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Photothermal catalysis for CO₂ convert into C₁–C₃ hydrocarbons by proton conductor BZCY532

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Abstract

Conversion of CO₂ into long-chain hydrocarbons is a potential applications in clean energy research. Here, we exhibit an efficient, stable and readily synthesized photocatalyst for the photocatalytic reduction of CO₂. This is the first time that the proton conductor BZCY 532 as photocatalysts can harvest UV light for multielectron, multiproton reduction of CO₂ to C₁ (methane), C₂ (ethane), and C₃ (propane) hydrocarbons. Under the photothermal coupling (350 °C + UV) condition, the total yield of CH₄, C₂H₆, and C₃H₈ were 39.13 umol g⁻¹, 8.64 umol g⁻¹ and 3.22 umol g⁻¹ over the course of more than 5 h runs, respectively. The light and temperature attribute influence the selectivity of C₁ and C₂, C₃. In this approach, Ni, Co-doped BZCY532 were also studied and the results show that Ni, Co-doped BZCY532 have higher activity. Ni₀.05 and Co₀.05 obtained the yield of total CH₄, C₂H₆, C₃H₈, which show about 5.6, 9.6, 3.9 and 6.8, 14.2, 6.7 times than BZCY532, respectively. The results proved that doping play a crucial role in improving photocatalytic activity of BZCY532. The formation of multi-carbon compounds maybe the faster proton transfer, which can harvest more electrons from the proton conductor catalysts and promote C–C coupling to form C₂ and C₃. These findings elucidate BZCY-based proton conductor catalyst can be good candidate for the nature of photocatalysis, which involves the stage for the chemical bond formation by light excitation.

1. Introduction

The excessive emission of CO₂ has potentially caused serious environmental problems. This makes it imperative to find an efficient energy conversion technology to realize a zero carbon footprint recycling of CO₂ [1, 2]. Photocatalytic reduction of CO₂ into valuable fuels and chemicals is a desirable way to resolve the carbon emission and energy crisis issues [3]. To achieve high CO₂ conversion, the development of efficient photocatalysts is particularly important [4].

CO₂ is an extremely stable molecular and carbon is in the highest oxidation state in CO₂, so the reduction of CO₂ can lead to a large variety of products with different carbon oxidation [5]. However, most of the reported catalysts can be reduced CO₂ into a variety of C₁ products, such as CH₄, CH₃OH, HCHO and HCOOH [6–9]. Photocatalytic formation of C₂ and C₃ compound, such as C₂H₄, C₂H₂, C₂H₆, C₃H₆, C₃H₈, has also been reported, but most of catalysts are loaded with noble metals (Au, Ag, Pt and Cu) nanoparticles due to excitation of their located surface plasmon resonances which can be stored photogenerated hot carries on the plasmonic nanoparticles and harvest photoredox reaction [10–12]. It is well known, the conversion of CO₂ into C₂ and C₃ need effective transfer of more electrons and protons, as well as stabilize the C₁ radicals or intermediates to ensure C–C bond formation, which is more difficult than C₁ evolution from CO₂ [13].

Perovskite-type (ABO₃) proton conductors has appreciable proton conduction at high temperature and chemical stability, thus it can provide possible electron transport [14]. The reaction of CO₂ and H₂O to form hydrocarbons involves multiple proton-coupled electron transfer. As a proton conductor can provide more
protons to conduct charge and facilitate the occurrence of the reactions, which may become candidate photocatalyst to convert CO₂ into high-carbon compounds. BaCeO₃ and BaZrO₃-based have been extensively studied, because of the high conductivities [15, 16]. Due to BaCeO₃ has poor chemical stability in acidic gases and BaZrO₃ has poor conductivity and need high temperature which limited its widespread application [17–19]. Many studies have shown that BaCeO₃ and BaZrO₃-based exhibited photocatalytic water splitting activity [20–22]. As we know, there is little attention has been paid to the application of proton conductors in photocatalytic of CO₂. Recently, Zou et al reported about the photocatalytic of BaZrO₃ and BaCeO₃ for CO₂ reduced into CH₄ under ultraviolet light [23, 24]. This studied motivated us to use proton conductors as photocatalyst to reduce CO₂ into hydrocarbons. BZCY (Ba, Zr, Ce, Y) have been widely investigate to achieve both chemical stability and proton conductivity [25–27]. Ce-doped can format a stable Ce⁴⁺/Ce⁶⁺ redox couple and Ce⁴⁺ turn to Ce³⁺ by absorbing photogenerated electron can increase the photocatalytic performance [28, 29]. Y-doped can improve the conductivity of proton conductors [30]. Hence, doping can format defects in the ABO₃, which increase proton conductivity. In our previous work, BaZr₀.₅Ce₀.₃Y₀.₂O₃₋ₓ (BZCY532) showed good proton conductivity in the most promising proton conductors [31, 32]. Therefore, BZCY532 was selected as photocatalyst for study photocatalytic reduction of CO₂.

To the best of our knowledge, there is no results have been reported about the photocatalytic activity of BaZr₀.₅Ce₀.₃Y₀.₂O₃ for reduction of CO₂ under UV light irradiation. In this study, we reported that BaZr₀.₅Ce₀.₃Y₀.₂O₃ (BZCY532) as a photocatalyst not only can successfully converted CO₂ and H₂O into CH₄, but also generated long-chain hydrocarbons of C₂H₆ and C₃H₈. Furthermore, Ba(Zr₀.₅Ce₀.₃Y₀.₂)₁−ₓCoₓO₃ and Ba(Zr₀.₅Ce₀.₃Y₀.₂)₁−ₓNiₓO₃ (x = 0.01, 0.03, 0.05, 0.07, 0.09) were also synthesized and investigated the photocatalytic activity, which showed higher conversion rates. This paper provides a new sight for photocatalytic reduction of CO₂.

2. Experimental

2.1. Materials and methods

BZCY532, Co-doped BZCY532, Ni-doped BZCY532 were synthesized by a conventional solid-state reaction method. Stoichiometric amounts of commercial BaCO₃, ZrO₂, Y₂O₃, CeO₂, CoO and NiO powders (purity >99.9%) were mixed for 5 h by ball-milling with slurry. The details of BZCY synthesis can refer to our previous studies [33, 34]. The intended composition of Co-doped BZCY532 and Ni-doped BZCY532 were Ba(Zr₀.₅Ce₀.₃Y₀.₂)₁−ₓCoₓO₃ and Ba(Zr₀.₅Ce₀.₃Y₀.₂)₁−ₓNiₓO₃ (x = 0.01, 0.03, 0.05, 0.07, 0.09), which were abbreviated as Co₀.₀₁, Co₀.₀₃, Co₀.₀₅, Co₀.₀₇, Co₀.₀₉, Ni₀.₀₁, Ni₀.₀₃, Ni₀.₀₅, Ni₀.₀₇, Ni₀.₀₉, respectively.

The phase composition of the photocatalysts were examined by x-ray diffraction (XRD, TD-3500, Tongda, China). The microstructure and morphology of various photocatalysts were investigated by desktop Scanning Electronic Microscope (SEM, Phenom Pro, Phenom World, Holland). The specific surface area were measured by BET (ASAP 2020, Micromeritics, American). Light absorption performance of photocatalyst were tested by Ultraviolet and visible diffuse relectance spectra (UV–vis, UV-3600, SHIMADZU, Japan). The electrochemical tests was used electrochemical workstation (CS-300, China). Chemical composition and chemical valence of photocatalyst surface were analysed by x-ray photoelectron spectroscopy (XPS, ESCALAB250, England). Photoluminescence (PL) was recorded with a Fluorescence spectrophotometer (Edinburgh, FLS-920, USA).

2.2. Catalytic measurements

Photocatalytic CO₂ reduction experiments were carried out in a gas-tight circulation system. 100 mg sample powder was evenly dispersed on the bottom of a Pyrex glass cell. The reaction setup was vacuum-treated several times and the high purity CO₂ (≥99.999%) was flown through the whole system for 5 min at a flow rate of 27 ml min⁻¹. 0.3 ml H₂O was injected in the reactor before the heating. The entire catalytic activity evaluation was performed at 350 °C, which was kept constant by an external heating sleeve (heat source). A 300 W Xe lamp (PLS-SXE300, Beijing Zhongjiaojinyuan Technology Co, Ltd.) with a UV-light filter (λ > 420 nm) was employed as the light source, which was kept 8–10 cm away from the upper surface of the catalyst. The first sample (0.5 ml) was taken after 1 h of reaction, after which samples were collected every 0.5 h. The photocatalytic reaction was typically performed for 4 h. After the irradiation, the products were analysed by Echror A90 gas chromatograph equipped with a flame ionization detector (FID, capillary column, HP-PLOTQ) detector.

3. Results and discussion

The XRD pattern of BZCY532, Ba(Zr₀.₅Ce₀.₃Y₀.₂)₁−ₓCoₓO₃, Ba(Zr₀.₅Ce₀.₃Y₀.₂)₁−ₓNiₓO₃ (x = 0.01, 0.03, 0.05, 0.07, 0.09) are displayed in figure 1. From the pattern, BZCY532 shows a typical cubic perovskite structure (space group Pm₃m). Ba(Zr₀.₅Ce₀.₃Y₀.₂)₁−ₓCoₓO₃ and Ba(Zr₀.₅Ce₀.₃Y₀.₂)₁−ₓNiₓO₃ compared with BZCY532...
didn’t present impurity phase, which illustrated that doping transition metals doesn’t cause the change of lattice structure. It can be seen from table 1 that the peak slightly shift to high angle with the increase of Co and Ni, which indicate that the ion radius of Co and Ni are smaller than B-sit elements (Zr, Ce, Y) and have entered the crystal lattice to replace some B-sit metal ions. At the same time, the crystallite size also increases with increase of Co and Ni. This is because CoO and NiO are sintering aids which can promote the growth of crystal particle with doping amount increases [35, 36].

The microstructure images of BZCY532 and Co-doped BZCY532 are present in figure 2. It can be seen that BZCY532 show irregular particles and has certain pores between the particles. This microstructure is favorable for gas adsorption and transmission and beneficial for the occurrence of catalysis. With the increase of Co-doped, the sample began to agglomerate. When the Co reached 0.09, the particle agglomeration became more obvious. This phenomenon we have explained in previous. CoO as a sintering aid promoted the sintering of BZCY532. Therefore, with the increase of doping amount, the particle size becomes larger, which eventually leads to agglomeration. The results of SEM was consistent with XRD pattern. Ni-doped has the same rules with Co-doped, but the agglomeration looked more obvious (Figure S1 is available online at stacks.iop.org/MRX/7/085504/mmedia). A catalytic reaction occurs at the surface of catalysts. The smaller the particles, the larger the specific surface area, which can provide more active sites for entire reaction, finally the photocatalytic efficiency is correspondingly improved. Therefore, the photoconversion efficiency of CO2 reduction can be improved by paying more attention to optimizing the content of Co and Ni-doping.

The surface area can be used as a factor to judge the catalytic activity. The higher the specific surface area, the more active sites, the higher photocatalytic activity. The BET surface date of BZCY532, Co-doped and Ni-doped have been acquire in table 1. It can be clearly seen that the specific surface area of BZCY532 is obviously larger than that of Co and Ni-doped BZCY532. At the same time, the specific surface area decreases with the increase of Co and Ni doping amount. This results were consistent with the analysis of XRD and SEM, which show that CoO and NiO as sintering agents promoted the agglomeration of BZCY532 particles. Therefore, the more doping

| Sample  | 2θ degree (110) | Crystallite size (nm) | S(BET), m² g⁻¹ |
|---------|----------------|----------------------|----------------|
| BZCY    | 29.457         | 254                  | 1.5363         |
| Co 0.01 | 29.575         | 257                  | 1.1149         |
| Co 0.03 | 29.608         | 270                  | 0.5592         |
| Co 0.05 | 29.577         | 311                  | 0.5887         |
| Co 0.07 | 29.520         | 410                  | 0.4919         |
| Co 0.09 | 29.502         | 437                  | 0.3855         |
| Ni 0.01 | 29.459         | 328                  | 0.5037         |
| Ni 0.05 | 29.493         | 373                  | 0.3058         |
| Ni 0.07 | 29.512         | 447                  | 0.1774         |
| Ni 0.09 | 29.457         | 529                  | 0.1615         |

Table 1. XRD analysis and specific surface area for BZCY532 at different Co, Ni-doping levels.
amount of Co and Ni, the more obvious the agglomeration will appear, the smaller the specific surface area will be.

The photocatalytic effectiveness were ultimately dependent on its light-absorbing capability and band-gap structure. The light absorption spectrum are shown in figure 3 within the wavelength range of 200–800 nm. From figure 3(a), the major peak of BZCY532 is around 280 nm and the absorption edge extended to almost 410 nm. Thus, BZCY532 has a good absorption in the ultraviolet region, which means that BZCY532 has a good response to ultraviolet light. Through the Tauc method, the band gap of BZCY532 was calculated to be 3.02 eV which indicated that BZCY532 is a wide-band gap semiconductor, so ultraviolet light can effectively excite BZCY532 semiconductor catalyst.

In the Co-doped and Ni-doped BZCY532, the absorption range of light extends from ultraviolet to visible light, and the absorbance increases with the increase of Ni and Co-doped, which indicated that the Co and Ni-doped can effectively enhanced visible light absorption (figures 3(b) and (c)). The calculated energy band gap for Ni, Co-doped BZCY532 changed from 1.3 to 2.3 eV, which indicated that the doping can narrow the optical band gap (Figure S2 and table S2). Although doping can enhance the material’s ability to absorb visible light, in order to compare with the catalytic performance of BZCY532, all photocatalytic tests use UV light as the light source.

The band gap energy is critical for photocatalytic activity, which can reflect the region and intensity of the light response and the ability of electrons to be excited from the valence band to conduction band. The conduction band (CB) and valence band (VB) values have an effect on the formation of different hydrocarbon fuels. For CO₂ reduction with H₂O, the redox potential of valence band edge should be more positive than the redox potential of H₂O/O₂ (H₂O → 1/2O₂ + 2H⁺ + 2e⁻, E’ ox = 0.82 eV), and the redox potential of conduction band edge should be more negative than the redox potential of CO₂/CH₄ (CO₂ + 8e⁻ + 8H⁺ → CH₄ + H₂O, E’ red = −0.24 eV). We performed electrochemical tests and used the Mott-Schottky curve to fit the CB value of BZCY532 in figure 4. Through the formula E_{CB} = E_{VB}−E_{F}, the VB value of BZCY also can be calculated which be calculated to be 2.77 eV and −0.25 eV, respectively. From the calculation results, it can be seen that the E_{VB} of BZCY532 is more positive than E’ (H₂O/O₂), so the oxidation ability is stronger and the E_{CB} is more negative than E’ (CO₂/CH₄), so the reducing ability is stronger. The CB and VB values of undoped BZCY532 was only to provide an evidence that BZCY532 has the photocatalytic potential for reduction in CO₂ with H₂O into hydrocarbons. This conclusion can prove that BZCY has potential of photocatalytic reduction of CO₂. The photocatalytic ability of Co and Ni-doped BZCY to reduce CO₂ are also worth looking forward.
To further understand the chemical composition and chemical state of BZCY532 and Co-doped and Ni-doped in BZCY532, XPS analysis was performed on the samples (Figure S3, S4). There are only Ba, Zr, Ce, Y, O, Ni, Co and a trace amount of C are detected. The C comes from the C film used in the sample test. Due to the low content of Ni and Co, and the close position of Co 2p and Ba 3d, so the survey spectrum can’t obtain much information, but show that Ni and Co successfully doped in BZCY532.

Surface oxygen vacancies act as trap states for photogenerated charge carries, which can reduce the probability of electron-hole recombination and improve the photocatalytic activity, whereas lattice oxygen (bulk oxygen vacancies) maybe as carrier recombination centers and play an important role in photocatalysis.
shows that photothermal heating also play an important role in the catalytic activity and products. Photothermal conditions can also cause products, such as CH4, C2H6, C3H8 to increase about 3.0 times and 3.3 times, respectively, when the catalytic reaction has both heat source and UV light source. UV-light can reveal the rate of photogenerated electron-hole recombination in catalysts. Figure 6 shows the PL spectra of the BZCY532 at different Ni and Co-doping levels. It can be seen that doping didn’t induce new spectral signals, but only affects the intensity of the spectral signals, a clear quenching of the PL emission peak is observed after doping, which indicated that doping of Ni and Co can effectively reduce the efficiency of carrier recombination. Especially when the doping amount of Co and Ni reach 0.05, the quenching is the most obvious and the carrier recombination efficiency is minimized. This conclusion shows that doping can reduce the possibility of carrier recombination and effectively improve the photocatalytic efficiency. It is beneficial for the occurrence of photocatalytic reactions.

Figure 7(a) shows the comparison of catalytic activity of thermal reduction (250 °C and 350 °C) and photothermal reduction (UV + 250 °C, 350 °C and UV + 350 °C). As depicted in figure 7(a) that the yield of CH4 increased 20 times when the temperature rises from 250 °C (0.57 μmol g⁻¹) to 350 °C (11.80 μmol g⁻¹). When the catalytic reaction has both heat source and UV light source, the yield of CH4 increased 22 times from UV + 250 °C (1.76 μmol g⁻¹) to UV + 350 °C (39.13 μmol g⁻¹). Compared thermal reduction and photothermal reduction under the same temperature, CH4 increased about 3.0 times and 3.3 times, respectively. The CH4 production yields of BZCY are in the order of 350 °C + UV-light > 250 °C > UV-light > 250 °C. It is worth noting that C2H6 and C3H8 are almost undetectable at 250 °C. This result clearly shows that photothermal heating also play an important role in the catalytic activity and products.

Figure 7(b) shows the reduction products C2H6 and C3H8 under the thermal only conditions at 350 °C and photothermal conditions (350 °C + UV-light), Obviously, the production of C2H6 and C3H8 increased significantly under heating with light, which indicates that the photothermal coupling is beneficial to increase the activity and selectivity of the catalytic reaction. After 5 h of reaction under photothermal coupling, the cumulative output of CH4 reached 39.13 umol g⁻¹, C2H6 was 8.64 umol g⁻¹, and C3H8 was 3.23 umol g⁻¹, the total of CO2 conversion rate is 0.11%. As we know, in all case C1 hydrocarbons have been the predominant products, such as CH4, CH3OH, HCOOH et al. Selective conversion of CO2 to higher grade carbon species (Cn, n ≥ 2) didn’t have much research. This experimental results showed that CH4, C2H6, C3H8 were the...
primary products in the photocatalytic CO$_2$ reduction system using BZCY as the photocatalyst and the product selectivity was found to follow the order: CH$_4$ $>$ C$_2$H$_6$ $>$ C$_3$H$_8$. The selective formation of CH$_4$, C$_2$H$_6$ and C$_3$H$_8$ might be attributed to the redox potential of CH$_4$/CO$_2$ ($E^0$ = −0.24 V versus NHE), C$_2$H$_6$/CO$_2$ ($E^0$ = −0.27 V versus NHE) and C$_3$H$_8$/CO$_2$ ($E^0$ = 0.14 V), which is much lower than that of CO/CO$_2$ ($E^0$ = −0.53 V versus NHE) or CH$_3$OH/CO$_2$ ($E^0$ = −0.38 V versus NHE) [11, 39]. This is a new discovery that proton conductor BZCY as a photocatalyst can successfully convert CO$_2$ with H$_2$O into C$_1$–C$_3$ hydrocarbons under certain temperature and light.

To further confirm that doping has stronger catalytic performance, the reduction of CO$_2$ with H$_2$O was carried out under the same photothermal conditions (350 °C + UV-light). The products were consistent with the previous catalytic of BZCY532, which were mainly CH$_4$, C$_2$H$_6$, and C$_3$H$_8$. The Ni$_{0.05}$ exhibited the highest performance for the catalytic reduction of CO$_2$ (CH$_4$ = 219.9 umol g$^{-1}$, C$_2$H$_6$ = 83.24 umol g$^{-1}$ and C$_3$H$_8$ = 12.7 umol g$^{-1}$) in Ni-doped BZCY532 (figures 8(a)–(c)), which is about 5.6, 9.6, 3.9 times than BZCY532 (CH$_4$ = 39.13 umol g$^{-1}$, C$_2$H$_6$ = 8.64 umol g$^{-1}$ and C$_3$H$_8$ = 3.22 umol g$^{-1}$) under the same condition. Figure 8(d)–(f) shown the products of Co-doped BZCY. It has the similar regularity that Co$_{0.05}$ emerged the highest activity for conversion CO$_2$ (CH$_4$ = 266.8 umol g$^{-1}$, C$_2$H$_6$ = 123.2 umol g$^{-1}$ and C$_3$H$_8$ = 21.27 umol g$^{-1}$), which is about 6.8, 14.2, 6.7 times than BZCY532 and 1.2, 1.5, 1.7 times than Ni$_{0.05}$.

Figure 5. O 1s XPS spectra of the BZCY532 and at different (a) Ni-doping (b) Co-doping levels.
The research showed higher photocatalytic efficiency of CH₄, C₂H₆ and C₃H₈ than titanate nanotubes decorated with nanoparticle elemental Cu and CdS Quantum Dots [40]. A comparison results between this work and other related papers for CO₂ photoreduction products were listed in table S3. That is to say that Ni, Co-doping can effectively improve the photocatalytic ability of the BZCY532, especially for Ni₀₀.⁰⁵ and Co₀₀.⁰⁵, but Co₀₀.⁰⁵ showed more outstanding catalytic ability of CO₂. This result corresponds to the previous PL and XPS analysis. Doping can effectively reduce the recombination rate of photo-generated electron-hole pairs and increase the surface oxygen vacancy concentration, which cause more effective electrons and holes participate in the photocatalytic reaction and quickly capture O in CO₂ and H₂O and generate more electrons and protons to convert CO₂ into hydrocarbons. This is also a new research that Co and Ni-doped in proton conductor BZCY532 as a photocatalyst can not only successfully convert CO₂ with H₂O into C₁–C₃ hydrocarbons, but also improve photocatalytic conversion efficiency.

Under the condition of 350 °C + UV, the three hydrocarbon products were CH₄, C₂H₆ and C₃H₈ and the selectivity was CH₄ > C₂H₆ > C₃H₈. The reason why the selectivity like this is that CH₄ production needs 8e⁻ and 8H⁺, C₂H₆ production involves 14e⁻ and 14H⁺ and C₃H₈ production requires 20e⁻ and 20H⁺. The transfer of 14 and 20 electrons–protons, which is more difficult than the 4 electrons and protons reaction of CH₄ from CO₂ (equations (1)–(3)). When the photocatalytic reduction reaction is performed at 250 °C, C₂H₆ and
C3H8 were nearly not detected and only traces of CH4, which because temperature can provide additional energy to reach the activation energy required for the reaction. Therefore, only supply of enough energy to generate more electrons and protons can promote the production of C2H6 and C3H8. Ni, Co-doped BZCY 532, the yield of CH4, C2H6 and C3H8 increased. On the one hand, doping Ni and Co can introduce more surface oxygen vacancies which can increase adsorption and activation of CO2 and as trap electrons to avoid recombination of electron-hole, on the other hand, doping can narrow the band gap which can improve the efficiency of light absorption and produces more photogenerated electrons and holes.

\[
\begin{align*}
\text{CO}_2 + 8 \text{H}^+ + 8e^- & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \\
2\text{CO}_2 + 14 \text{H}^+ + 14e^- & \rightarrow \text{C}_2\text{H}_6 + 4\text{H}_2\text{O} \\
2\text{CO}_2 + 20 \text{H}^+ + 20e^- & \rightarrow \text{C}_3\text{H}_8 + 6\text{H}_2\text{O}
\end{align*}
\]

In order to understand the reaction process, a possible catalytic mechanism of BZCY532 catalysts for the reduction of CO2 to CH4, C2H6 and C3H8 were proposed (figure 9). H2O is the essential proton donor for the reduction of CO2, but the possible H2 evolution from the reduction of H2O become a fiercely competing reaction with photocatalytic CO2 reduction reactions [41]. Rapid proton transfer or consume H2 can suppress the H2 evolution, then can enhance the overall efficiency of CO2 photoreduction. BZCY532 has optimization of proton conductivity depends on the proton transport, defect formation and chemical stability, so the holes oxidize H2O into O2 and H+; the H+ can be quickly transferred to the conduction band with the surface formed CO2 δ− and electron becomes ·COOH. Then the H+ continue transfer to ·COOH with electron to form HCOOH. After a series of intermediates combine with couple of H+ and electron, dehydrate and hydrogenation to form the final products CH4, this called formaldehyde pathway of CO2 to CH4 which process can be express to \( \text{CO}_2 \rightarrow \text{HCOOH} \rightarrow \text{H}_2\text{CO} \rightarrow \text{CH}_3\text{OH} \rightarrow \text{CH}_4 \). Intermediate products are HCOOH, HCO3−, CH3OH and so on, which can be preferentially adsorbed upon the active photocatalyst sites. The other way of CO2 to CH4 called Carbene pathway, which goes through deoxygenation followed by hydrogenation. The process can be described as \( \text{CO}_2 \rightarrow \text{CO} \rightarrow \cdot \text{C} \rightarrow \cdot \text{CH}_3 \rightarrow \text{CH}_3\text{OH/CH}_4 \) [42, 43]. Although ·CH3 may be convert CH3OH or CH4 are competing reactions, in our experimental results, no methanol was detected, which can be ascribe to the fast proton make the combination \( \cdot \text{CH}_3 + \text{H}^+ \rightarrow \text{CH}_4 \). Carbene pathway can avoid too much intermediate products, and the only intermediate product CO can react with H2 through Fischer-Tropsch reaction, the whole process nearly only need transfer of protons and electrons [44, 45].

In this research, no other intermediates or side products were detected. We can propose that carbene pathway is the most possible way for BZCY532 convert CO2 in to CH4, C2H6 and C3H8. This is plausible because the local proton activity within the BZCY532 might be enhanced and various intermediates involved in the formation of C2H6 and C3H8 can be stabilized in the BZCY532 to facilitate the multi-electron transfer as we mentioned earlier. The formation of C2H6 and C3H8 requires even more electrons and protons, and stabilize ·CH3 to promote C–C coupling reactions. The studied have been show that graphene appears to stabilize ·CH3 radicals and allows for enhance probability of \( (\cdot \text{CH}_3 + \cdot \text{CH}_3 \rightarrow \cdot \text{C}_2\text{H}_6) \) [46]. Considering that BZCY532 can successfully convert CO2 into C2H6 and C3H8, which indicated that the photoreconversion reactions that need more protons seem to be preferentially favored in the BZCY532 and the local activity in the BZCY532 may have the ability to stabilize the adsorption of intermediate ·CH3 radicals on the surface and promotes C–C and C–C–C coupling to facilitate the multi-electrons and protons transfer for the formation of C2H6 and C3H8. Ni and Co-doped BZCY532 increase the surface oxygen vacancies, which can produce more reactive sites to promote the CO2 absorption and activation and stabilize the adsorption of

![Figure 7. (a) CH4 and (b) C2H6 and C3H8 generation of BZCY532 catalyst under different conditions.](image-url)
intermediate CH$_3$ to promote C–C and C–C–C coupling (Figure S5). Therefore, the yield of CH$_4$, C$_2$H$_6$ and C$_3$H$_8$ are increased, respectively. However, there are no studies on the photocatalytic reduction of CO$_2$ into C$_1$–C$_3$ by BZCY532, so how does BZCY532 stabilize the intermediate ions needs further research in the future.

4. Conclusions

The photocatalytic activity of BZCY532 as a new photocatalyst to convert CO$_2$ into hydrocarbon have been investigated. The BZCY532 samples obtained at 1450 °C can successfully converted CO$_2$ and H$_2$O into CH$_4$ and long-chain hydrocarbons of C$_2$H$_6$ and C$_3$H$_8$ under photothermal coupling (350 °C + UV). Doping Ni and Co can effectively improve the photocatalytic efficiency, Ni$_{0.05}$ and Co$_{0.05}$ showed the higher photocatalytic activities. Under the same condition, Co$_{0.05}$-doped showed highest photocatalytic activities than the samples with other doping amount. Doping Ni and Co on BZCY532 promote the absorption of light and results in the more surface oxygen vacancy can provide active sites to promote the CO$_2$ adsorption and activation, at the same time, doping reduce the possibility of carrier recombination. All of that are beneficial for the occurrence of photocatalytic reactions. The formation of high carbon hydrocarbon of C$_2$H$_6$ and C$_3$H$_8$ requires multiple electron and proton transfer steps and should stabilize the C$_1$ radicals or intermediates to ensure them participate in C–C bond formation. BZCY532 as
proton conductor photocatalyst promotes the protons transfer for formation of CH₄ and has the ability to stabilize the adsorption of intermediate -CH₃ radicals on the surface to promote C–C (C₂H₆) and C–C─C coupling (C₃H₈). Ni, Co-doped in BZCY532 bring about higher catalytic efficiency, the electron and proton transmission and C–C bond formation. This paper provide new ideas for the production of higher grade carbon species (Cn, n ≥ 2). The detailed mechanism would be further studied.

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Conflicts of interest

There are no conflicts to declare.

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