at the 3500–3000 cm⁻¹

region corresponds to the stretching mode of all of the OH-containing species and N-H stretching from the residual amino groups [40,41]. The shoulder located at 1630 cm⁻¹ represents the H-O-H bending mode of all of the water molecules present at the surface of the material. The peaks in the 1628–1232 cm⁻¹ region correspond to the characteristic stretching of the C-N heterocycles, including the trigonal N-(C)₃ and bridging H-N-(C)₂ units [42]. Finally, the sharp absorption peak at 805 cm⁻¹ can be attributed to the breathing mode of the triazine units [43]. The FT-IR spectra of the modified materials demonstrate no significant changes. More specifically, there is no observable shift in the peaks, indicating that the chemical bonding of the main g-C₃N₄ network is unaffected [38].



Figure 2. FT-IR spectra of the g-C₃N₄ photocatalysts.

3.4. Optical Characteristics

The measured diffuse reflectance spectra of the g-C₃N₄ photocatalysts are shown in the inset of Figure 3. They were used for the construction of the absorption functions $(F \times E)^{1/2} = f(E)$ presented in Figure 4, which allowed the determination of the materials' band gap energy (E_g), as described in Ref. [44]. It is evident that after modification, the light absorption of the materials is increased. However, the E_g only slightly decreased from 2.73 eV for bulk g-C₃N₄, which is in agreement with the literature [16,17], to 2.71 eV for the modified samples.

The properties of the photogenerated charge carriers were evaluated with fluorescence measurements at $\lambda_{ex} = 365$ nm (Figure 4). All of the samples showed a broad band with λ_{em} at around 455 nm, which is in agreement with the absorption edge wavelength measured by UV-vis spectroscopy. Such a signal can be attributed to the band–band PL phenomenon, which mainly results from the $n-\pi^*$ electronic transitions in g-C₃N₄ [45]. The strongest emission intensity is displayed by bulk g-C₃N₄, which suggests a faster electron–hole radiative recombination rate. On the other hand, the modified samples show significantly weaker emission intensity, which becomes even more prominent as the iron content increases. This indicates a lower recombination rate and higher charge transfer efficiency, suggesting a potential improvement in the photocatalytic activity of the materials.



Figure 3. UV-Vis diffuse reflectance (inset) and plots of $(F \times E)^{1/2}$ vs. photon energy of the g-C₃N₄ photocatalysts.



Figure 4. PL spectra of the $g-C_3N_4$ photocatalysts.

Photoelectrochemical measurements are one of the characterization techniques that allow the prediction of the photocatalyst behavior. Since the photocatalyst is irradiated under an external potential that has been applied to the working electrode, the recombination of electrons and holes is strongly suppressed. Based on the photocurrent generation (Figure 5), it is clear that the highest amount of charge carriers is produced in the case of bulk g-C₃N₄. This is connected to a higher specific surface area. However, a higher amount of produced charge carriers does not mean higher photocatalytic activity, especially since bulk g-C₃N₄ has the highest recombination rate of charge carriers (Figure 4). It is known that the redox potential of Fe³⁺/Fe²⁺ is below the CB of g-C₃N₄. After iron modification, the photogenerated electrons could be trapped by the Fe²⁺ sites, leading to the reduced recombination of the photogenerated electron–hole pairs. With a higher iron concentration, more photogenerated electron trapping sites exist, thus leading to the further decrease of the PL intensity.



Figure 5. Photocurrent generation of g-C₃N₄ photocatalysts recorded under 1 V external potential.

3.5. Mössbauer and EPR Spectroscopy

Mössbauer spectroscopy was used to investigate the nature of the iron of the modified $g-C_3N_4$ photocatalysts. The 80 K spectra of samples CN-Fe0.3 and CN-Fe1.1 are shown in Figure 6. The most prominent characteristic of both spectra are the two distinct doublets that are characteristic of the Fe²⁺ ions in two different chemical environments [46]. These environments may be associated with the iron that is present in the $-C_3N_4$ network gaps or on the layer surface. The spectra also show a lower intensity doublet showing the presence of Fe³⁺ ions. A subspectrum that can be attributed to magnetic Fe₂O₃ [47], which is most likely due to the reaction of weakly stabilized Fe^{3+/2+} ions with air, is also observed in all of the spectra. At 80 K there is no sign of any subspectral broadening that would suggest the existence of superparamagnetic nanoparticles. Thus, the only crystalline iron-containing phase observed through Mössbauer spectroscopy is that of the Fe₂O₃ oxide.



Figure 6. Mössbauer spectra of the samples CN-Fe0.3 (**a**) and CN-Fe1.1 (**b**), where the Fe²⁺ species are in green, the Fe³⁺ species are in blue, and the Fe₂O₃ subspectra are in red.

By comparing the relative spectral areas of the corresponding peaks (Table S2), it is evident that iron in the g-C₃N₄ matrix is mainly present in the form of Fe²⁺ species. This indicates that during melamine polycondensation, the Fe³⁺ ions of the iron nitrate precursor are reduced to Fe²⁺. It should be also noted that the Mössbauer peaks of the sample CN-Fe0.3 are less intense than those of sample CN-Fe1.1, which confirms the lower amount of Fe present in the photocatalyst. The EPR spectra of the modified samples (Figure S3) display a broad line that is characteristic of iron ion–ion interactions [48]. However, as expected, the Fe²⁺ ions were not visible in the EPR measurements.

Recent studies have revealed that transition metal ions such as Au³⁺, Ag⁺, Cu²⁺, and Fe³⁺ may be reduced during g-C₃N₄ synthesis at ~550 °C [49,50]. During melamine polycondensation, apart from NH₃, reactive species such as CNH₂, H₂NCN, and CN₂⁺ are also released. These species can progressively reduce Fe³⁺ to Fe²⁺ until the formed ions are stabilized in the g-C₃N₄ network [51].

3.6. Photocatalytic Activity

Figure 7 shows the dependence of product yields on the irradiation time (0–8 h). The main products of the photocatalytic reduction of CO_2 are methane (Figure 7a) and carbon monoxide (Figure 7b). However, the hydrogen generated from the photocatalytic water splitting is also present in much higher concentrations (Figure 7c).



Figure 7. Time dependence of yields of (**a**) CH₄, (**b**) CO, and (**c**) H₂.

Photocatalytic CO_2 reduction is a complex process with a number of reactions occurring simultaneously. The g-C₃N₄ band gap energy around 2.7 eV (Figure 3) corresponds to a wavelength of approximately 460 nm, and since the photocatalytic reduction was conducted under the irradiation of 365 nm, each incident photon should lead to the generation of an electron and hole. The product yields and the apparent quantum yields (AQY) are shown in the Supplementary Materials (Table S1). Among the photocatalysts, the CN-Fe0.1

demonstrated the highest CH_4 and H_2 AQY at 0.0020% and 0.0733%, respectively. One of the most important properties of a photocatalyst is the CB and VB edge potentials. XPS analysis was used to determine the potential of the valence bands of each photocatalyst (Figure 8).



Figure 8. VB edge potentials measured by XPS.

As can be seen, the VB edge potential shifted to more positive values after the modification, which indicates the increased oxidation efficiency of the photogenerated holes [21]. By combining the band gap energy and VB edge potential values, the CB edge potentials of the materials were also calculated. Thus, the electronic band structures of the g-C₃N₄ photocatalysts were created (Figure 9). As the E_g of the photocatalysts remains practically unchanged after the modification, the CB edge potential shifts to less negative values, indicating a slight decrease in the reduction strength of the photogenerated electrons. However, the potential of CB is still higher than the redox potential that is required for the CO₂ reactions (Equations (1)–(5)).

The potentials of valence and conduction bands slightly differ for each $g-C_3N_4$ material; however, it is approximately inside the interval -1.5 V (CB potential) and 1.2 V (VB potential) vs. NHE (pH = 7). It is the relatively high reduction strength (negative potential of CB) that makes $g-C_3N_4$ such an attractive material.

The potential of CB is negative enough to allow any of the partial redox reactions to proceed (Equations (1)–(5)) [52,53]. However, the direct reduction of a CO₂ molecule by a single electron is not possible due to a very negative required potential of -1.9 V (Equation (6)) [2,5,54,55].

$$CO_2 + 2e^- + 2H^+ \to HCOOH E^0 = -0.61 V$$
 (1)

$$CO_2 + 2e^- + 2H^+ \to CO + H_2O E^0 = -0.53 V$$
 (2)

$$CO_2 + 4e^- + 4H^+ \rightarrow HCHO + H_2O E^0 = -0.48 V$$
 (3)

$$CO_2 + 6e^- + 6H^+ \rightarrow CH_3OH + H_2O E^0 = -0.38 V$$
 (4)

$$CO_2 + 8e^- + 8H^+ \to CH_4 + 2H_2O E^0 = -0.24 V$$
 (5)

$$CO_2 + e^- \to CO_2^- E^0 = -1.90 \text{ V}$$
 (6)

All of the redox potentials are stated vs. NHE at pH = 7.





Based on the equations above, it is clear that the photocatalytic reduction of CO_2 is a multielectron process that also requires the presence of a hydrogen cation. The necessity of a hydrogen cation is the reason why the reaction has to be conducted in aqueous phase or in the presence of water vapor.

There are two possible ways that water can be oxidized by photogenerated holes toward H^+ (Equations (7) and (8)) [56].

$$2H_2O + 4h^+ \to O_2 + 4H^+ E^0 = +0.82 V \tag{7}$$

$$H_2O + h^+ \to OH + H^+ E^0 = +2.32 V$$
 (8)

It is clear that Equation (8) would be more probable since it requires just one hole and one water molecule; however, its redox potential is much more positive than the VB potential of $g-C_3N_4$, and therefore, this reaction cannot proceed in the presence of $g-C_3N_4$ material, leaving Equation (7) as the main source of the required H⁺ ions. This significantly complicates the situation. First of all, the reaction (Equation (7)) is much less probable since it requires two water molecules o and four holes at the same time, but oxygen is also produced along with H⁺. The reduction of oxygen molecules to a superoxide radical (Equation (9)) is one of the competitive reactions for the reduction of CO₂ [27,57].

$$O_2 + e^- \to O_2^- E^0 = -0.33 \,\mathrm{V}$$
 (9)

The presence of oxygen not only competes with CO_2 molecules to be adsorbed on the surface of the photocatalyst but also consumes the necessary electrons that are needed for the reduction.

Another competitive reaction is the reduction of the generated H^+ ions to hydrogen (Equation (10)).

$$2H^+ + 2e^- \to H_2 E^0 = -0.41 V \tag{10}$$

It is this competitive reaction that is responsible for the presence of hydrogen among the detected products (Figure 7c). Methane and carbon monoxide were other detected reaction products that can be generated according to Equations (2) and (5). Unfortunately, the possible products in the liquid phase were below the detection limit, and therefore, their presence could not be confirmed.

It is clear that the photocatalytic reduction of CO_2 is a very complex process that follows several multielectron steps. Nevertheless, the presence of the Fe^{3+}/Fe^{2+} couple (Figure 6) can complicate the situation even more. Many publications say that the presence of iron ions can be beneficial due to the possibility of photo-Fenton process occurring along with the photocatalysis [58–60]. What does this mean in the case of a photocatalytic CO_2 reduction? Part of the photogenerated electrons can directly transfer to Fe^{3+} ions and form Fe^{2+} (Equation (11)).

$$Fe^{3+} + e^- \to Fe^{2+} E^0 = 0.77 V$$
 (11)

Holes, however, stay in the valence band and can participate in the oxidation reaction. The presence of Fe^{3+} can improve the separation of generated charge carriers; however, the negative side effect is the consumption of electrons needed for the photocatalytic reduction of CO_2 ; therefore, finding an optimum amount of iron ions is necessary [15].

Since the Fe²⁺ ions are unstable, they easily oxidize back into Fe³⁺ in the presence of oxygen and form either O_2^- (Equation (12)) or H₂O₂ (Equation (13)).

$$Fe^{2+} + O_2 + e^- \to Fe^{3+} + O_2^- E^0 = -0.05 V$$
 (12)

$$2Fe^{2+} + O_2 + 2H^+ \to 2Fe^{3+} + H_2O_2 E^0 = +0.68 V$$
(13)

The above-mentioned equations clearly suggest the consumption of electrons in both redox Fe^{3+}/Fe^{2+} reactions. Higher amounts of iron ions would clearly explain the lower yields of the CO₂ reduction products. On the other hand, the oxygen used in Equations (12) and (13) does not compete with CO₂ molecules needed for adsorption on the surface of the photocatalyst.

In addition, the holes in g-C₃N₄ VB have sufficient potential to oxidize H₂O to H₂O₂ (+0.69 V vs. NHE) [27,61] and the potential of H_2O_2/OH (1.07 V vs. NHE) [27] is more positive than the redox potential of Fe³⁺/Fe²⁺ (0.77 V vs. NHE) [27,61,62]; the produced H₂O₂ reacts with Fe²⁺ to produce ·OH species. Hydroxyl radical species are very strong oxidizing agents and are very beneficial when the removal of organics in water is the goal. However, the goal is to create organic compounds for the photocatalytic reduction of CO₂. Therefore, a higher amount of Fe would lead to a higher amount of hydroxyl radicals that would be able to oxidize the already generated organic products (CH₄) [27]. This is the reason why the CH_4 yields were lower in the case of photocatalysts containing 0.3 and 1.1 wt.% of Fe (Table S1). Furthermore, when the iron content exceeds an optimal value, the photocatalytic performance decreases, which is possibly due to the competitive capture between the adsorbed CO_2 and Fe^{2+} sites. In this case, an excess of Fe^{2+} sites could trap more photogenerated electrons, leading to fewer electrons being available to react with the adsorbed CO₂ molecules. On the other hand, the higher Fe content in the photocatalyst clearly leads to a higher selectivity toward CO production (Figure 7b). This suggests higher selectivity for CO₂ reduction to CO. Higher amounts of iron ions are incorporated into the g- C_3N_4 lattice and affect its electronic properties, which were confirmed by the valence band position shift after the addition of Fe (Figure 9), forming impurities that lead to an enhanced separation of charge carriers. On the other hand, this means a higher amount of hydroxyl radicals and a higher rate of reverse oxidation for the produced hydrocarbons [63].

4. Conclusions

Iron-modified $g-C_3N_4$ photocatalysts were prepared using a simple thermal treatment of melamine mixed with specific amounts of iron nitrate. The XRD and FT-IR measurements did not reveal any iron in the photocatalysts due to its very low concentrations (0.1, 0.3 and 1.1 wt.%). However, its presence in the form of Fe²⁺, Fe³⁺, and Fe₂O₃ was demonstrated by Mössbauer spectroscopy, with Fe²⁺ being the main species.

The addition of iron resulted in a decrease in the photocurrent and specific surface area due to the partial blocking of the $g-C_3N_4$ pores by iron. However, this led to the reduced recombination of the photogenerated electron–hole pairs, which is important for high photocatalytic efficiency.

The photocatalytic activity measurements of the prepared materials in the CO_2 reduction showed that the photocatalyst with the lowest amount of iron exhibited the biggest methane and hydrogen evolution in comparison with pure $g-C_3N_4$ and $g-C_3N_4$ with higher iron amounts. Excess iron consumes electrons that are needed for the reduction reactions and generates hydroxyl radicals that oxidize organic products from the CO_2 reduction. The iron-modified (0.1 wt.%) $g-C_3N_4$ proved to be a promising photocatalyst for CO_2 conversion into valuable hydrocarbons.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/photochem1030030/s1, Figure S1: The batch reactor used for the photocatalytic reduction of CO₂, Figure S2: N₂ adsorption-desorption isotherms (a) and pore size distribution curves (b) of the g-C₃N₄ photocatalysts, Figure S3: EPR spectra of samples CN-Fe0.3 and CN-Fe1.1, Table S1: Recalculated product yields to μ mol·s⁻¹ and apparent quantum yields (AQY) for each product in the presence of the photocatalysts, Table S2: Mössbauer parameters for samples CN-Fe0.3 and CN-Fe1.1 and corresponding assignments. Isomer Shift (IS), line width (HWHM), Quadrupole Splitting (QS), Hyperfine Magnetic Feld (HMF) and the subspectral area (= relative amount of iron).

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