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# Highly Stable Photocatalytic Dry and Bi-Reforming of Methane with the Role of a Hole Scavenger for Syngas Production over a Defective Co-Doped $g-C_3N_4$ Nanotexture

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Abstract: Photocatalytic reduction of CO<sub>2</sub> with CH<sub>4</sub> through the dry reforming of methane (DRM) is an attractive approach to recycling greenhouse gases into valuable chemicals and fuels; however, this process is quite challenging. Although there is growing interest in designing efficient photocatalysts, they are less stable, and have lower photoactivity when employed for DRM reactions. Herein, we developed a noble metal-free hierarchical graphitic carbon nitride (HC<sub>3</sub>N<sub>4</sub>) loaded with cobalt (Co) for highly efficient and stable photocatalytic dry reforming of methane to produce synthesis gases (CO and H<sub>2</sub>). The performance of the newly designed  $Co/HC_3N_4$  composite was tested for different reforming systems such as the dry reforming of methane, bi-reforming of methane (BRM) and reforming of  $CO_2$  with methanol–water. The performance of  $HC_3N_4$  was much higher compared to bulk g- $C_3N_4$ , whereas Co/HC<sub>3</sub>N<sub>4</sub> was found to be promising for higher charge carrier separation and visible light absorption. The yield of CO and  $H_2$  with  $HC_3N_4$  was 1.85- and 1.81-fold higher than when using  $g-C_3N_4$  due to higher charge carrier separation. The optimized 2% Co/HC<sub>3</sub>N<sub>4</sub> produces CO and H<sub>2</sub> at an evolution rate of 555 and 41.2  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>, which was 18.28- and 1.74-fold more than using  $HC_3N_4$  during photocatalytic dry reforming of methane (DRM), with a  $CH_4/CO_2$  feed ratio of 1.0. This significantly enhanced photocatalytic CO and H<sub>2</sub> evolution during DRM was due to efficient charge carrier separation in the presence of Co. The CH<sub>4</sub>/CO<sub>2</sub> feed ratio was further investigated, and a 2:1 ratio was best for CO production. In contrast, the highest H<sub>2</sub> was produced with a 1:1 feed ratio due to the competitive adsorption of the reactants over the catalyst surface. The performance of the composite was further investigated for bi-reforming methane and methanol. Using photocatalytic CO<sub>2</sub> reduction with  $CH_4/H_2O$ , the production of CO and  $H_2$  was reduced, whereas significantly higher CO and  $H_2$ evolved using the BRM process involving methanol. Using methanol with CO<sub>2</sub> and H<sub>2</sub>O, 10.77- and 1.39-fold more  $H_2$  and CO efficiency was achieved than when using dry reforming of methane. The composite was also very stable for continuous synthesis gas production during DRM in consecutive cycles. Thus, a co-assisted g-C<sub>3</sub>N<sub>4</sub> nanotexture is promising for promoting photocatalytic activity and can be further explored in other solar energy applications.

 $\label{eq:keywords: photocatalysis; dry reforming of methane; bi-reforming of methane; synthesis gas production; hierarchical g-C_3N_4; co-loaded g-C_3N_4$ 



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# 1. Introduction

The industrialization and rapid growth of the economy has resulted in an increase in greenhouse gases, especially carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>), in the atmosphere. Both CO<sub>2</sub> and CH<sub>4</sub> have become the main causes of climate change and global warming [1,2]. Among other methods, the direct conversion of CO<sub>2</sub> into valuable chemicals via catalytic reforming processes is intriguing and promising [3]. Through the dry reforming of methane (DRM) or catalytic CO<sub>2</sub> reforming of CH<sub>4</sub>, CO<sub>2</sub> can be used with methane to recycle both the gases into valuable chemicals and fuels [4]. DRM has a variety of exceptional benefits, including the reduction of both greenhouse emissions and the direct creation of syngas with an equimolar blend of CO and H<sub>2</sub> [5]. However, DRM is more susceptible to coking, operates at higher reaction temperatures, and decreases catalyst stability [6,7].

As an alternative, using phototechnology is a potential method for the photocatalytic conversion of CO<sub>2</sub> and CH<sub>4</sub> to fuels under typical operating conditions. From this perspective, Shi et al. [8] reported the production of C<sub>2</sub>H<sub>6</sub>, CH<sub>3</sub>COOH, CH<sub>3</sub>COCH<sub>3</sub>, and CO products during the photocatalytic dry reforming of methane with a Cu/CdS-loaded TiO<sub>2</sub>/SiO<sub>2</sub> composite. Similar to this, DRM has been studied over a Pt-loaded TiO<sub>2</sub> catalyst, and under UV light irradiation, CO and H<sub>2</sub> were shown to be the primary products [9]. Au/Rh-modified TNTs have recently been used in the photocatalytic dry reforming of methane to produce syngas [10]. Similarly, Rh/TiO<sub>2</sub>-B nanobelts were tested for the photocatalytic dry reforming of methane for synthesis gas production under UV-visible light irradiation [11]. Recently, we studied Ti<sub>3</sub>C<sub>2</sub>-supported TiO<sub>2</sub> for the photocatalytic dry reforming of methane for synthesis gas production under UV-visible light irradiation [12]. Obviously, TiO<sub>2</sub> has been extensively studied, but its poor activity is linked to the quick recombination rate of photo-generated charges, and it is only active under UV light [13]. Therefore, efficient and low-cost photocatalysts that are functional under solar energy are in high demand.

Among noble metal-free semiconductors, graphitic carbon nitride  $(g-C_3N_4)$  is becoming more important to scientists due to its several benefits, including affordability, improved potential for negative reduction, chemical and thermal stability, and its ability to be utilized under solar energy [14,15]. Its smaller specific surface area, compact layered structure, and faster rate of photoinduced charge carrier recombination are some of its key disadvantages [16,17]. To maximize photocatalytic efficiency, a number of enhancing techniques, including loading with metals and semiconductor coupling, have been investigated [18–20]. Limited reports are available on using  $g-C_3N_4$  for the photocatalytic dry reforming of methane. Previously, we reported on a  $GO/g-C_3N_4$  composite for use in the photocatalytic DRM process; photocatalytic efficiency was increased due to efficient charge carrier separation [21]. As cocatalysts, many noble metals, such as Pt, Au, Ag, and Ru, are frequently used to form and transport charge carriers to enhance  $g-C_3N_4$  photocatalytic efficiency [22,23]. However, due to their high price and restricted availability, noble metals' application for commercial hydrogen production is severely constrained. Due to their low cost, earth abundance, and reducibility, transition metals, including Ni, Co, Mn, and Fe, are seen as viable replacements for noble metals.

Cobalt (Co) is currently seen to be particularly promising due to numerous important properties like loosely bounded d-electrons, active sites, and effective electron trapping [24,25]. In addition to that, cobalt oxide has a narrow band gap, high surface area, exhibits strong light absorption, and has excellent electrical conductivity [26,27]. More carbon atoms can be attached to the active sites of the photocatalyst, increasing its stability and preventing the production of coke [28]. For instance, we studied hydrogen generation using Ni and Co loaded over TiO<sub>2</sub>, and found promising results and stability during the steam reforming of phenol to produce hydrogen [29]. Co-loaded TiO<sub>2</sub> was found to have increased H<sub>2</sub> evolution because it reduces overpotential and makes photoinduced electron transfer easier [30]. Another study found that loading g-C<sub>3</sub>N<sub>4</sub> with a CoP cocatalyst free of noble metals increased the efficiency of H<sub>2</sub> evolution [31]. To encourage solar energy-assisted

hydrogen synthesis, additional research into cobalt with noble metal-free semiconductors is in high demand.

In this study, a facile approach to developing highly efficient and stable Co-doped g- $C_3N_4$  composites for the photocatalytic dry reforming of methane has been investigated. A hierarchical structured g- $C_3N_4$  (HC<sub>3</sub>N<sub>4</sub>) was synthesized through the controlled decomposition of melamine and urea and was loaded with Co using an impregnation approach. The role of structure and morphology was extensively investigated using a variety of characterization approaches with a variety of experimental validations. The performance evaluation was conducted based on synthesis gas (CO, H<sub>2</sub>) production during the photocatalytic dry reforming of methane (DRM) and bi-reforming with  $CH_4/H_2O$  and  $CH_3OH/H_2O$  systems. The effects of different  $CH_4/CO_2$  feed ratios were investigated to understand the role of reactants' attachment to catalysts' active sites. Comparatively, Co/HC<sub>3</sub>N<sub>4</sub> was found to be more promising for CO production compared to H<sub>2</sub>, and trends were consistent in all types of photocatalyst. Their stability was further investigated in cyclic runs, and catalysts were further characterized after the reactions. A reaction mechanism is further proposed to understand the role of catalysts and reactants in photoactivity and products' selectivity.

### 2. Results and Discussion

# 2.1. Characterization of Materials

The XRD results for the samples of  $g-C_3N_4$ ,  $HC_3N_4$ , and  $Co/HC_3N_4$  are shown in Figure 1a. For  $g-C_3N_4$ , two diffraction peaks at 20 of 12.84° and 27.42°, indexed to the (100) and (002) planes, respectively, were produced. The peak at the 12.84° plane is accounted for by the formation of tri-s-triazine chains, whereas another peak at 27.42° is attributed to aromatic rings in the fundamental in-plane periodic structure, as reported previously [32]. There was no change in the crystalline structure and peak position for the  $HC_3N_4$ , which confirms the successful synthesis of the hierarchical structured  $g-C_3N_4$ . Furthermore, crystalline planes were not minimally altered when Co was loaded over  $HC_3N_4$ , confirming the successful synthesis of a Co-loaded  $HC_3N_4$  composite.

With the help of UV-vis DRS, the optical characteristics of  $g-C_3N_4$ ,  $HC_3N_4$ , and  $Co/HC_3N_4$  were further investigated, and the results are displayed in Figure 1b. There was little difference in the UV-visible light absorption spectra between  $g-C_3N_4$  and  $HC_3N_4$ , definitely due to the crystalline structure remaining unchanged. When Co was loaded onto  $HC_3N_4$ , light absorption was somewhat boosted towards the visible region. Band gap energy values for  $g-C_3N_4$ ,  $HC_3N_4$  and  $Co/HC_3N_4$  were estimated as 2.87, 2.89 and 2.86, respectively. This demonstrates that the influence of co-loading on the change in the band gap energy of  $HC_3N_4$  was negligible. Recently, a  $g-C_3N_4$  compound based on  $Co_3O_4$  was created, and cobalt was found to increase visible light absorption [26].

Through PL analysis, the effectiveness of  $g-C_3N_4$ ,  $HC_3N_4$ , and  $Co/HC_3N_4$  was further studied, and the results are shown in Figure 1c. With pure  $g-C_3N_4$ , more charge carrier recombination led to a higher PL intensity. However,  $HC_3N_4$  showed a lower peak intensity than  $g-C_3N_4$ , which is explained by less charge recombination. This demonstrates that hierarchical structure has a greater potential to lengthen the life of holes and electrons. When Co was loaded onto  $HC_3N_4$ , the lowest PL intensity was achieved due to efficient charge separation in the presence of cobalt. This shows that cobalt not only helps to increase active sites but also functions as a sink to capture and transport carriers of photoinduced charge. In many reports, enhanced charge separation in the presence of metals has been reported. For example,  $g-C_3N_4$  PL intensity was significantly reduced with Co-loading [26].

FESEM was used to examine the structure and morphology of  $g-C_3N_4$ ,  $HC_3N_4$ , and  $Co/HC_3N_4$ , and the results are shown in Figure 2. When melamine was thermally treated in an environment of airtight packed non-uniform sheets of  $g-C_3N_4$ , an uneven structure was obtained, as shown in Figure 2a. Figure 2b shows the morphology of hierarchical and exfoliated sheets of  $g-C_3N_4$  ( $HC_3N_4$ ) produced during the thermal decomposition of melamine with urea. Obviously, gaps are presented between the sheets, which would be useful for the penetration of more light irradiation, in addition to promoting the sorption

process. When Co was loaded onto  $HC_3N_4$ , there was not much difference in the morphology of the pure  $HC_3N_4$  and  $Co/HC_3N_4$  samples. This reveals that Co has no effect in altering morphology; however, it was deposited over the layered structure during the impregnation method. The EDX mapping analysis further confirms the uniform distribution of Co over the  $HC_3N_4$  surface, as shown in Figure 2d. The color images in Figure 2e–h further confirm the presence of Co, C, N, and O over the entire surface. All these findings confirm the successful fabrication of Co-loaded  $HC_3N_4$  using a facile method.



**Figure 1.** (a) XRD analysis of  $g-C_3N_4$ ,  $HC_3N_4$ ,  $Co/HC_3N_4$ , (b) UV-vis DRS analysis of  $g-C_3N_4$ ,  $HC_3N_4$ ,  $Co/HC_3N_4$ , (c) PL analysis of  $g-C_3N_4$ ,  $HC_3N_4$ ,  $Co/HC_3N_4$ .



**Figure 2.** SEM images of (**a**) g-C<sub>3</sub>N<sub>4</sub>, (**b**) HC<sub>3</sub>N<sub>4</sub>, (**c**) Co/HC<sub>3</sub>N<sub>4</sub>; (**d**) EDX mapping of Co/HC<sub>3</sub>N<sub>4</sub>, (**e**-**h**) color images showing the distribution of Co, C, N, and O over the Co/HC<sub>3</sub>N<sub>4</sub> surface.

The elemental state and composition of Co/HC<sub>3</sub>N<sub>4</sub> were examined using X-ray photoelectron spectroscopy (XPS), and the results are presented in Figure 3. Figure 3a displays the N1s spectra with binding energies of 397.5, 399.0 and 401.5 eV, which are associated with C–N=C, N–(C)<sub>3</sub>, and C-NH<sub>2</sub>, respectively [33]. The high-resolution C 1s spectra in Figure 3b has binding energies of 284.6 and 288.1 eV that are attributed to C–C and N–C=N bonds in the sp<sup>2</sup>-hybridized aromatic ring units, respectively [34]. Four peaks in the Co 2p resolution spectrum in Figure 3c were located at binding energies of 780.8, 787.2, 797.3, and 802.3 eV. The binding energies assigned to the spin orbits Co 2p 3/2 and Co 2p1/2, respectively, were 780.6 and 797.3 eV and indexed to Co<sup>2+</sup>. The presence of cobalt in the oxide state is further supported by the two satellite peaks at 787.2 and 802.3 eV. All these results point to the successful loading of Co onto HC<sub>3</sub>N<sub>4</sub> and to the presence of trapping and transporting charge carriers.



Figure 3. XPS analysis of Co/HC $_3$ N $_4$  for (a) N 1s, (b) C 1s, (c) Co 2p.

# 2.2. Photocatalytic Dry Reforming of Methane

To confirm that the results obtained during the photocatalytic reaction were solely obtained during the photocatalytic process, the photocatalytic activity of the synthesized samples was first assessed in a control experiment. To make sure that no product gases  $(CO, H_2)$  were produced from the organic residues, the blank experiments were carried out utilizing N<sub>2</sub> gas in the photoreactor under light illumination without any feed gases  $(CO_2, CH_4)$ . The measurement of product gases  $(CO, H_2)$  using an experiment without a photocatalyst was also carried out. This demonstrates that the photocatalytic reaction products were generated via a photocatalytic DRM process when light irradiation was present.

# 2.2.1. The Effect of Co-Loading on HC<sub>3</sub>N<sub>4</sub> Photoactivity

The performances of  $g-C_3N_4$  and  $HC_3N_4$  were initially investigated for photocatalytic  $CO_2$  reduction with  $CH_4$  through a DRM reaction for the CO and  $H_2$  production, and their results are presented in Figure 4. CO and  $H_2$  yield rates of 18 and 14.78 µmol  $g^{-1}$  were produced with  $g-C_3N_4$  and were increased to 33.35 and 26.8 µmol  $g^{-1}$ , respectively, in the presence of  $HC_3N_4$ . This reveals that the hierarchical structure of  $g-C_3N_4$  has an obvious effect on promoting photocatalytic activity. This augmented photoactivity was due to more light penetration in the nanosheets and its efficient interaction with reactants enabling more production and utilization of photoinduced charge carriers.



**Figure 4.** Photocatalytic CO<sub>2</sub> reduction with CH<sub>4</sub> over g-C<sub>3</sub>N<sub>4</sub>, HC<sub>3</sub>N<sub>4</sub>, and Co-doped HC<sub>3</sub>N<sub>4</sub> composite samples with a CO<sub>2</sub>/CH<sub>4</sub> ratio of 1.0.

Figure 4 also shows the results of a photocatalytic dry reformation of methane (DRM) reaction that uses g-C<sub>3</sub>N<sub>4</sub>, HC<sub>3</sub>N<sub>4</sub>, and Co/HC<sub>3</sub>N<sub>4</sub> samples as photocatalysts to produce syngas (CO and H<sub>2</sub>). In all types of photocatalyst, CO was the main product during the DRM process, and its yield rate was significantly increased with Co-loading onto HC<sub>3</sub>N<sub>4</sub>. Using 1% Co, a CO yield of 717.2 µmol g<sup>-1</sup> was produced, which is 21.5- and 39.85-fold more than was produced with pure HC<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> samples. The highest CO yield rate of 1172.86 µmol g<sup>-1</sup> was obtained, which was 1.42- to 65-fold higher than using 3 and 1% Co-loading and pure g-C<sub>3</sub>N<sub>4</sub> and HC<sub>3</sub>N<sub>4</sub> catalysts. The trends for H<sub>2</sub> production were similar to the CO, wherein the yield rate was much lower. Using 2% Co/HC<sub>3</sub>N<sub>4</sub>, the highest H<sub>2</sub> yield of 92.36 µmol g<sup>-1</sup> was produced, which is 1.49-, 2.1-, 3.5-, and 6.25-fold higher than 3% Co/HC<sub>3</sub>N<sub>4</sub>, 1% Co/C<sub>3</sub>N<sub>4</sub>, HC<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> samples, respectively. Due to the efficient separation of charge carriers in the presence of Co, the amount of CO and H<sub>2</sub> produced during the DRM reaction significantly increased [26]. However, any further increase in Co-loading beyond 2% Co decreases photocatalytic activity of HC<sub>3</sub>N<sub>4</sub> due to the creation of charge recombination centers, which lowers the charge separation efficiency.

Previously, photocatalytic H<sub>2</sub> production with Co<sub>3</sub>O<sub>4</sub>/ZnIn<sub>2</sub>S<sub>4</sub> was conducted, and it was observed that 3 wt. % Co<sub>3</sub>O<sub>4</sub> produced the highest photocatalytic efficiency to maximize H<sub>2</sub> production [35]. In a recent paper, we described the photocatalytic dry reforming of methane using a V<sub>2</sub>AlC MAX/g-C<sub>3</sub>N<sub>4</sub> composite. The primary products obtained were CO and H<sub>2</sub>, with yield rates of 118.74 and 89.52 mol g<sup>-1</sup> h<sup>-1</sup>, respectively [36]. The higher efficiency of V<sub>2</sub>AlC/g-C<sub>3</sub>N<sub>4</sub> was due to efficient charge carrier separation during the photocatalytic process. In several other reports, the dry reforming of methane over various photocatalysts has been investigated, and the enhanced productivity was most probably due to the effective process of charge separation in the presence of cocatalysts and metals. Recently, with the use of Ti<sub>3</sub>C<sub>2</sub> with TiO<sub>2</sub>, CO and H<sub>2</sub>, yield rates of 99.8 and 5.6 µmol g<sup>-1</sup> h<sup>-1</sup> were observed during a DRM reaction with a GO/g-C<sub>3</sub>N<sub>4</sub> composite. The significantly enhanced photocatalytic activity compared to pure materials was because of the effectual separation and utilization of photoinduced electrons and holes during the oxidation and reduction reactions.

# 2.2.2. The Effect of $CH_4/CO_2$ Feed Ratio for CO and $H_2$ Production

Different  $CH_4/CO_2$  feed ratios were chosen while keeping all other variables constant in order to examine the impact of feed ratios on the photocatalytic activity of 2 wt. %  $Co/HC_3N_4$ . Different feed ratios (CH<sub>4</sub>/CO<sub>2</sub>) and their relationships to CO and H<sub>2</sub> evolution are depicted in Figure 5a. The chosen feed ratios for assessing the effect on CO and  $H_2$  evolution under visible light irradiation were  $CO_2/CH_4$  1:1, 1:2, and 2:1. Using a  $CH_4/CO_2$  input ratio of 1:1 affords the maximum rate of CO generation; however, a larger feed ratio reduces that production rate. The production of CO was reduced by adjusting to a feed ratio of 2:1. This revealed that a higher concentration of CH<sub>4</sub> is more beneficial to enhancing the photocatalytic DRM reaction to maximize CO evolution. The highest CO production of 2703  $\mu$ mol g<sup>-1</sup> was achieved using a CH<sub>4</sub>/CO<sub>2</sub> ratio of 2:1, which is 1.22- and 1.61-fold higher than using 1:1 and 2:1 feed ratios of  $CH_4/CO_2$  under identical operating conditions. When increasing the  $CH_4$  concentration, there is more attachment of  $CH_4$ over the catalyst surface, resulting in greater production of protons that were effectively consumed in the reduction of  $CO_2$  to CO. In addition to this, there is the possibility of activating both a reversed water-gas shift (RWGS) reaction and reforming reactions, resulting in more production of CO [22,37]. Previously, it has been reported that  $CO_2$  attachment to the g- $C_3N_4$  surface is efficient to due to the basic nature of g- $C_3N_4$  compared to the acidic nature of  $CO_2$ . Thus, by increasing the initial concentration of  $CH_4$ , both the reactants may be effectively adsorbed for the DRM reaction to proceed. In photocatalysis, the attachment of both reactants is important for the oxidation and reduction reactions to proceed [19]. On the other hand, decreased CO evolution at much higher and lower concentrations may be due to the greater attachment of  $CO_2$  to the catalyst surface, the lower production of protons in the presence of a lesser amount of CH<sub>4</sub>, and inappropriate adsorption of both the reactants [38].

Figure 5b shows the effectiveness of Co/HC<sub>3</sub>N<sub>4</sub> composites for the photocatalytic dry reforming of methane with various CH<sub>4</sub>/CO<sub>2</sub> feed ratios to produce H<sub>2</sub>. Interestingly, varied CH<sub>4</sub>/CO<sub>2</sub> feed ratios produce radically different outcomes for H<sub>2</sub> generation compared with CO production. A large amount of H<sub>2</sub> was produced using a CH<sub>4</sub>/CO<sub>2</sub> feed ratio of 1.0 with an H<sub>2</sub> yield of 164.80 µmol g<sup>-1</sup>, which was decreased to 118.67 and 95.27 µmol g<sup>-1</sup> with the increase in the CH<sub>4</sub>/CO<sub>2</sub> feed ratio. These results can be discussed based on different hypotheses, such as the reactants' adsorption compositions and competitive reactions occurring over the photocatalyst surface. At a CH<sub>4</sub>/CO<sub>2</sub> feed ratio of 1.0, there should be an effective attachment of both the reactants, resulting in a higher rate of oxidation and reduction reactions. Due to the lesser availability of protons, there wer fewer changes in the consumption of hydrogen to be used for the RWGS reaction; thus, a higher amount of H<sub>2</sub> was produced. Likewise, when the feed ratio was increased further by increasing the CH<sub>4</sub> concentration, it became possible for the coupling of methane to produce products

other than hydrogen, resulting in a lower production of hydrogen [39,40]. Therefore, an optimized  $CH_4/CO_2$  feed ratio is required to maximize the production of both CO and  $H_2$  during the photocatalytic dry reforming of methane reactions.



**Figure 5.** Effect of  $CH_4/CO_2$  feed ratio in a photocatalytic DRM process over a  $Co/HC_3N_4$  composite on (a) CO evolution and (b)  $H_2$  evolution.

In several other works, the effects of  $CH_4/CO_2$  feed ratios on product yield and selectivity with various types of photocatalyst have been reported. For instance, the effectiveness of GO/g- $C_3N_4$  was studied using various  $CH_4/CO_2$  feed ratios. It was observed that the highest CO production was obtained with a  $CO_2$ : $CH_4$  ratio of 1.0, whereas  $H_2$  production was favored in a methane-rich feed mixture with a  $CH_4$ : $CO_2$  feed ratio of 2:1 [21]. Similarly, the effects of different feed ratios in DRM and BRM reactions on the performance of  $Ti_3C_2/g$ - $C_3N_4/LDH$  for CO and  $H_2$  evolution have been investigated.

Using a DRM process with a  $CO_2:CH_4$  feed ratio of 2:1, the highest yield of CO was obtained; however, a  $CO_2:CH_4$  feed ratio of 1:2 was conducive to enhancing  $H_2$  evolution. In the case of the BRM process, again, the highest CO was observed when a  $CO_2:CH_4$  feed ratio of 2:1 with  $H_2O$  was tested. Similar trends for  $H_2$  evolutions were observed, in which the maximum yield was obtained with a  $CO_2:CH_4$  feed ratio of 1:2 with  $H_2O$  [41].

# 2.2.3. Photocatalytic CO<sub>2</sub> Bi-Reforming of Methane and Methanol

In photocatalytic CO<sub>2</sub> reforming systems, the product yield and selectivity are entirely dependent on the type of feed mixture and its composition. Therefore, the performance and selectivity of Co/g-C<sub>3</sub>N<sub>4</sub> was further investigated using various reforming systems such as the bi-reforming of methane (CO<sub>2</sub> with CH<sub>4</sub>/H<sub>2</sub>O) and the bi-reforming of methanol (CO<sub>2</sub> with CH<sub>3</sub>OH/H<sub>2</sub>O) under identical reaction conditions. To explore photocatalytic CO<sub>2</sub> reduction through bi-reforming, equal concentrations of CO<sub>2</sub> and CH<sub>4</sub> feed mixture (CH<sub>4</sub>/CO<sub>2</sub> = 1.0) were passed through a water saturator to carry moisture before entering the reactor. To explore the bi-reforming of CO<sub>2</sub> with methanol as a hole scavenger, 10 vol. % methanol/water was first prepared and used to saturate CO<sub>2</sub> gas with methanol/water vapors.

Photocatalytic CO<sub>2</sub> reduction through the bi-reforming of methane (CH<sub>4</sub>/H<sub>2</sub>O) for the production of CO and  $H_2$  is shown in Figure 6a. Over the course of the entire irradiation period, it was evidently possible to produce continuous CO and H<sub>2</sub>; nevertheless, CO production was more significant than H<sub>2</sub> production, and these results are consistent with those of the DRM reaction. Maximum CO and  $H_2$  evolutions of 689 and 95.8 µmol  $g^{-1}$  were attained over 2% Co/HC<sub>3</sub>N<sub>4</sub> after 4 h of irradiation time. By comparing the results with the DRM process, it was detected that both the CO and  $H_2$  production were decreased by introducing water with CH<sub>4</sub>/CO<sub>2</sub> during the BRM process of CO<sub>2</sub> reduction. These results could be explained based on several hypotheses due to the complex photocatalysis process, which involves competitive oxidation and reduction reactions. When using feed mixtures of  $CO_2$  and  $CH_4$ , they have equal potential to attach to the photocatalyst surface, promoting both oxidation and reduction reactions.  $CO_2$  is consumed to produce CO through the use of electrons and protons, whereas CH<sub>4</sub> is oxidized to produce protons. On the other hand, when the  $CO_2/CH_4$  mixture was used with water, there may be more attachment of water molecules over the  $Co/g-C_3N_4$  surface and fewer active sites available for the attachment of CO<sub>2</sub> molecules to be consumed in the reduction reaction. Therefore, although the oxidation reaction will be efficient, the reduction reaction will be lacking, resulting in a lower overall photocatalytic efficiency. Thus, efficient attachment of both the reactants is necessary to maximize oxidation and reduction reactions for the production of CO and  $H_2$ over a Co/HC<sub>3</sub>N<sub>4</sub> photocatalyst.

The photocatalytic reduction of  $CO_2$  with methanol and water solution through BRM was further investigated, and the results are presented in Figure 6b. The main products obtained were CO and H<sub>2</sub>, with smaller amount of CH<sub>4</sub>. Using both H<sub>2</sub>O and CH<sub>3</sub>OH as sacrificial reagents, continuous generation of CO, CH<sub>4</sub>, and H<sub>2</sub> was achieved throughout the irradiation period. Similar to DRM and BRM process,  $CO_2$  reduction with methanol and water was conducive to producing the highest yield of CO and H<sub>2</sub> over the Co/HC<sub>3</sub>N<sub>4</sub> composite photocatalyst. This BRM system with methanol and water gave the highest yields of 3086, 1776 and 20.96  $\mu$ mol g<sup>-1</sup> for CO, H<sub>2</sub> and CH<sub>4</sub>, respectively, after four hours of irradiation time. The amount of CO produced with the methanol-water system was 1.39 and 4.42 times higher than using the  $CO_2$ -CH<sub>4</sub> and  $CO_2$ -CH<sub>4</sub>-H<sub>2</sub>O reforming systems. Similarly, the yield of  $H_2$  was 10.8- and 18.5-fold more than when it evolved through the involvement of the DRM and BRM reactions. All these findings reveal that methanol as a sacrificial reagent is more able to produce significant amounts of H<sub>2</sub> and CO, while keeping all other parameters constant. This further demonstrates that  $HC_3N_4$  in any type of reforming system is likely to boost CO generation as the primary product, and produce an appreciable amount of H<sub>2</sub> due to the suitable reduction potential of  $CO_2/CO$  (-0.50 eV) and  $H^+/H_2$  (-0.41 eV) with the CB of g-C<sub>3</sub>N<sub>4</sub> (-1.30 eV).



**Figure 6.** Photocatalytic  $CO_2$  reduction through bi-reforming reactions: (**a**)  $CO_2$  reduction with  $CH_4$  and  $H_2O$  and (**b**)  $CO_2$  reduction with methanol and water.

This demonstrates that for the conversion of CO<sub>2</sub> to CO and H<sub>2</sub>, methanol works better than Co/HC<sub>3</sub>N<sub>4</sub> as a sacrificial reagent. The increased attachment of methanol to the surface of g-C<sub>3</sub>N<sub>4</sub> was the cause of its photocatalytic activity. Sacrificial reagents, in general, trap holes and are helpful in producing electrons, resulting in an abundance of protons and electrons to produce H<sub>2</sub>. As a result, the photoactivity of CO and H<sub>2</sub> production was higher with OH-based sacrificial reagents such as CH<sub>3</sub>OH. This is because methanol and water have more potential to adhere to the catalytic surface than CH<sub>4</sub>. Due to the unique surface functional group of g-C<sub>3</sub>N<sub>4</sub>, methanol will more effectively adsorb over the Co/HC<sub>3</sub>N<sub>4</sub> surface. This facilitates an effective CO<sub>2</sub> photoreduction process by facilitating CH<sub>3</sub>OH's attachment to the g-C<sub>3</sub>N<sub>4</sub> surface [15].

In various reports, the effect of different sacrificial reagents has been investigated. For example, the effect of different reducing agents during  $CO_2$  reforming reactions (carried out to examine the performance of  $Ti_3C_2/TiO_2$ ) was reported. It was observed that using a  $CO_2$ -H<sub>2</sub>O feed mixture, the highest amount of CO was produced, whereas the bi-reforming of methane ( $CO_2$ -CH<sub>4</sub>-H<sub>2</sub>O) was more promising for increasing the H<sub>2</sub> evolution rate. These results were possibly due to the acidic characteristic of the catalysts. The favorable H<sub>2</sub> production achieved with BRM reforming systems was possibly due to higher CH<sub>4</sub> and H<sub>2</sub>O adsorption over the catalyst's active sites, which causes hydrogen-rich synthesis gas production [12]. Previously, the performances of GO/g-C<sub>3</sub>N<sub>4</sub> composites under different reforming systems (such as the dry reforming of methane and the bi-reforming of methane) have been investigated. It was found that DRM is the most efficient method of producing more CO and H<sub>2</sub>, compared to BRM and CO<sub>2</sub> reduction with H<sub>2</sub>O [21].

# 2.2.4. Performance Analysis

A performance comparison of the  $Co/HC_3N_4$  composite under different operating conditions and reforming systems is summarized in Table 1. The performance of the composite was investigated using the dry reforming of methane (DRM), the bi-reforming

of methane (BRM) and  $CO_2$  reforming with a methanol–water mixture in a fixed-bed photoreactor system. Using all types of reforming systems, CO was identified as the main product. However, the production of H<sub>2</sub> was dependent on the kind of reforming systems, whereas the highest H<sub>2</sub> yield was produced using methanol as the sacrificial reagent.

Catalyst	Feed Ratio	Production Rate $(\mu mol g^{-1} h^{-1})^*$			Selectivity (%)		
		CH <sub>4</sub>	СО	H <sub>2</sub>	CO	H <sub>2</sub>	CH <sub>4</sub>
HC <sub>3</sub> N <sub>4</sub>	$CH_4/CO_2 = 1.0$	-	30.36	23.69	56.17	43.83	
$2\%Co/HC_3N_4$	$CH_4/CO_2 = 1.0$	-	555	41.2	93.09	6.91	
$2\%Co/HC_3N_4$	CH <sub>4</sub> /CO <sub>2</sub> : 2:1	-	676	29.7	95.79	4.21	
2%Co/HC <sub>3</sub> N <sub>4</sub>	CH <sub>4</sub> /CO <sub>2</sub> : 1:2	-	420	23.8	94.64	5.36	
2%Co/HC <sub>3</sub> N <sub>4</sub>	CO <sub>2</sub> -CH <sub>4</sub> -H <sub>2</sub> O	-	175	24	87.9	12.1	
2%Co/HC <sub>3</sub> N <sub>4</sub>	CO <sub>2</sub> -CH <sub>3</sub> OH-H <sub>2</sub> O	4.42	771	444	63.5	36.5	0.4

Table 1. Performance comparison of different systems producing CO and H<sub>2</sub> via a DRM process.

\* Yield rate was calculated based on 4 h of irradiation time and 150 mg of catalyst loading.

Using HC<sub>3</sub>N<sub>4</sub>, CO and H<sub>2</sub> production rates of 30.36 and 23 µmol g<sup>-1</sup> h<sup>-1</sup> were produced, due to modifying structure to exfoliated nanosheets. With loading optimized 2% Co with HC<sub>3</sub>N<sub>4</sub>, CO and H<sub>2</sub> yield rates of 555 and 41.2 µmol g<sup>-1</sup> h<sup>-1</sup> were produced during DRM process with a CH<sub>4</sub>/CO<sub>2</sub> feed ratio of 1.0. The yield of CO and H<sub>2</sub> over Co/HC<sub>3</sub>N<sub>4</sub> was 18.28- and 1.74-fold higher than when using HC<sub>3</sub>N<sub>4</sub>, respectively. The production of CO was increased to 676 µmol g<sup>-1</sup> h<sup>-1</sup> with a CH<sub>4</sub>/CO<sub>2</sub> feed ratio of 2:1, whereas H<sub>2</sub> production was decreased. The CO production was further increased to 771 µmol g<sup>-1</sup> h<sup>-1</sup> when methanol was used as the sacrificial reagent. Similar to this, the highest H<sub>2</sub> of 444 µmol g<sup>-1</sup> h<sup>-1</sup> was produced over 2% Co/HC<sub>3</sub>N<sub>4</sub> with methanol as the sacrificial reagent, which is 10.78, 14.95- and 18.67-fold higher than that produced when using CH<sub>4</sub>/CO<sub>2</sub> feed ratios of 1:1, 2:1, and 2:1, respectively. More importantly, in the bi-reforming of methane (CO<sub>2</sub>-CH<sub>2</sub>-H<sub>2</sub>O), the lowest photocatalytic efficiency was observed. All these findings point to the higher efficiency of the Co/HC<sub>3</sub>N<sub>4</sub> composite in the conversion of stable CO<sub>2</sub> and CH<sub>4</sub> compounds to CO and H<sub>2</sub> through a photocatalytic process.

Few reports are available on the photocatalytic dry reforming of methane under UV and visible light irradiations. In a recent work, a covalent organic framework (COF)-based composite was tested for the photocatalytic dry reforming of methane. CO and H<sub>2</sub> yield rates of 56.18 and 1.54 µmol  $g^{-1}$  h<sup>-1</sup>, respectively, were obtained, which were significantly higher than those obtained with pure materials [42]. Similarly, we reported a V<sub>2</sub>AlC MAX/g-C<sub>3</sub>N<sub>4</sub> composite for the photocatalytic dry reforming of methane, and the main products obtained were CO and H<sub>2</sub>, with yield rates of 118.74 and 89.52 µmol g<sup>-1</sup> h<sup>-1</sup>, respectively [36]. In several other reports, the dry reforming of methane over various photocatalysts has been investigated. Recently, with the use of Ti<sub>3</sub>C<sub>2</sub> with TiO<sub>2</sub>, CO and H<sub>2</sub>, yield rates of 85 and 18 µmol g<sup>-1</sup> h<sup>-1</sup> were reported [12]. Similarly, CO and H<sub>2</sub> yield rates of 99.8 and 5.6 µmol g<sup>-1</sup> h<sup>-1</sup> were observed during a DRM reaction over a GO/g-C<sub>3</sub>N<sub>4</sub> composite. By comparing the results with previous works, it can be seen that noble metal-free HC<sub>3</sub>N<sub>4</sub> loaded with Co is a very promising material for maximizing the dry reforming of methane to produce synthesis gas.

### 2.3. Stability Analysis

Given that the catalyst deactivates during the dry reformation of methane, it is imperative to conduct stability research into the synthesized 2% Co/HC<sub>3</sub>N<sub>4</sub> composite for syngas (CO and H<sub>2</sub>) through a DRM reaction. Figure 7a shows the findings of a stability test that was carried out in this work to assess how well the synthesized composite performed in producing syngas (CO and H<sub>2</sub>) over several cycles, when exposed to visible light. The catalyst was uniformly dispersed throughout the reactor for the stability test, and the CH<sub>4</sub>/CO<sub>2</sub>, input feed ratio, was maintained at 1.0 for each cycle. Evidently, consistent CO and H<sub>2</sub> generation was achieved throughout each of the stability tests. For CO yield, it was increased in the second cyclic run, and this was made possible by the reductive characteristics of cobalt under light irradiation. However, in the third cyclic run, still, higher and continuous production of CO was obtained compared to the first cyclic run. Recently, a covalent organic framework (COF)-based composite was tested and reported to increase CO evolution in the second cyclic run during the photocatalytic dry reforming of methane [42]. On the other hand, during the whole irradiation and throughout all of the cyclic runs, H<sub>2</sub> was continuously and steadily produced. This demonstrated that the catalyst remained stable throughout the DRM process for the evolution of CO and H<sub>2</sub>. After three cycles, it is evident from the CO and H<sub>2</sub> evolution data that the composite performs extremely well as a photocatalyst during the DRM process when exposed to visible light. Previously, we investigated DRM over  $V_2AIC/g-C_3N_4$ ; however, therein, the photocatalytic activity for CO and H<sub>2</sub> declined over the irradiation time [36].



**Figure 7.** (a) Photocatalytic dry reforming of methane (DRM) over 2% Co/HC<sub>3</sub>N<sub>4</sub> composite per 4 h in consecutive three cycles; (b) XRD analysis of fresh and used 2% Co/HC<sub>3</sub>N<sub>4</sub> composite; (c) FTIR analysis of fresh and used 2% Co/HC<sub>3</sub>N<sub>4</sub> composite.

XRD analysis was used to further compare the 2% Co/HC<sub>3</sub>N<sub>4</sub> composites before and after the reaction, and the results are displayed in Figure 7b. The fresh and used samples both had similar peaks, proving that the peak position had not altered. The composite obtained after the reaction showed no new peaks, demonstrating the material's excellent stability and the absence of structural change or carbon generation. This demonstrates that using cobalt in combination with g-C<sub>3</sub>N<sub>4</sub> rendered higher stability for the DRM process. Figure 7c shows the results of an FTIR study that was carried out to further evaluate the used photocatalyst before and after three cycles of the photocatalytic DRM reaction. The FTIR spectra of the composite are nearly identical before and after the reaction. The FTIR spectra exhibit the same peaks before and after the reaction; no additional peaks are present, thereby confirming the higher stability of g-C<sub>3</sub>N<sub>4</sub> when loaded with cobalt during the DRM process.

# 2.4. Proposed Mechanism

When it comes to improved photocatalytic activity, a photocatalyst's performance is determined by effective charge separation and charge carrier mobility ( $e^-$  and  $h^+$ ). Similar to this, fast charge separation and consideration of the reduction potential of the products (CO and H<sub>2</sub>) in relation to the semiconductors' conduction band locations are also required for photocatalytic reduction via DRM and BRM processes. Additionally, other factors including light absorption capacity, reactant activation, and their adsorption over the catalyst's surface are essential factors required for an effective photocatalysis process. Furthermore, increased exposed surface area encourages more light absorption, which produces a lot of charge to boost the reduction and oxidation reactions.

Due to compact nanosheets with bulk structures, the  $g-C_3N_4$  performs charge separation less effectively, resulting in a lower amount of CO and  $H_2$  evolution. On the other hand, when  $g-C_3N_4$  was exfoliated to produce a hierarchical structure, there were obvious gaps to enable efficient light penetration with defects, itself then enabling efficient charge carrier separation. The layered structure of  $HC_3N_4$  allows strong light penetration with efficient charge carrier separation, resulting in higher photocatalytic efficiency.

Figure 8 provides a schematic representation of the suggested mechanism for the dry reforming of methane over a  $Co/HC_3N_4$  composite. As was previously mentioned, CO and H<sub>2</sub> were the primary products of the photocatalytic DRM reaction over the  $Co/HC_3N_4$  composite, which were produced through the involvement of two electrons. This suggests that numerous charge carriers and effective charge carrier separation are required for the increased and selective production of syngas (CO and H<sub>2</sub>). In order to facilitate quick charge separation, Co was found to be a promising vehicle to trap and transport photoinduced charge carriers. The reactions involved during the oxidation and reduction reactions are discussed in Equations (1)–(11) [12,43].



**Figure 8.** Proposed mechanism for the photocatalytic dry and bi-reforming of methane to produce CO and  $H_2$  over a Co/HC<sub>3</sub>N<sub>4</sub> composite.

Oxidation reactions:

$$CH_4 + h^+ \rightarrow \bullet CH_3^- + H^+ \tag{1}$$

$$\bullet CH_3^- + h^+ \rightarrow \bullet CH_2^- + H^+$$
<sup>(2)</sup>

$$\bullet CH_2^- + h^+ \rightarrow \bullet CH^- + H^+$$
(3)

$$\bullet CH^- + h^+ \to C^{\bullet} + H^+ \tag{4}$$

Reduction reactions:

$$\mathrm{CO}_2 + \mathrm{e}^- \rightarrow \bullet \mathrm{CO}_2^-$$
 (5)

$$\bullet CO_2^- + 2H^+ + e^- \rightarrow CO + H_2O \tag{6}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \tag{7}$$

Series reactions for CO and H<sub>2</sub> formation:

$$\bullet CH_3^- + H_2O + 6h^+ \to CO + 5H^+$$
(8)

$$\bullet CH_2^- + H_2O + 5h^+ \rightarrow CO + 4H^+$$
<sup>(9)</sup>

$$\bullet CH^- + H_2O + 4h^+ \rightarrow CO + 3H^+$$
<sup>(10)</sup>

$$C^{\bullet} + H_2O + 3h^+ \rightarrow CO + 2H^+$$
(11)

$$2\mathrm{H}^{+} + 2\mathrm{e}^{-} \to \mathrm{H}_{2} \tag{12}$$

During the photocatalytic dry reforming of methane, methane is oxidized by holes to produce intermediate  $\bullet$ CH<sub>x-1</sub> and protons (H<sup>+</sup>) through the involvement of the reactions in Equations (1)–(4). The efficiency of these reactions depends on the attachment of  $CH_4$ to the catalyst surface, and also on the availability of holes to proceed with the oxidation reaction. Due to this series of reactions (as detailed in Equations (1) and (4)), final products of  $H^+$  and  $C^{\bullet o}$  are produced. The protons produced are further used in a series of reactions to produce CO during the reduction reaction. During the reduction reaction,  $CO_2$  is reduced with electrons to produce intermediate  $\bullet CO_2^-$  through the reaction in Equation (5) with the involvement of electrons. The intermediate products ( $\bullet CO_2^-$ ) and  $CO_2$  can be converted to CO and water molecules through the involvement of two protons, as shown in Equations (6) and (7). The  $CH_4$  intermediates, with the involvement of water molecules and holes, produce CO and protons, as discussed in Equations (8)-(11). However, in all these reactions, the important factor is the utilization of C<sup>o</sup> with water molecules and holes to produce CO and protons (Equation (11)). Finally,  $H_2$  is produced through the use of two electrons, as shown in Equation (12) [22,37]. The production of CO occurred through several parallel reactions with the involvement of holes, protons, and electrons over the highly efficient Co/HC<sub>3</sub>N<sub>4</sub> composite photocatalyst. Thus, the production of CO was higher compared to hydrogen production during the dry reforming of methane over the Co/HC<sub>3</sub>N<sub>4</sub> composite photocatalyst.

# 3. Experimental

# 3.1. Synthesis of Hierarchical Graphitic Carbon Nitride (HC<sub>3</sub>N<sub>4</sub>)

Hierarchical and bulk samples of carbon nitrides were created using melamine as the precursor, using the hydrothermal method.  $g-C_3N_4$  was synthesized using only melamine and heating for two hours at 550 °C, as reported previously [44]. For the synthesis of HC<sub>3</sub>N<sub>4</sub>, equal amounts of melamine and urea were heated at 550 °C with total time of 2 h in an air atmosphere. The final product obtained was given the name (HC<sub>3</sub>N<sub>4</sub>).

# 3.2. Synthesis of Co-Doped g-C<sub>3</sub>N<sub>4</sub> (Co/HC<sub>3</sub>N<sub>4</sub>)

The co-loaded  $HC_3N_4$  nanotextures were produced using an impregnation method. A predetermined amount of  $HC_3N_4$  was dispersed in methanol, and then varied amounts of cobalt nitrates dissolved in methanol were added to the above suspension under continuous stirring. The slurry was agitated for two hours before being dried overnight at 100 °C. The finished product was denoted Co/HC<sub>3</sub>N<sub>4</sub>. Different Co-loading amounts (1, 2 and 3 wt. %) were prepared using various cobalt nitrate loadings with HC<sub>3</sub>N<sub>4</sub>; these were then labeled 1% Co/HC<sub>3</sub>N<sub>4</sub>, 2% Co/HC<sub>3</sub>N<sub>4</sub>, and 3% Co/HC<sub>3</sub>N<sub>4</sub>, respectively.

### 3.3. Characterization

The material's structure, crystallinity, morphology, element dispersion, light absorption, and ability to separate charges were all investigated using a range of instruments. An XRD analysis was performed to determine the crystalline structure using the Bruker Advance D8 diffractometer. Morphology analysis was carried out using a Hitachi SU8020 SEM (Scanning electron microscope). We used a PerkinElmer equipment to obtain FTIR spectra. XPS analysis was carried out using an Axis Ultra DLD instrument. Using the UV-3600 Plus Spectrometer, the band gap energy and light absorption were estimated. A PL analysis was then carried out utilizing a spectrometer from HORIBA Scientific with a laser of wavelength 325 nm. A Raman analysis was performed using HORIBA Scientific with a laser of wavelength 532 nm.

### 3.4. Photocatalytic Activity Test

A photoactivity test to assess the performance of synthesized photocatalysts was conducted in a stainless steel photoreactor. The light source used was a 200 W Hg lamp with light intensity 100 mW cm<sup>-2</sup>, which was equipped with a cooling fan to remove lamp heat. Typically, a 150 mg powder photocatalyst was uniformly dispersed within the stainless-steel chamber, equipped with a quartz glass. Mass flow controls were used to control the flow rate of  $CO_2$  and  $CH_4$ . In order to saturate the catalyst and purge the reactor before the experiment began, the feed mixture ( $CO_2$  and  $CH_4$ ) was continually pumped through the reactor for 30 min at a total flow rate of 20 mL/min and a  $CO_2/CH_4$  molar feed ratio of 1.0. The effects of different  $CH_4/CO_2$  feed ratios were further investigated to understand the role of feed composition on the photocatalytic performance. For this purpose, different feed mixtures of  $CH_4/CO_2$  were used, while keeping a total flow rate of 20 mL/min. During the photocatalytic bi-reforming of methane, the mixture of  $CO_2/CH_4$ was passed through the water saturator before entering the reactor. To further investigate the effect of the reducing agent through the bi-reforming of  $CO_2$  with methanol/water, CO<sub>2</sub> was passed through a 10% methanol/water solution at a total flow rate of 20 mL/min. A gas chromatographer (GC-Agilent Technologies 6890 N, USA) connected to a thermal conductivity detector (TCD) and a flame-ionized detector (FID) was used to evaluate the products.

# 4. Conclusions

In conclusion, self-assembly was used to produce  $Co/HC_3N_4$ , which offers a potential method of carrying out the photocatalytic dry reforming of methane by utilizing both  $CH_4$  and  $CO_2$ . The DRM was tested using a variety of catalyst materials, including pure and composite samples, to examine their photocatalytic activity. In all types of photocatalysts,

CO was identified as the main product, with a lower amount of  $H_2$  during CO<sub>2</sub> reduction with CH<sub>4</sub> through DRM and with CH<sub>4</sub>/H<sub>2</sub>O through the BRM process. Excellent photocatalytic activity for the formation of syngas was achieved by the Co/HC<sub>3</sub>N<sub>4</sub>, which was much higher than that achieved when using pure HC<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> samples. When the CH<sub>4</sub>/CO<sub>2</sub> feed ratio was altered, the yields of CO and H<sub>2</sub> also varied. A CH<sub>4</sub>/CO<sub>2</sub> feed ratio of 2:1 was favorable for maximizing CO evolution, whereas a CH<sub>4</sub>/CO<sub>2</sub> feed ratio of 1 was more suitable for obtaining the highest H<sub>2</sub> productivity. Among the different reforming systems, the bi-reforming of CO<sub>2</sub> with methanol and water was the most efficient system for maximizing the production of both CO and H<sub>2</sub> due to the production of more electrons and protons. The cobalt-assisted HC<sub>3</sub>N<sub>4</sub> was also promising in its demonstration of higher photostability in multiple cycles for the continuous production of CO and H<sub>2</sub> during the DRM process. In general, excellent interfacial contact between Co and HC<sub>3</sub>N<sub>4</sub> enables promising charge carrier separation with higher photostability, and is promising for other energy-based and environmental applications.

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