Efficient photocatalytic CO\textsubscript{2} reforming of methane on Ru/La-g-C\textsubscript{3}N\textsubscript{4} by promoting charge transfer and CO\textsubscript{2} activation

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Abstract: Artificial photosynthesis, in which solar energy drives CO\textsubscript{2} to produce hydrocarbon fuels, is considered an effective way to solve the increasingly serious energy crisis and mitigate the greenhouse effect. Here, layered porous Ru-loaded and La-doped g-C\textsubscript{3}N\textsubscript{4} nanosheets (Ru-LGCN) were prepared by one-step Calcination, followed by in situ photoreduction deposition of Ru. The layered Ru-LGCN showed excellent photocatalytic CO\textsubscript{2} reforming of methane performance under visible light, and the generation rates of CO, CH\textsubscript{3}OH, CH\textsubscript{2}OH and CH\textsubscript{3}CH(OH)CH\textsubscript{2} were 133, 154, 251 and 133 \textmu mol·h\textsuperscript{-1}·g\textsuperscript{-1}, respectively. The reason for the enhanced photocatalytic activity of Ru-LGCN is the synergistic effect of bimetallic Ru and La. It is worth noting that the doped La can provide a good channel for charge transfer between LGCNs and CO\textsubscript{2}. This change in the charge behavior of the transport path is beneficial to break the C=O bonds on the active site La and generate methyl radicals on Ru, resulting in the generation of C2+ hydrocarbons.

Introduction

The energy crisis, caused by the depletion of non-renewable fossil resources, and the environmental crisis, caused by the emission of greenhouse gas CO\textsubscript{2} from the burning of fossil fuels, have been recognized as the two most important global challenges for scientists in the past decade.\textsuperscript{[1,2]} Therefore, driven by inexhaustible renewable energy of solar, the photocatalytic process is considered a way to convert greenhouse gas CO\textsubscript{2} into renewable high-value hydrocarbon fuels (such as CO, CH\textsubscript{3}OH, CH\textsubscript{3}CH\textsubscript{2}OH). Thus, photocatalysis provides effective and attractive solutions to these crises. Initially, Inoue and co-workers reported the photocatalytic reduction and conversion of CO\textsubscript{2} on semiconductor photocatalysts, such as TiO\textsubscript{2}, ZnO, CdS, GaP, and SiC, in 1979.\textsuperscript{[3]} To improve the activity, durability, and selectivity of the photocatalytic reaction, scientists have made numerous attempts, including the design and synthesis of new photocatalysts and the construction of photocatalytic systems. Among them, the successful conversion of CO\textsubscript{2} using CH\textsubscript{4} as a reducing agent has received increasing attention in recent years.\textsuperscript{[4-7]} For example, Shi and co-workers synthesized C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{5}OH from a mixture of CO\textsubscript{2} and CH\textsubscript{4}, using the Cu/CdS-TiO\textsubscript{2}/SiO\textsubscript{2} composite photocatalyst at 373 K.\textsuperscript{[7]} BalázsLászló and co-workers reported titanium nanotubes (TNTs) modified with gold and rhodium can effectively convert CO\textsubscript{2} and CH\textsubscript{4} into CO and H\textsubscript{2}.\textsuperscript{[8]} Tahir and co-workers also obtained similar results, replacing the photocatalyst with a Cu-modified g-C\textsubscript{3}N\textsubscript{4} catalyst to produce CO/H\textsubscript{2} at 373 K.\textsuperscript{[9]}

However, owing to the limitations of stable molecular bonds and multi-step reaction kinetics, the photocatalytic reaction efficiency has always been at a low level. Many strategies have been developed to overcome these challenges. In terms of energy band structure and electron-hole pair separation, element doping is the most effective method to improve the photocatalytic performance of GCN. Wang and co-workers found that potassium-doped g-C\textsubscript{3}N\textsubscript{4} obtained effective visible light-driven...
CO₂ reduction, and DFT calculations and XPS tests proved that potassium doped was interlayer doping, which changed the electronic structure of g-C₃N₄.[10] Yu and co-workers revealed that the reason for the enhanced performance of sulfur-doped g-C₃N₄ photocatalytic CO₂ reduction is that the band gap of g-C₃N₄ becomes narrower and the absorbance increases after doping the sulfur element.[11] Fu and co-workers prepared layered porous O-doped g-C₃N₄ nanotubes by continuous thermal oxidation striping and capillary condensation of bulk g-C₃N₄ and showed excellent photocatalytic reduction performance of CO₂ due to the hierarchical structure of nanotubes and the O doping effect.[12]

Among these dopant atoms, it is shown that the alkaline metal elements in g-C₃N₄ connect adjacent layers, increase the photogenerated carrier concentration, and further promote charge separation. In addition, through the intercalation of alkali metals and nitrogen species, a bidirectional channel is constructed between adjacent layers to reduce the potential barrier and guide the flow of charge to the desired location, that is, the reactive site. This allows the redox reaction to be separated in space, which not only reduces the annihilation rate of photogenerated carriers but also increases the rate of chemical reactions on the photocatalyst surface.

We recently reported that Zn-doped g-C₃N₄ photocatalyst can effectively convert CO₂ and methane to C₂-hydrocarbons through photocatalytic reforming.[13] In particular, the Zn atom enters the g-C₃N₄ lattice, where it is chemically coordinated in the form of Zn-N bonds. The Zn-N bond can act as an electron channel, which accelerates the charge separation inside g-C₃N₄ and enables the rapid transfer of electrons from g-C₃N₄ to the photocatalyst of deposited Ru. Owing to the unique properties of ligand formation/coordination with other elements and the complex optical properties of trivalent lanthanide ions (La³⁺), we incorporated lanthanide ions into carbon nitride.[14-16] The La element is introduced into the intermediate layer of carbon nitride to enhance charge transfer and photocatalytic activity through the interaction of La and the functional group of g-C₃N₄.

Herein, we successfully synthesized a series of Ru loaded and La-doped g-C₃N₄ (named Ru-LGCN) photocatalysts through continuous thermal oxidative exfoliation and condensation of urea and lanthanum salt, followed by in situ photodeposition deposition of Ru. The structural characteristics and physical-chemical properties of the photocatalysts were studied through DFT theoretical calculation, as well as CO₂-TPD, CH₄-TPD, PL, and BET tests. Then, the effects of La and Ru on the structure, morphology, and photocatalytic activity of g-C₃N₄ were discussed, and the mechanism of Ru-LGCN photocatalytic CO₂-CH₄ conversion was proposed.

Results and Discussion

As shown in Fig. 1, the successful synthesis of GCN and La-doped g-C₃N₄ was confirmed. The characteristic diffraction peaks of g-C₃N₄ near 13.1° and 27.4° were assigned to plane (100) for intra-planar structural packing and (002) plane for interlayer stacked conjugated aromatic structure of GCN, respectively. These assignments are consistent with previous literature reports.[17-19] In the XRD pattern of La-doped GCN, with the continuous increase of La ions content, the (002) diffraction peaks gradually shift to a lower 2θ value. This indicates that the interstitial doping of La ions produces continuously enlarged interlayer distance.[20] The metal ions La³⁺ are doped into the nanocrystals of g-C₃N₄, where they coordinate with the electron-donating N-containing functional groups of g-C₃N₄. Therefore, owing to the interaction between La and GCN and the release of NH₃ during the calcination process, La was successfully doped into the crystal.[21-22]

The TEM and SEM images containing information regarding morphologies and particle sizes are shown in Fig. 2. It can be seen that 0.6LGCN is composed of small nanosheets, which are uniform in size and shape compared with bulk g-C₃N₄. Fig. 2c shows that there is a disordered but well-developed 0.6LGCN pore system, with a pore size close to 20 nm. Fig. 2e illustrates the selected area electron diffraction pattern of the as-prepared nanocomposite, which indicates the crystalline structure of Ru nanoparticles. The lattice planes (101), (200), and (102) correspond to the crystalline lattice of Ru nanocrystals loaded on 0.6LGCN, which demonstrates the existence of Ru. The elemental mapping images of the samples, shown in Fig. 2f, reveal the uniform distribution of C and N elements in the catalyst, as well as O and La in the corresponding samples. In particular, the metal ions La³⁺ are uniformly distributed in the GCN matrix. This phenomenon is consistent with the XRD characterization results. The XRD pattern does not find the characteristic diffraction of lanthanum oxide or lanthanum carbonate.

The nitrogen adsorption–desorption isotherms and Barret–Joyner–Halenda (BJH) pore size distribution curves for samples LGCN and GCN are shown in Fig. 3. The results show that GCN has a classic IV type hysteresis loop, indicating the mesoporous structure (2–50 nm) of the sample. In addition, 0.6LGCN is classified as an H4 hysteric loop according to the adsorption isotherm, which is attributed to adsorption-desorption in narrow slit pores. The isotherm can also be estimated from the BJH pore size distribution (2-25 nm).[23-24] The calculated pore diameter distribution curve shows that 0.6LGCN mesoporous distribution is narrow, and the maximum pore diameter radius is 25 nm. These data show that acetic acid lanthanum (III) can be used as a precursor to improve the specific surface area and porous structure. The reason for this result is that a large amount of NH₃ is released during the calcination process, and the gas escaping process increases the pore volume and dictates the pore size distribution, thus increasing the specific surface area. These
trends are observed in Fig. 2c. Similar results for other photocatalysts are summarized in Table 1. From Table 1, the addition of La precursors increased the specific surface area and pore size, reaching the maximum value at 0.12LGCN sample. Further increase in La precursors results in the decrease of specific surface area and pore size. The results show that a moderate amount of La doping is beneficial to the construction of more surface active sites, whereas a large amount of La doping may partially destroy the structure of g-C$_3$N$_4$, resulting in the reduction of its specific surface area. In addition, loading a small amount of Ru may cover the pore structure, resulting in a further reduction in surface area. The adsorption of CO$_2$ on the surface of the photocatalyst is the first step in the photocatalytic CO$_2$ reduction process. To evaluate the CO$_2$-capture ability of different catalysts, the CO$_2$ adsorption isotherms of GCN, 0.6LGCN and 0.5Ru-0.6LGCN was shown in Fig. S5. The results showed that La doping provides more CO$_2$ adsorption sites and the addition of Ru actually caused a slight decrease in the amount of CO$_2$ adsorbed.
### Table 1. Specific surface area, pore volume, and pore diameter of pure GCN and La-doped LGCN samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{BET}/\text{m}^2\cdot\text{g}^{-1} )</th>
<th>( V_{pore}/\text{cm}^3\cdot\text{g}^{-1} )</th>
<th>( d_{pore}/\text{nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-( \text{C}_3\text{N}_4 )</td>
<td>12.9212</td>
<td>0.0336</td>
<td>17.02</td>
</tr>
<tr>
<td>0.12LGCN</td>
<td>58.8733</td>
<td>0.2575</td>
<td>12.94</td>
</tr>
<tr>
<td>0.30LGCN</td>
<td>56.7329</td>
<td>0.2400</td>
<td>12.18</td>
</tr>
<tr>
<td>0.40LGCN</td>
<td>53.1657</td>
<td>0.2110</td>
<td>10.92</td>
</tr>
<tr>
<td>0.60LGCN</td>
<td>49.0890</td>
<td>0.1779</td>
<td>9.49</td>
</tr>
<tr>
<td>0.80LGCN</td>
<td>37.9122</td>
<td>0.1312</td>
<td>7.11</td>
</tr>
<tr>
<td>0.5 Ru-0.60LGCN</td>
<td>45.1850</td>
<td>0.1562</td>
<td>9.18</td>
</tr>
</tbody>
</table>

As shown in Fig. S1, the FTIR spectra of pure GCN and nLGCN were recorded in the range of 500–4000 cm\(^{-1}\), and the detailed information of the organic structure was recorded. Several typical \( \text{g-C}_3\text{N}_4 \) absorption peaks were measured. The peak at 810 cm\(^{-1}\) can be attributed to the breathing mode of tri-s-triazine. The wide absorption near 3200 cm\(^{-1}\) is due to the stretching vibration of N–H bond. It is also worth noting that strong absorption occurs at 2166 cm\(^{-1}\), compared to pure GCN, and increases with increasing La. This result corresponds to the suspended cyanide group (C≡N triple bond), one of the intermediates of urea pyrolysis. Several peaks between 1100 cm\(^{-1}\) and 1700 cm\(^{-1}\) can be attributed to the typical stretching pattern of the CN-heterocyclic system.\(^{[25-26]}\)

To fully investigate the light absorption properties of as-prepared photocatalysts and thoroughly understand their optical structures, UV-vis, XPS, and PL spectra were recorded. Fig. 4a exhibits a sudden rise in absorption intensity from 450 nm up to the UV region for the GCN, which indicates a relatively narrow band gap of ~2.73 eV. Additionally, intensive absorption peaks emerging in the UV region were attributed to the band gap between HOMO and LUMO in the polymeric melon units in accordance with other characterization results.\(^{[27]}\) Meanwhile, a

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**Figure 4.** (a) UV-vis diffuse reflectance spectra of GCN and nLGCN. (b) XPS valence band spectra of GCN and 0.60LGCN. (c, d) PL spectra of different catalysts excited at 380 nm.
gradual red shift in the absorption edge of LGCN was observed after the introduction of La, indicating a narrower band gap. All band gaps, calculated using the Tauc equation and acquired via the intercept value of the tangent to the curve (ahν)^2 versus photon energy hν, are given in Fig. 4a. As shown in Fig. 4b, the XPS valence band spectra of GCN and 0.6LGCN were tested to explore the influence of La doping on the valence band of the semiconductor photocatalyst. The test results showed that the valence band positions of GCN and 0.6LGCN were both 1.69 eV, so we speculated that the doping of La did not affect the valence band position. To more clearly prove the feasibility of CO₂ reforming, the energy band structure diagrams of GCN and 0.6LGCN were shown in Fig. S4. Therefore, the estimated calculation results implied that broadening the light response range and efficiently utilizing visible light can be achieved by doping La into GCN. A photoluminescence (PL) test (excited at 380 nm) was used to explain the migration, transfer, and recombination processes of the photogenerated electron-hole pairs in a semiconductor (Fig. 4c and d). Obviously, the PL spectrum intensity of LGGCN photocatalyst decreased significantly, compared with that of GCN. With the increase in La content, PL intensity gradually decreased, suggesting the possibility of carrier recombination can be reduced. It also indicates the photoinduced carriers can be appointed to a shorter distance, which needs to travel along with the C- and N-forming π-conjugated graphitic planes. Similarly, the intensity of peaks decreased with the incorporation of metal Ru, which is due to the photogenerated charge transfer between the Ru and GCN. Therefore, the synergy created by Ru and La is expected to favor the photocatalytic performance.

To better understand the electronic properties of La-doped g-C₃N₄ layer, the electronic projected density of states (PDOS) was calculated for g-C₃N₄ and LGGCN. From Fig. 5a and b, the pristine g-C₃N₄ is a semiconductor with a band gap of 1.18 eV, which is underestimated by the DFT-PBE method. The La doping lowers the energy of both the valence and conduction bands in LGGCN, and the doped structure displays a typically heavy n-doped electronic structure with Eᵥ located at the bottom of the conduction band. To obtain a better impression of the nature of conducting states for the photogenerated carriers, the charge distribution associated with states at valence band maximum (VBM) and conduction band minimum (CBM) is depicted in Fig. 5c and d. Interestingly, the charge distribution for states at VBM and CBM is consistent with the plotting of PDOS from different elements, as shown in Fig. 5b. The spatially separate states of VBM and CBM located at separated regions on the layer. The CBM states are mainly contributed by electronic orbitals from La atom and neighboring C and N atoms, whereas the VBM states mainly contain orbitals from N atoms far from La atom. This result is consistent with the plotting of PDOS from different elements, as shown in Fig. 5b. The spatially separate states of VBM and CBM in LGGCN can effectively prohibit recombination and promote the separation of photogenerated carriers. That is to say, the excited electrons will migrate to the CBM, which is located around the doped La atoms, and participate in the reduction of adsorbed CO₂. Simultaneously, the holes will migrate in the opposite direction to the VBM and participate in the oxidation process.

**Figure 5.** Electronic projected density of states (PDOS) of (a) g-C₃N₄ and (b) CN-La (LGGCN) monolayers. Contributions of electrons from different elements are distinguished by color. Top view of partial charge density associated with frontier states in the (c) valence band (pᵥ) and (d) conduction band (pᶜ) for LGGCN layer. The energy ranges associated with pᵥ and pᶜ are indicated by the green shaded region in (b) and extend from Eᵥ = 1.7 eV < E < Eᶜ = 1.3 eV for the valence band and Eᶜ–0.3 eV < E < Eᶜ+0.1 eV for the conduction band. The isosurface value for both is pᵥ and pᶜ is 4×10⁻⁹ eV/Bohr³.
peak was attributed to desorption of CO₂ from weak basic sites, probably –NH₂ sites, while the latter one could be assigned to chemical absorption sites with strong basicity. Moreover, three low-temperature peaks are located at approximately 80°C, 150°C, and 300°C for 0.5Ru-0.6LGCN and 0.6LGCN. It is suggested that a physical absorption peak under 100°C, a 150°C weak basic absorption corresponding to the species of bicarbonates, and a decomposition of carbonates peak at 265°C are collectively due to La in the lattice. Moreover, a similar strong basic site on 0.6LGCN was detected at 420°C, compared to the pristine GCN. However, little difference was observed when loading Ru on the catalysts, which indicates little carbon dioxide is absorbed on the metal. Fig. 6b describes the CH₄ absorption performance of photocatalytic composites. The absorption temperatures below and above 200°C on the products correspond to weak and strong absorption of methane. Interestingly, the stability of the major absorption intensities of the composites at around 130°C reveals that a large proportion of CH₄ is attached to g-C₃N₄ by physical adsorption. In contrast to CO₂ curves, two middle absorption bumps stand out after depositing Ru on GCN and 0.6LGCN. This is likely attributed to partially absorbed CH₄ on the metal by chemisorption.

Figure 6. (a) CO₂-TPD curves and (b) CH₄-TPD curves of GCN, 0.5Ru-GCN, 0.6LGCN and 0.5Ru-0.6LGCN.

Figure 7. Top and side view of optimized structure for (a) pristine graphitic-carbon nitride (g-C₃N₄) monolayer, (b) La-doped g-C₃N₄ (LGCN), and the adsorption of CO₂ on CN-La (LGCN) (c) via the doped La atom and (d) without La atom. The O atom in CO₂ connected to La and the one far from the layer is distinguished by a subscript in (c).
Therefore, it facilitates the generation of long-chain products during CH₂ oxidation.

To verify the crucial role of the doped La atoms in enhancing the photocatalytic activity of g-CN₄, ab initio density functional calculations were executed to simulate the interaction between a CO₂ molecule and the La-doped g-CN₄ (LGCN) layer. The optimized structures for monolayers of pristine g-CN₄ and LGCN are shown in Fig. 7a and b. The most stable configuration for the doped La atom is inside one of the big C-N rings of g-CN₄. The doped structure becomes corrugated in the side view, compared to the flat 2D pristine structure. The adsorption of CO₂ on the LGCN surface via La atom doping and without La atom doping is compared, and the optimized structures are shown in Fig. 7c and d. When CO₂ is adsorbed near the La atom, the molecule is attached to the layer by connecting one O atom (O₁) to the La atom. However, when CO₂ is adsorbed far from the La atom, the molecule is adhered to the surface close to the center of the big C-N ring and almost parallel to the local plane. Our DFT calculations show that in the case of La doping, the La-O₁ bond length is about 2.759 Å, and the corresponding adsorption energy of one CO₂ molecule \( \Delta E_{\text{ad}} \), which is defined as \( \Delta E_{\text{ad}} = E_{\text{ad}}(\text{LGCN} / \text{CO}_2) - E_{\text{ad}}(\text{LGCN}) - E_{\text{ad}}(\text{CO}_2) \), is -0.81 eV. In the case without La, however, the shortest distance from CO₂ to the LGCN layer is about 3.223 Å, and a lower value for \( \Delta E_{\text{ad}} \) of -0.56 eV is obtained. The larger \( \Delta E_{\text{ad}} \) in the case with La indicates the preference for CO₂ adsorbed on LGCN near the location of La atoms. The detailed results for the \( \Delta E_{\text{ad}} \) calculations are given in Table S1.

The electronic structure changes associated with the adsorption of CO₂ on the LGCN layer were calculated by DFT to further explore the effects of the doped La atoms on the charge transfer between LGCN and CO₂. The total charge density \( \rho \) for CO₂ adsorbed on the LGCN layer was shown in Fig. S6. The differential charge density \( \Delta \rho = \rho_{(\text{LGCN})} - \rho_{(\text{LGCN}/\text{CO}_2)} \) related to the assembly of CO₂ adsorbed LGCN layer from structures of only LGCN and only CO₂ was calculated. As depicted in Fig. 8a and b, the \( \Delta \rho \) (visualized by contour plots) shows that when compared to the case without La, a much larger charge redistribution occurs near CO₂ when it is adsorbed on the layer via La. Additionally, there is a significant electron transfer to the O₁ atom from the other local atoms. Quantitative measurements for charge transfer using Bader charge analysis show that without La doping, each O atom in CO₂ gains about 1.063 electrons. However, in the case with La doping, the O₁ atom gains 1.110 electrons and the O₂ atom gains 0.985 electrons. The extra electron flow to the O₁ atom caused by the La-O₁ bond can effectively modify the chemical activity of the adsorbed CO₂ molecule. The measurements for the bond length in CO₂ show that when attached to La, the length of the C-O₁ bond (1.187 Å) is larger than the C-O₂ bond (1.165 Å), while the values of the C-O bond length are approximately equal (1.175 Å and 1.177 Å) when adsorbed without La. The elongated C-O₁ bond indicates that the charge redistribution weakens the C-O₁ bond and enhances the activity of CO₂ adsorbed via La.

Since the charge transfer between the LGCN layer and CO₂ is restricted by the potential energy barriers, the regional electrostatic potential (V) in the adsorption region was investigated. The results for V distributed in the xz-plane at the interface, which is marked by the horizontal dashed line in the top view of Fig. 8a and b, are shown in Fig. 8c and d. The blue potential wells are caused by atoms close to the plane, and the high potential in red represents the vacuum region. When CO₂ is adsorbed on the LGCN layer without La, a potential barrier...
approximately 3.83 eV higher than the $E_F$ was observed at the interface. This barrier is shown by solid black contours. The barrier much higher than $E_F$ can dramatically hinder the charge transfer through the interface. However, when CO$_2$ is adsorbed via La, the potential barrier at the interface is significantly reduced to 2.42 eV lower than $E_F$. In this case, electrons at the Fermi level can easily migrate across the interface since the barrier is below $E_F$. These results show that the doped La can provide a good channel for charge transfer between LGCN and CO$_2$.

The XPS analysis for the synthesized catalysts was conducted to confirm the presence of C-N-La bonds. The La 3D high-resolution XPS spectrum (Fig. S3) of the purchased bare La$_2$O$_3$ sample exhibited peaks at 831.46 eV and 835.12 eV, as well as 848.25 eV and 852.37 eV, corresponding to the La 3d$_{5/2}$ and La 3d$_{3/2}$ states, respectively.$^{[38]}$ Compared to those of 0.6LGCN (Fig. S3), a negative shift in the binding energies suggests that electrons on La migrate to other atoms rather than O. It is further observed that in the high N 1s high-resolution XPS spectra (Fig. S2) of GCN and 0.6LGCN, a slight red shift indicates the electron density around the N atom is decreasing.$^{[39-40]}$ Thus, La tends to bind to N atoms. We also measured the XPS spectrum of Ru 3p. As shown in Fig. S3, a featured signal at 461.02 eV indicates Ru mainly existed in the zero-valence state. In addition, we also apply XPS analysis to Ru 3p of the composites after

Table 2. Product distribution involved in the controlled contrast experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Condition</th>
<th>Rate of formation (μmol h$^{-1}$ g$^{-1}$)</th>
<th>CO</th>
<th>CH3CH3</th>
<th>CH3CH2OH</th>
<th>CH3CH(OH)CH3</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>UV-Vis &amp; 100 °C</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.5Ru-0.6LGCN</td>
<td>Dark &amp; 100 °C</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GCN</td>
<td>UV-Vis &amp; 100 °C</td>
<td>8.40</td>
<td>16.67</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.6LGCN</td>
<td>UV-Vis &amp; 100 °C</td>
<td>13.13</td>
<td>15.69</td>
<td>0.65</td>
<td>5.00</td>
<td>133.33</td>
</tr>
<tr>
<td>0.5Ru-GCN</td>
<td>UV-Vis &amp; 100 °C</td>
<td>133.33</td>
<td>153.68</td>
<td>130.38</td>
<td>133.33</td>
<td>133.33</td>
</tr>
</tbody>
</table>

Figure 9. In situ FTIR spectra of the adsorbed species after introduction of CO$_2$ and CH$_4$ and irradiation for: i) 0 min, ii) 30 min, iii) 60 min, iv) 90 min, v) 120 min on 0.5Ru-0.6LGCN.
Figure 10. (a-d) Photocatalytic yield of the products over the various Ru-LGCN photocatalysts: (a) CO, (b) CH₃OH, (c) CH₃CH₅, (d) CH₃CH₂OH, (e) CH₃CHO, and (f) CH₃CH(OH)CH₃.

The paths and intermediates of photocatalytic CO₂ reforming of CH₄ were studied by in-situ FTIR spectra. Fig. 9 shows the in-situ FTIR spectra obtained by using 0.5Ru-0.6LGCN as photocatalyst with different irradiation time. The absorption peak located at near 1305 cm⁻¹ was typical vibration absorption of methane, while the absorption peak near 2356 cm⁻¹ was characteristic absorption of CO₂.[8, 41-42] It should be noted that the intensity of these absorption peaks decreased gradually after irradiation, and some new peaks appeared. More specifically, the characteristic vibration absorption peak at 2206 cm⁻¹ can prove the presence of CO (C≡O) (as shown in Fig. 9b), and the intensity of the new absorption peak increases with the increase of irradiation time.[43] Specifically, as shown in Fig. 9a, the absorption peak at 1035 cm⁻¹ was due to the vibration absorption of ν(C-O). The decrease of absorption peak intensity at 1340 cm⁻¹ was caused by the vibration absorption of the ν₅(C-O) of decreasing CO₂. In addition, the vibration absorption is coincident with the absorption vibration of the methyl deformation mode around 1350 cm⁻¹. As shown in Fig. 9c, the wide bands of 3010 cm⁻¹, 2960 cm⁻¹, 2946 cm⁻¹ and 2925 cm⁻¹ were attributed to the vibration absorption of ν(C-H) of alkyl groups (i.e. -CH₃, -CH₂, and -CH). Interestingly, in the process of photocatalytic CO₂ reforming CH₄, the key CO₂ absorption existed in the dicentate carbonate (i.e. β-CO₃²⁻ and m-CO₃²⁻) states, and the key transition state •CO₂⁻ (at 1674 cm⁻¹) was formed, as shown in Fig. 9d. The observation of •CO₂⁻ by the in-situ FTIR spectra showed that the activation of CO₂ in the form of CO₂ (carbonate) + e⁻ → •CO₂⁻ could be achieved by transferring photogenerated electrons to the CO₂ adsorption sites La. In Fig. 9a, the new absorption peak at ~1715 cm⁻¹ corresponds to the characteristic absorption of δ(CH₃). On the basis of the above analysis, the reaction mechanism of photocatalytic CO₂ reforming CH₄ to C₂+ hydrocarbons on La doped g-C₃N₄ photocatalyst was described as the Equations (1) - (13).

\[
0.5\text{Ru/0.60LGCN} + h\nu \rightarrow h^+ + e^- \tag{1}
\]
Here, layered porous Ru-modified and La-doped g-C3N4 nanosheets (Ru-LGCN) were prepared by continuous thermal oxidative exfoliation and condensation of urea and lanthanum salt, followed by in situ photoreduction deposition of Ru. The layered Ru-LGCN showed excellent photocatalytic CO2 reformation of methane performance under simulated sunlight, and optimal yields of CO, CH3OH, CH3H, and CH3CHOHCH2 were 401.03, 750.02, 460.56 and 460.12 μmol/g, respectively, for 3 h over 0.5Ru-0.6LGCN photocatalyst. The CO2-TPD and CH4-TPD tests and theoretical calculations show that the reason for the enhanced photocatalytic activity of Ru-LGCN is the synergistic effect of bimetallic Ru and La. The spatially separate states of VBM and CBM in LGCN can effectively prohibit the recombination of photogenerated carriers. That is to say, the excited electrons will migrate to the CBM which is located around the doped La atoms and participate in the reduction of adsorbed CO2, while the holes will migrate in the opposite direction to the VBM and participate in the oxidation process. It is worth noting that the doped La can provide a good channel for charge transfer between LGCN and CO2. This change in the charging behavior of the transport path is beneficial to break the C=O bond on the active site La and generate methyl radicals on Ru particles, resulting in the generation of series C2+ hydrocarbons.

**Conclusion**

The 0.5Ru/0.6LGCN photocatalyst was stimulated by UV-Vis irradiation to produce photogenerated electrons (e−) in the valence band and photogenerated holes (h+) in the conduction band, respectively (as shown in Eq. (1)). Correspondingly, photogenerated electrons and holes played the major role in the REDOX process of photocatalytic CO2 reforming of CH4. Photogenerated holes participated in the oxidation reaction of CH4 to generate methyl radical (•CH3) and H+ at the same time (Eqs. (2), (3) and (4)).[8, 44] Here, two •CH3 radicals were coupled to form ethane (Eq. (5)). Methanol could be produced by coupling reaction of •CH3 radicals with OH (Eq. (6)). The ethane was further oxidized with the hole (h+) to form •CH2CH2 radicals and further reacted with OH− to form ethanol. Acetaldehyde can be formed by the oxidation reaction of ethanol (Eqs. (8), (9) and (10)).[45] Two •CH3 radicals conjugated with CH radicals to form isopropyl radicals, which then reacted with OH− to form isopropyl alcohol. Of course, the reaction of the •CH2CH3 radical with the hole (h+) and further coupling of the methyl radical could also obtain isopropyl radical and isopropyl alcohol (Eqs. (7), (11) and (12)). In addition, the main chemical reaction paths in the photocatalytic reaction process are summarized in Scheme 1.

The photocatalytic performance of Ru modified and La doped g-C3N4 photocatalyst for the photocatalytic CO2 reforming of methane was investigated under simulated solar irradiation. Fig. 10a-f summarized the yields changed of various photocatalytic products with time. The products obtained by photocatalytic reforming mainly include CO, CH3OH, CH3H, and CH3CHOHCH2, and the reaction paths were shown in Scheme 1. The results showed that the photocatalytic activity had an obvious volcanic relationship with the contents of La and Ru. The optimal yields of CO, CH3OH, CH3H, and CH3CHOHCH2 were 401.03, 750.02, 460.56 and 460.12 μmol/g, respectively, for 3 h over 0.5Ru-0.6LGCN photocatalyst. As shown in Table 2, the control experiment showed that even if the reaction system temperature was 100°C, the photocatalytic reforming reaction could only be carried out in the presence of both photocatalyst and light irradiation. Therefore, the reaction of photocatalytic CO2 reforming of CH4 was carried out under photocatalysis, and the photons provided enough energy to generate photogenerated electrons and holes to activate the REDOX reaction. In order to verify the carbon source, no hydrocarbons were observed after a 3-hour reaction in pure nitrogen, ruling out the possibility of photocatalytic generation of hydrocarbons from carbon residues or adsorbed during the preparation of the photocatalysts. Finally, the stability of the 0.5Ru-0.6LGCN catalyst was tested, as shown in Fig. S7. The yields of productions did not change significantly after five-time cycled test.

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La doped g-C$_3$N$_4$ can provide a good channel for charge transfer between La and CO$_2$, which is consistent with theoretical calculations. This change of the charge behavior of the transport path is beneficial to break the C=O bond on the active site of La and generate methyl radicals.