High selective photocatalytic CO₂ conversion into liquid solar fuel over a cobalt porphyrin-based metal–organic framework

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Abstract

In the present study, porphyrin-based metal–organic framework (Co/PMOF) was synthesized and characterized by different spectra analyses. The photoluminescence properties of porphyrin and Co/PMOF revealed that the photoluminescence of Co/PMOF was quenched compared to the porphyrin, indicating that the lifetime of photo-generated charge carriers in Co/PMOF is longer than porphyrin. The prepared Co/PMOF was applied as an efficient photocatalyst for CO₂ photoconversion to formate in the presence of triethanolamine (TEOA) as a sacrificial agent under visible-light irradiation. The photoreaction results showed that 23.21 μmol HCOO[−] was produced over Co/PMOF during the 6 h photocatalytic reaction under visible illumination, showing much better activity than the porphyrin, 4.56 μmol HCOO[−]. No other products were detected, suggesting that this reaction over Co/PMOF has high selectivity. Co/PMOF reusability and stability were examined through recycling tests and there were no remarkable losses of photoactivity even after three cycles of photoreaction. Moreover, FTIR measurement and UV–Vis spectra demonstrated no notable changes in Co/PMOF structure. As a result, superior photocatalytic behavior of Co/PMOF was implied for CO₂ photoreduction which highlights the great potential of assembly porphyrin and cobalt into MOFs for CO₂ photoreduction.

Keywords Photocatalyst · Liquid solar fuel · Metal organic framework · Porphyrin · CO₂ photoreduction

1 Introduction

In recent years, heavy dependence on fossil fuels for energy has resulted in excessive CO₂ emissions and global warming [1, 2]. Great efforts have been made to reduce CO₂ emissions through carbon capture and sequestration/separation from post-combustion effluents [3, 4]. These processes are energy-intensive and therefore costly; moreover, there are many uncertainties with regard to CO₂ long-term storage in geological formations [2, 5]. An alternative and the more preferable way is catalytic converting of CO₂ to valuable fuels or useful chemicals with input energy (e.g. UV and/

or visible light, sunlight) [6–8]. In this respect, various semiconductors, metal-incorporated zeolites, and metal complexes have been investigated for CO₂ photoreduction [9–11], but the molecular systems are mostly limited to expensive noble metal catalysts [12]. TiO₂-based photocatalysts have been widely investigated due to their stability and availability at low cost [13–15]. However, their efficiency for CO₂ photoreduction is not satisfactory, due to the weak CO₂ adsorption on the catalyst surface. Furthermore, most of the investigated photocatalysts are active only in the UV region [15]. It is desirable to develop highly efficient photocatalytic materials that can reduce CO₂ under visible light, which still remains a remarkable challenge to this field of research.

Metal–organic frameworks (MOFs) as a new class of hybrid materials, which is assembled by two main inorganic components (metal ions or clusters) and organic linkers, have attracted tremendous attention because of their unique properties such as large surface area, tunable porous structure and tailorable chemistry [15, 16]. These properties make MOFs very promising for a variety of applications, including gas storage [17, 18], chemical separation [19, 20], catalysis [21–23], sensing [24], and drug delivery [25]. Recently, MOFs provide

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a unique opportunity for integrating different molecular functional components to achieve light-harvesting and emerging as a new type of promising photocatalysts [26]. The progress of MOFs as photocatalysts for CO₂ reduction was fast in these recent years. Fu et al. [27] synthesized NH₂-MIL-125(Ti) using 2-aminoterephthalate (H₂ATA) as a linker and applied it as a photocatalyst for CO₂ reduction in the presence of triethanolamine (TEOA) as a sacrificial agent. The obtained results showed that the parent MIL-125 (Ti) was inactive whereas the NH₂-MIL-125 (Ti) demonstrated moderate activity with the 8.14 μmol HCOO[−] under similar conditions. In another study, NH₂-Uio-66(Zr) demonstrated higher photoactivity for CO₂ reduction than previously studied NH₂-MIL-125(Ti) under visible-light irradiation. Furthermore, a mixed NH₂-Uio-66 (Zr) was prepared by mixing ATA and 2,5-diaminoterephthalic acid (H₂DTA) and showed improvement in CO₂ photoreduction, more than 50% higher than over pure NH₂-Uio-66(Zr). This performance improvement is due to the increase in CO₂ adsorption and also light absorption in the visible region [15]. In 2020, Cheng et al. [28] utilized 2,4,6-tris(4-pyridyl) pyridine (tpy) to improve the photocatalytic performance of NH₂-Uio-66. Since tpy has a strong electron-donating ability, the charge can transfer effectively and CO₂-to-CO conversion is greatly improved compared to NH₂-Uio-66. Organic ligands play a crucial role in the MOFs application [29]. Porphyrins are versatile functional molecules in catalysis [30, 31], light-harvesting [32–34] and have been utilized as building blocks for MOFs [35–39]. Porphyrins are assembled in MOFs structure to synthesize supramolecular solids which yield high-performance photoactive materials [29]. Xu et al. [2] utilized photoactive zirconium-porphyrin MOF based on tetrakis (4-carboxyphenyl) porphyrin (TCPP), PCN-222, as a photocatalyst to reduce CO₂ in the presence of TEOA as a sacrificial agent. The results implied that TCPP ligand acts as antenna to absorb visible light and transfer electrons from the excited TCPP linker to the Zr₆ centers which reduce CO₂ to HCOO[−] product. After 10 h illumination, PCN-222 captured and photoreduced CO₂ selectively, 30 μmol HCOO[−]. In another study, TCPP coordinated to Al³⁺ to form MOF and applied as a photocatalyst for CO₂ reduction with triethylamine (TEA). Then, the methanol formation rate from CO₂ (38 ppm h^{−1} g^{−1}_{cat}) was greatly improved by introducing Cu²⁺ to the porphyrin-based MOF structure (260 ppm h^{−1} g^{−1}_{cat}) [40]. It is worthy to note that cobalt oxide and hydroxide are considered as one of the most promising electroactive materials for high-performance electrochemical capacitors [41]. On the other hand, cobalt-based compounds and composites have been widely used as electrocatalysts, secondary batteries and also pseudocapacitors [42]. Furthermore, among all the transition metals such as copper, vanadium and chromium, cobalt is utilized as the most effective dopant to increase the light response and photoactivity of TiO₂ [43]. Also, cobalt has been recognized as an active component for photo/electrochemical

water oxidation [44]. In general, cobalt-based materials have drawn much interest due to their low cost, low toxicity, earth abundance, and notably, conveniently redox transformation between different chemical valence states which leads to high performance with tunable properties [45–47]. Call et al. [47] used [{meso-tetra(4-sulfonatophenyl)porphyrinato}-cobalt (III)], CoTPPS as a catalyst for CO₂ photoreduction in fully aqueous media in the presence of [Ru(bpy)₃]²⁺ as a photosensitizer and ascorbate as a sacrificial agent under visible-light irradiation. To perform the photocatalytic reaction, 0.1 M NaHCO₃ was added to the solution and the obtained results showed 92.6 μmol CO and 19.7 μmol H₂ were produced after 4 h irradiation. On the other hand, Zhang et al. [48] utilized 3D network MOF-525 (Zr₆O₄(OH)₄(TCPP-H₂)₃) to synthesize MOF-525-Co photocatalyst and applied it for CO₂ photoreduction. It is worthy to note that the efficiency of 3D porphyrin-based MOFs is low because of the slow separation of the photo-generated electron–hole pairs [49]. In contrast, 2D MOFs have high exposed active sites and abundant accessible active sites on double sides due to their specific 2D morphology, which are led to increasing interfacial charge transfer and also prolonging the lifetime of the photo-generated electron–hole pairs [50–53].

In the present study, tetrakis (4-carboxyphenyl) porphyrin (TCPP) is applied as a linker and used cobalt as a node to synthesize high selective 2D Co/PMOF. Then, it is used as a photocatalyst for CO₂ reduction into formate (HCOO[−]) under visible-light irradiation in the presence of TEOA as a sacrificial agent. It is expected that the prepared Co/PMOF exhibits high photocatalytic performance and also high selectivity for CO₂ reduction because of the acceleration of the TCPP carboxylate group in ligand-to-metal charge transfer and also the aforementioned properties of the cobalt. The XRD, SEM, EDX, UV–Vis, FTIR and PL were used for characterization of synthesized Co/PMOF. The recycle tests are performed to determine the structural stability and the reusability of the photocatalyst. Finally, the proposed mechanism and the reaction pathway are provided.

2 Experimental

2.1 Materials

Tetrakis (4-carboxyphenyl) porphyrin (TCPP) was purchased from TCI AMERICA. Acetonitrile (MeCN), triethanolamine (TEOA), *N,N*-dimethylformamide (DMF) and Co(NO₃)₂·6H₂O were supplied by Merck. All purchases materials were utilized as received without further purification. The CO₂ gas with ultra-high purity (99%) was used as the feed gas. The deionized water was used to synthesize the catalyst.

2.2 Preparation of catalyst

To prepare Co/PMOF, 0.39 g TCPP was introduced into 0.13 L DMF and the solution was stirred to proceed the reaction for 20 min. Then 2.017 mmol (or 0.6 g) $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to the solution. The solution was stirred for an additional 30 min, thereafter, introduced into a 250 mL Teflon-lined autoclave and heated at 180 °C for 24 h. After cooling to room temperature, the solid was centrifuged and washed with DMF and acetone several times. Eventually, the obtained powder was dried at 60 °C.

2.3 Photocatalyst characterization

Powder XRD patterns were collected on Bruker SMART APEXII X-ray diffractometer equipped with Cu K α radiation source ($\lambda = 1.5418 \text{ \AA}$). Scanning electron microscopy (SEM) images were taken using a JEOL 6360 operated at 15 kV. The elemental composition analysis of the prepared catalyst was performed by energy-dispersive X-ray spectrometer (EDX). The Fourier transform infrared spectroscopy (FTIR) was recorded with an ALPHA (Bruker, Germany) FTIR spectrophotometer. Samples of 1–2 mg were mixed with 100 mg KBr and pressed into translucent disks at room temperature. All spectra were taken in the range 400–4000 cm^{-1} at a resolution of 4 cm^{-1} . N_2 adsorption–desorption isotherms of the prepared photocatalyst were obtained at 77 K using a Quantachrome Autosorb-1 MP analyzer. Before the measurements, the sample was outgassed under vacuum for 6 h at 150 °C. UV–vis spectra were recorded on a Cary 100 Scan UV–Vis spectrophotometer (Varian, USA) at room temperature (23–25 °C). The photoluminescence (PL) spectra of samples were carried out with a JASCO spectrophotometer Model FP-6200 equipped with a thermostat bath, using a 1.0 cm quartz cell. Elemental analyses were carried out on a Perkin-Elmer 2400 element analyzer. Also, the weight percentage of the metal in the photocatalyst was measured by inductively coupled plasma optical emission spectrometry (ICP-OES Optima 5300 DV—Perkin-Elmer).

2.4 Photoreactor system

The photoreaction was performed in a batch outer irradiation-type quartz photoreactor designed by our laboratory, Fig. S1. To keep the solution temperature constant, 30 °C, the photoreactor was equipped with a cooling water recirculation system. Herein, three 125 W high-pressure mercury lamps were utilized as the light source of photoreaction, which are externally arranged around the photoreactor. To filter out UV light, a glass bulb with a special coating was employed (Osram GmbH, Germany), as shown in Fig. S2. 50 mg of the photocatalyst was dispersed in a 60 ml solution that contained MeCN and TEOA (5:1 v/v) and stirred during

the 6 h irradiation by a magnetic stirrer. After that, the photoreactor was sealed and before irradiation, the photocatalyst suspension was degassed by CO_2 for 30 min to completely remove trapped air and dissolved O_2 . The amounts of liquid products were analyzed using an HPLC (Agilent 1200) with Kromasil 5u C18 column. Furthermore, the reaction solution has been examined with a gas chromatography system (Agilent) equipped with a DB-5 column and a flame ionization detector (FID) to detect alcohols. The results showed no signal for alcohols. To detect possible gaseous product (CH_4 , CO), an on-line commercial gas chromatograph GC-CGCA-1 apparatus were applied which is equipped with parallel setup of two packed columns (Molecular sieve and Propak Q). No signal can also be detected for gaseous products.

2.4.1 Results and discussion

XRD analysis was performed to investigate the prepared Co/PMOF crystal structure. As can be seen from Fig. 1, all the main peaks for the as-prepared catalyst are identical to those of the simulated pattern confirming the successful formation of the photocatalyst. Furthermore, similar XRD patterns were obtained for PMOF structures in the previous studies [40, 54, 55], which can be concluded that the photocatalyst has been successfully synthesized. The crystallite size of prepared Co/PMOF calculated from the XRD spectra with Scherrer equation as follows [56, 57]:

$$D = 0.9\lambda / \beta \cos \theta, \quad (1)$$

where D is the mean crystal size of the catalyst, λ is the X-ray wavelength used for the diffraction measurements (1.5418 Å), β is the full width at half maximum (FWHM) of the diffraction peak (radian) and θ is the diffraction angle at the peak maximum. The estimated value is 30.61 nm. Generally, the relatively strong diffraction intensity, Fig. 1, and the obtained crystal size show good crystallinity of Co/PMOF structure. The morphology of the Co/PMOF was analyzed by SEM. As shown in Fig. S3a, the Co/PMOF consists of nanoplates. To confirm the presence of the Co in Co/PMOF structure, the EDX analysis was performed. In Fig. S3b, the EDX pattern indicates a clear signal of the Co which implies Co was successfully incorporated into the Co/PMOF framework. Quantification of the results on the average gives 37.3% C, 5.05% N, 19.23% O, and 38.42% Co (all wt.%). Furthermore, Table 1 shows the composition of Co/PMOF applying elemental analysis and ICP-OES. According to the obtained results, prepared catalyst contains 35.6% C, 4.81% N, 21.13% O, and 38.46% Co (all wt.%). The FTIR spectra of TCPP, Co/PMOF were illustrated in Fig. S4. The FTIR spectrum of TCPP, Fig. S4, demonstrates typical symmetric and asymmetric stretching bands of the pyrrole ring of ν

Fig. 1 XRD pattern of as-prepared Co/PMOF and simulated pattern of Co/PMOF

Table 1 Elemental analysis and ICP-OES (wt.%) of the Co/PMOF

Sample	C	N	O	Co
Co/PMOF	35.6	4.81	21.13	38.46

(N–H), (C–H), (C=C) and (C=N) in the range of the 700–1700 cm^{-1} . The broadband appeared about 3400 cm^{-1} in both structures is assigned to the OH vibration of adsorbed water. The bands appearing at 1650 and 1179 cm^{-1} are assigned to $\nu(\text{C}=\text{O})$ stretch and $\nu(\text{C}-\text{O})$ stretch of the carboxylic acid groups, respectively. The FTIR spectra illustrate band at 1500 cm^{-1} which is due to the $\nu(\text{C}=\text{C})$ stretching vibration in pyrrole ring. Notably, the disappearance of the N–H vibration at 974 cm^{-1} and appearance a new peak at 1007 cm^{-1} resulting from the replacement of hydrogen by metal cation. Furthermore, according to the literatures [58–60], three peaks at 1696, 1623, and 1579 cm^{-1} assigned to the metal-coordinated carboxylate groups in Co/PMOF. Notably, a peak at 1650 cm^{-1} was observed in TCPP, which is assigned to carboxylic stretching band and its intensity is disappeared in Co/PMOF. Generally, the obtained FTIR spectra of Co/PMOF is consistent with previous studies [52, 61–63], which is implied that the MOF structure was successfully. Figure 2 shows the UV–Vis spectra of TCPP and Co/PMOF. A typical strong Soret band with λ_{max} at 420 and 426 nm ($S_0 \rightarrow S_2$ absorption process) is demonstrated for TCPP and Co/PMOF, respectively. Also, four weak split Q bands with λ_{max} at 516, 553, 594 and 650 nm were observed for TCPP. Notably, a slight redshift in the Soret band (from 420 to 426 nm) with two Q bands, 559 and 597 nm, due to the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ transitions, confirms cobalt is successfully inserted in the TCPP structure. The obtained results are consistent with the results of reported works [6, 52, 62, 64–66]. The N_2 adsorption–desorption isotherms measured at liquid nitrogen temperature (77 K) is shown in

Fig. 2 UV–Vis spectra of TCPP, fresh and used Co/PMOF

Fig. S5. Co/PMOF shows a typical II N_2 adsorption isotherm which is observed in nanoporous or macropores materials or open voids [40]. The BET surface area and pore volumes are 957 m^2/g and 0.348 cm^3/g for Co/PMOF, respectively. Also, the average pore diameter of the Co/PMOF is 12.3 Å. On the other hand, the kinetic diameter of the CO_2 is 3.3 Å which is smaller than the average pore diameter of the Co/PMOF. It can be concluded that the CO_2 molecule can diffuse in the porosity of the photocatalyst and the reaction can occur in the porosity besides the surface. Photoluminescence (PL) is a useful approach to study the electron-transfer process [15, 67]. Therefore, the photoluminescence properties of TCPP, Co/PMOF were investigated in the solid-state with an excitation wavelength of 420 nm. The emission peaks are demonstrated in Fig. 3. TCPP and Co/PMOF display an intense emission between 600 and 730 nm. The photoluminescence of Co/PMOF was quenched and implied that the photo-generated charge carriers separate effectively. In other words, the recombination of photo-generated electron–hole pairs is reduced in Co/PMOF compared to the TCPP [59, 68, 69].

Fig. 3 The photoluminescent spectra of TCP and Co/PMOF

Therefore, it can be concluded that the lifetime of photo-generated charge carriers in Co/PMOF is longer than TCP due to the transferring electrons from the excited TCP to the conduction band of metal. A similar electron transfer from the photoexcited organic linker (TCP) to the metal was previously investigated by PL studies [59, 68–70]. This phenomenon can be validated by photoreactor tests indicated in Fig. 4. Also, the proposed mechanism of CO_2 photoreduction over Co/PMOF will be discussed in the following. Photocatalytic reduction of CO_2 over Co/PMOF was performed in MeCN as solvent and TEOA as a sacrificial agent (60 ml, 5:1 v/v) under visible-light irradiation for 6 h, Fig. 4. Remarkably, Co/PMOF demonstrates significant photocatalytic activity toward CO_2 reduction. The HCOO^- was continuously produced with the time of irradiation and finally the amount reached to $23.21 \mu\text{mol}$ in 6 h. Since no other products were formed in both gas and liquid phase, confirming that the Co/PMOF has highly selective toward the CO_2 reduction. The comparison of CO_2 photoreduction over TCP (4.56 $\mu\text{mol HCOO}^-$) and Co/PMOF (23.21 $\mu\text{mol HCOO}^-$) revealed that the photoactivity can be dramatically enhanced by assembling the TCP ligand onto MOFs structure. Generally, the amount of produced HCOO^- over Co/PMOF is much higher than observed values in other studies, Table S1. In addition, blank tests were performed to ensure that the HCOO^- was produced through a photocatalytic reaction rather than photocatalyst organic decomposition, Fig. 4. No HCOO^- was generated while the photoreaction was conducted without either Co/PMOF or TEOA which implies the critical role of photocatalyst and electron donor in the CO_2 photoreduction process. Since no HCOO^- was formed in the dark, concluding that the reaction is photocatalyst. In addition, N_2 was applied as a feed gas instead of CO_2 under otherwise similar reaction conditions. After 6 h photoreaction, no HCOO^- formation was observed which confirms the origin of HCOO^- is not from residual organic components of catalyst and is derived only from CO_2 . All these blank experiments confirm that the photoreaction only

Fig. 4 Amount of the HCOO^- produced as a function of the time of the visible-light irradiation over a Co/PMOF, b TCP, c no Co/PMOF, d no TEOA, and e no CO_2

proceeded when both catalyst and TEOA present with light irradiation. In addition, according to Fig. S6, photocatalytic deactivation was observed after 7 h and the amount of produced HCOO^- reaches 23/99 μmol in 24 h. The deactivation is not clear but the possible explanation for this might be that the active sites on the photocatalyst surface are partially saturated with intermediate product/by product. Notably, further study is required for elucidating the exact nature and causes of these deactivation species. Besides, as shown in Fig. S7, there is no remarkable decrease in the photocatalytic activity even after three cycles, suggesting that the catalyst structure has great performance and stability in recycling tests. In addition, the FTIR, XRD, and UV–vis measurements of before and after three cycles of the reaction were compared together to investigate the stability of the Co/PMOF structure. The results of the UV–vis absorption spectra demonstrated there is no remarkable shift in the UV–vis peaks, confirming the Co/PMOF structure is stable even after three cycles, Fig. 2. As shown in Fig. S4, the diffraction peaks of Co/PMOF at around $1400\text{--}1600 \text{ cm}^{-1}$ were changed. Furthermore, The XRD patterns of fresh and used catalyst show that the intensity of XRD pattern of the used catalyst is approximately reduced, Fig. S8. This result may be explained by the fact that some of the adsorbed species have been adsorbed chemically that remained on the photocatalyst even after washing by methanol and drying under vacuum which can be also the cause of the catalyst deactivation after 7 h, as is shown in Fig. S6. However, it is worthy to note that the changes are not dramatic and the main peaks have been retained which implies the catalyst structure is stable and kept unchanged. Overall, these results indicate that Co/PMOF possesses high durability toward CO_2

photoreduction under visible-light irradiation. According to the previous studies, in the TCPP based MOF photocatalysts, the carboxylate groups in the ligand structure accelerate the ligand-to-metal charge transfer (LMCT). On the other words, it is expected that the formed C-O-metal bond between TCPP and Co play the electron charge transfer channel role and accelerate the electron injection from excited TCPP units to the conduction band of metal nodes in the MOF structure [29, 39, 71–73]. Meanwhile, TCPP ligand behaves as a light-harvesting unit which has been well documented in previous studies [65, 74]. Notably, the photocatalytic properties of porphyrin molecules are significantly controlled and even modified by the presence of the metal cations in the porphyrin ring [75]. Once metal inserted into the porphyrin ring, dissociation of the metal ion is extremely difficult under most reaction conditions and consequently, the catalyst lifetime is prolonged. On the other hand, Co/PMOF has high metal coordination stability because of the chelation effect of the aromatic ligand. Besides, Co/PMOF has occupied cis-coordination sites. This metal coordination mode prevents a variety of possible side reactions related to the cis-coordination, and subsequently leads to a more effective and selective catalytic process [76, 77]. Consequently, it can thus be suggested that under illumination TCPP behaves as an antenna to absorb visible light to its excited state. After that, the CO₂ molecules receive electrons to reduce into HCOO[−] in the presence of TEOA as a hydrogen source. On the other hand, according to the previous studies [2, 48, 78–80], TEOA can be oxidized to its aldehyde form during CO₂ photoreduction process, as shown in Fig. S9. During this process, TEOA acts as an electron donor and furthermore providing a basic environment for accelerating the CO₂ photoreduction process [2, 15]. Also, the expected proposed mechanism is schematically shown in Fig. S10. It is worthy to note that, the presence of a base in the CO₂ reaction system leads to the hydrogenation of CO₂ to formate as mentioned in the prior studies. There are several possible explanations for this result: (1) the OH[−] ions in solution could act as strong hole-scavengers, consequently, the hole-electron pairs recombination is reduced, leading to facilitate the CO₂ photoreduction [81, 82]. Besides, the yields of hydrocarbons could be reduced resulting from the electron competition between H⁺ in the solution and CO₂ reduction (H⁺ + e[−] → H) [83] (2) compared to the acidic solution, CO₂ can be dissolved more and easily in a base solution which would increase yields of hydrocarbons in the photoreduction process [83, 84]. In general, therefore, it seems that an electron (e[−]) and positive hole (h⁺) are formed in the MOF when irradiated with visible light. Then, CO₂ interacts with the excited state of MOF (Co/PMOF*), and •CO₂[−] radicals are formed. During the protonation with the TEOA solution, the •CO₂[−] radicals can react with protons (H⁺) and an electron

to form acid formic. The expected proposed reaction pathway is given as follows [2, 15, 85–87]:

Light absorption by photocatalyst:

Electron transfer to a CO₂ molecule:

3 Conclusion

Photoreduction of CO₂ to useful chemicals (e.g. HCOO[−]) is one of the best solutions for both global warming and energy shortage problems. In this context, porphyrin-based metal–organic framework (Co/PMOF) was synthesized for high selective CO₂ photoreduction under visible-light irradiation in the presence of TEOA as a sacrificial agent. The results showed 23.21 μmol HCOO[−] was produced which shows much better activity than the TCPP ligand alone, 4.56 μmol. The high CO₂ uptake capacity in the PMOF might allow it to interact much better with CO₂ in MeCN, so benefiting its photoconversion. The stability and reusability of the Co/PMOF structure were investigated via recycling tests. The results implied that Co/PMOF has high durability toward the CO₂ photoreduction under visible-light irradiation. Moreover, there is no indicative loss of photocatalytic activity even after three cycles of photoreaction. The present study implies the integration of great properties of porphyrin, light-harvesting, and cobalt that led to high photoactivity and selectivity Co/PMOF. Also, it is expected to open a promising door to apply porphyrin-based MOF structures as a high photoactive and selective photocatalyst to produce liquid fuels.

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Declarations

Conflict of interest There are no conflicts to declare.

References

- Wu, J. C. S. (2009). Photocatalytic reduction of greenhouse gas CO₂ to fuel. *Catalysis Surveys from Asia*, 13(1), 30–40. <https://doi.org/10.1007/s10563-009-9065-9>
- Xu, H.-Q., Hu, J., Wang, D., Li, Z., Zhang, Q., Luo, Y., et al. (2015). Visible-light photoreduction of CO₂ in a metal-organic framework: boosting electron-hole separation via electron trap states. *Journal of the American Chemical Society*, 137(42), 13440–13443. <https://doi.org/10.1021/jacs.5b08773>
- White, C. M., Strazisar, B. R., Granite, E. J., Hoffman, J. S., & Pennline, H. W. (2003). Separation and capture of CO₂ from large stationary sources and sequestration in geological formations—coalbeds and deep saline aquifers. *J. Air Waste Manag.*, 53(6), 645–715.
- Setoyama, T. (2014). The contribution of catalysis for the realization of GSC in the twenty-first century. *Catalysis Surveys from Asia*, 18(4), 183–192. <https://doi.org/10.1007/s10563-014-9180-0>
- Li, D., Liu, T., Yan, Z., Zhen, L., Liu, J., Wu, J., et al. (2020). MOF-derived Cu₂O/Cu nanospheres anchored in nitrogen-doped hollow porous carbon framework for increasing the selectivity and activity of electrochemical CO₂-to-formate conversion. *ACS Applied Materials & Interfaces*, 12(6), 7030–7037. <https://doi.org/10.1021/acsaami.9b15685>
- Sadeghi, N., Sharifnia, S., & Sheikh-Arabi, M. (2016). A porphyrin-based metal organic framework for high rate photoreduction of CO₂ to CH₄ in gas phase. *Journal of CO₂ Utilization*, 16, 450–457. <https://doi.org/10.1016/j.jcou.2016.10.006>
- Akhter, P., Hussain, M., Saracco, G., & Russo, N. (2015). Novel nanostructured-TiO₂ materials for the photocatalytic reduction of CO₂ greenhouse gas to hydrocarbons and syngas. *Fuel*, 149, 55–65. <https://doi.org/10.1016/j.fuel.2014.09.079>
- Mateo, D., Asiri, A. M., Albero, J., & García, H. (2018). The mechanism of photocatalytic CO₂ reduction by graphene-supported Cu₂O probed by sacrificial electron donors. *Photochemical & Photobiological Sciences*, 17, 829–834.
- Inoue, T., Fujishima, A., Konishi, S., & Honda, K. (1979). Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders. *Nature*, 277(5698), 637–638. <https://doi.org/10.1038/277637a0>
- Tong, H., Ouyang, S., Bi, Y., Umezawa, N., Oshikiri, M., & Ye, J. (2012). Nano-photocatalytic materials: possibilities and challenges. *Advanced Materials*, 24(2), 229–251.
- Liu, Q., Zhou, Y., Kou, J., Chen, X., Tian, Z., Gao, J., et al. (2010). High-yield synthesis of ultralong and ultrathin Zn₃GeO₄ nanoribbons toward improved photocatalytic reduction of CO₂ into renewable hydrocarbon fuel. *Journal of the American Chemical Society*, 132(41), 14385–14387. <https://doi.org/10.1021/ja1068596>
- Sato, S., Morikawa, T., Kajino, T., & Ishitani, O. (2013). A highly efficient mononuclear iridium complex photocatalyst for CO₂ reduction under visible light. *Angewandte Chemie*, 125(3), 1022–1026.
- Habisreutinger, S. N., Schmidt-Mende, L., & Stolarczyk, J. K. (2013). Photocatalytic Reduction of CO₂ on TiO₂ and Other Semiconductors. *Angewandte Chemie International Edition*, 52(29), 7372–7408. <https://doi.org/10.1002/anie.201207199>
- Dhakshinamoorthy, A., Navalon, S., Corma, A., & Garcia, H. (2012). Photocatalytic CO₂ reduction by TiO₂ and related titanium containing solids. *Energy & Environmental Science*, 5(11), 9217–9233.
- Sun, D., Fu, Y., Liu, W., Ye, L., Wang, D., Yang, L., et al. (2013). Studies on photocatalytic CO₂ reduction over NH₂-UiO-66(Zr) and its derivatives: towards a better understanding of photocatalysis on metal-organic frameworks. *Chemistry—A European Journal*, 19(42), 14279–14285. <https://doi.org/10.1002/chem.201301728>
- Li, S.-L., & Xu, Q. (2013). Metal-organic frameworks as platforms for clean energy. *Energy & Environmental Science*, 6(6), 1656–1683. <https://doi.org/10.1039/c3ee40507a>
- Shimomura, S., Higuchi, M., Matsuda, R., Yoneda, K., Hijikata, Y., Kubota, Y., et al. (2010). Selective sorption of oxygen and nitric oxide by an electron-donating flexible porous coordination polymer. *Nature Chemistry*, 2(8), 633–637.
- Rowsell, J. L. C., & Yaghi, O. M. (2004). Metal-organic frameworks: a new class of porous materials. *Microporous and Mesoporous Materials*, 73(1–2), 3–14. <https://doi.org/10.1016/j.micromeso.2004.03.034>
- Bastin, L., B́arcia, P. S., Hurtado, E. J., Silva, J. A. C., Rodrigues, A. E., & Chen, B. (2008). A microporous metal-organic framework for separation of CO₂/N₂ and CO₂/CH₄ by fixed-bed adsorption. *Journal of Physical Chemistry C*, 112(5), 1575–1581. <https://doi.org/10.1021/jp077618g>
- Li, J.-R., Sculley, J., & Zhou, H.-C. (2012). Metal-organic frameworks for separations. *Chemical Reviews*, 112(2), 869–932. <https://doi.org/10.1021/cr200190s>
- Lei, Z., Xue, Y., Chen, W., Qiu, W., Zhang, Y., Horike, S., et al. (2018). MOFs-based heterogeneous catalysts: new opportunities for energy-related CO₂ conversion. *Advanced Energy Materials*, 8(32), 1801587. <https://doi.org/10.1002/aenm.201801587>
- Kimura, K. W., Fritz, K. E., Kim, J., Suntivich, J., Abruña, H. D., & Hanrath, T. (2018). Controlled selectivity of CO₂ reduction on copper by pulsing the electrochemical potential. *ChemSuschem*, 11(11), 1781–1786.
- Lee, J., Farha, O. K., Roberts, J., Scheidt, K. A., Nguyen, S. T., & Hupp, J. T. (2009). Metal-organic framework materials as catalysts. *Chemical Society Reviews*, 38(5), 1450–1459. <https://doi.org/10.1039/b807080f>
- Zhang, H., Li, J., Xi, S., Du, Y., Hai, X., Wang, J., et al. (2019). A graphene-supported single-atom FeN₅ catalytic site for efficient electrochemical CO₂ reduction. *Angewandte Chemie*, 131(42), 15013–15018.
- Taylor-Pashow, K. M. L., Rocca, J. D., Xie, Z., Tran, S., & Lin, W. (2009). Postsynthetic modifications of iron-carboxylate nanoscale metal-organic frameworks for imaging and drug delivery. *Journal of the American Chemical Society*, 131(40), 14261–14263. <https://doi.org/10.1021/ja906198y>
- Wang, J.-L., Wang, C., & Lin, W. (2012). Metal-organic frameworks for light harvesting and photocatalysis. *ACS Catalysis*, 2(12), 2630–2640. <https://doi.org/10.1021/cs3005874>
- Fu, Y., Sun, D., Chen, Y., Huang, R., Ding, Z., Fu, X., et al. (2012). An amine-functionalized titanium metal-organic framework photocatalyst with visible-light-induced activity for CO₂ reduction. *Angewandte Chemie International Edition*, 51(14), 3364–3367. <https://doi.org/10.1002/anie.201108357>
- Cheng, X., Zhang, J., Tan, X., Zheng, L., Tan, D., Liu, L., et al. (2020). Improved photocatalytic performance of metal-organic frameworks for CO₂ conversion by ligand modification. *Chemical Communications*, 56(55), 7637–7640. <https://doi.org/10.1039/d0cc02707c>
- Rahimi, R., Shariatnia, S., Zargari, S., Yaghoubi Berijani, M., Ghaffarinejad, A., & Shojai, Z. S. (2015). Synthesis, characterization, and photocurrent generation of a new nanocomposite based Cu-TCPP MOF and ZnO nanorod. *RSC Advance*, 5(58), 46624–46631. <https://doi.org/10.1039/c5ra02882e>
- Sharghi, H., Beyzavi, M. H., & Doroodmand, M. M. (2008). Reusable porphyrinatoiron(III) complex supported on activated silica as an efficient heterogeneous catalyst for a facile, one-pot, selective synthesis of 2-arylbenzimidazole derivatives in the presence of atmospheric air as a “green” oxidant at

- ambient temperature. *European Journal of Organic Chemistry*, 2008(24), 4126–4138. <https://doi.org/10.1002/ejoc.200800351>
31. Shinokubo, H., & Osuka, A. (2009). Marriage of porphyrin chemistry with metal-catalysed reactions. *Chemical Communications*, 9, 1011–1021. <https://doi.org/10.1039/b817941g>
 32. Harriman, A. (1981). Luminescence of porphyrins and metalloporphyrins. Part —Copper(II), chromium(III), manganese(III), iron(II) and iron(III) porphyrins. *Journal of the Chemical Society, Faraday Transactions*, 77(2), 369–377. <https://doi.org/10.1039/f19817700369>
 33. Harriman, A., Porter, G., & Richoux, M.-C. (1981). Photosensitized reduction of water to hydrogen using water-soluble zinc porphyrins. *Journal of the Chemical Society, Faraday Transactions*, 77(5), 833–844. <https://doi.org/10.1039/f29817700833>
 34. Knoer, G., & Vogler, A. (1994). Photochemistry and photophysics of antimony(III) hyper porphyrins: activation of dioxygen induced by a reactive sp excited state. *Inorganic Chemistry*, 33(2), 314–318. <https://doi.org/10.1021/ic00080a021>
 35. Burnett, B. J., Barron, P. M., Hu, C., & Choe, W. (2011). Stepwise synthesis of metal-organic frameworks: replacement of structural organic linkers. *Journal of the American Chemical Society*, 133(26), 9984–9987. <https://doi.org/10.1021/ja201911v>
 36. Lipstman, S., & Goldberg, I. (2010). New cyclic tetrameric and square-grid polymeric modes of supramolecular self-assembly of zinc tetra(4-pyridyl)porphyrin. *CrystEngComm*, 12(1), 52–54. <https://doi.org/10.1039/b914799c>
 37. Barron, P. M., Wray, C. A., Hu, C., Guo, Z., & Choe, W. (2010). A Bioinspired synthetic approach for building metal-organic frameworks with accessible metal centers. *Inorganic Chemistry*, 49(22), 10217–10219. <https://doi.org/10.1021/ic101459j>
 38. Chung, H., Barron, P. M., Novotny, R. W., Son, H.-T., Hu, C., & Choe, W. (2009). Structural variation in porphyrin pillared homologous series: influence of distinct coordination centers for pillars on framework topology. *Crystal Growth & Design*, 9(7), 3327–3332. <https://doi.org/10.1021/cg900220g>
 39. Sadeghi, N., Sharifnia, S., & Do, T.-O. (2018). Enhanced CO₂ photoreduction by a graphene-porphyrin metal-organic framework under visible light irradiation. *Journal of Materials Chemistry A*. <https://doi.org/10.1039/c8ta07158f>
 40. Liu, Y., Yang, Y., Sun, Q., Wang, Z., Huang, B., Dai, Y., et al. (2013). Chemical adsorption enhanced CO₂ capture and photoreduction over a copper porphyrin based metal organic framework. *ACS Appl. Mater. Inter.*, 5(15), 7654–7658. <https://doi.org/10.1021/am4019675>
 41. Sulciute, A., Baltrusaitis, J., & Valatka, E. (2015). Structure, morphology and electrochemical properties of zinc-cobalt oxide films on AISI 304 type steel. *Journal of Applied Electrochemistry*, 45(5), 405–417.
 42. Lee, K. K., Chin, W. S., & Sow, C. H. (2014). Cobalt-based compounds and composites as electrode materials for high-performance electrochemical capacitors. *Journal of Materials Chemistry A*, 2(41), 17212–17248.
 43. Jiang, P., Xiang, W., Kuang, J., Liu, W., & Cao, W. (2015). Effect of cobalt doping on the electronic, optical and photocatalytic properties of TiO₂. *Solid State Sciences*, 46, 27–32. <https://doi.org/10.1016/j.solidstatesciences.2015.05.007>
 44. Zhang, G., Huang, C., & Wang, X. (2015). Dispersing molecular cobalt in graphitic carbon nitride frameworks for photocatalytic water oxidation. *Small (Weinheim an der Bergstrasse, Germany)*, 11(9–10), 1215–1221. <https://doi.org/10.1002/smll.201402636>
 45. Kanan, M. W., & Nocera, D. G. (2008). In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and CO₂. *Science*, 321(5892), 1072–1075. <https://doi.org/10.1126/science.1162018>
 46. Zhang, J., Grzelczak, M., Hou, Y., Maeda, K., Domen, K., Fu, X., et al. (2012). Photocatalytic oxidation of water by polymeric carbon nitride nanohybrids made of sustainable elements. *Chemical Science*, 3(2), 443–446. <https://doi.org/10.1039/c1sc00644d>
 47. Call, A., Cibian, M., Yamamoto, K., Nakazono, T., Yamauchi, K., & Sakai, K. (2019). Highly efficient and selective photocatalytic CO₂ reduction to CO in water by a cobalt porphyrin molecular catalyst. *ACS Catalysis*, 9(6), 4867–4874. <https://doi.org/10.1021/acscatal.8b04975>
 48. Zhang, H., Wei, J., Dong, J., Liu, G., Shi, L., An, P., et al. (2016). Efficient visible-light-driven carbon dioxide reduction by a single-atom implanted metal-organic framework. *Angewandte Chemie*, 128(46), 14522–14526.
 49. Wang, C., Liu, X.-M., Zhang, M., Geng, Y., Zhao, L., Li, Y.-G., et al. (2019). Two-dimensional cobaltporphyrin-based cobalt-organic framework as an efficient photocatalyst for CO₂ reduction reaction: a computational study. *ACS Sustainable Chemistry & Engineering*, 7(16), 14102–14110. <https://doi.org/10.1021/acssuschemeng.9b02699>
 50. Cao, F., Zhao, M., Yu, Y., Chen, B., Huang, Y., Yang, J., et al. (2016). Synthesis of two-dimensional CoS_{1.097}/nitrogen-doped carbon nanocomposites using metal-organic framework nanosheets as precursors for supercapacitor application. *Journal of the American Chemical Society*, 138(22), 6924–6927.
 51. Zhao, W., Peng, J., Wang, W., Liu, S., Zhao, Q., & Huang, W. (2018). Ultrathin two-dimensional metal-organic framework nanosheets for functional electronic devices. *Coordination Chemistry Reviews*, 377, 44–63. <https://doi.org/10.1016/j.ccr.2018.08.023>
 52. Zhao, M., Wang, Y., Ma, Q., Huang, Y., Zhang, X., Ping, J., et al. (2015). Ultrathin 2D metal-organic framework nanosheets. *Advanced Materials*, 27(45), 7372–7378. <https://doi.org/10.1002/adma.201503648>
 53. Cheng, J., Chen, S., Chen, D., Dong, L., Wang, J., Zhang, T., et al. (2018). Editable asymmetric all-solid-state supercapacitors based on high-strength, flexible, and programmable 2D-metal-organic framework/reduced graphene oxide self-assembled papers. *J. Mater. Chem. A*, 6(41), 20254–20266. <https://doi.org/10.1039/c8ta06785f>
 54. Hamad, S., Hernandez, N. C., Aziz, A., Ruiz-Salvador, A. R., Calero, S., & Grau-Crespo, R. (2015). Electronic structure of porphyrin-based metal-organic frameworks and their suitability for solar fuel production photocatalysis. *Journal of Materials Chemistry A*, 3(46), 23458–23465. <https://doi.org/10.1039/C5TA06982C>
 55. Cichocka, M. O., Liang, Z., Feng, D., Back, S., Siahrostami, S., Wang, X., et al. (2020). A porphyrinic zirconium metal-organic framework for oxygen reduction reaction: tailoring the spacing between active-sites through chain-based inorganic building units. *Journal of the American Chemical Society*, 142(36), 15386–15395.
 56. Hossein Habibi, M., Nasr-Esfahani, M., Emtiazi, G., & Hosseinkhani, B. (2010). Nanostructure thin films of titanium dioxide coated on glass and its anti UV effect for living organisms. *Current Nanoscience*, 6(3), 324–329. <https://doi.org/10.2174/157341310791171180>
 57. Ahmad Beigi, A., Fatemi, S., & Salehi, Z. (2014). Synthesis of nanocomposite CdS/TiO₂ and investigation of its photocatalytic activity for CO₂ reduction to CO and CH₄ under visible light irradiation. *Journal of CO₂ Utilization*, 7, 23–29. <https://doi.org/10.1016/j.jcou.2014.06.003>
 58. Sohrabi, S., Dehghanpour, S., & Ghalkhani, M. (2018). A cobalt porphyrin-based metal organic framework/multi-walled carbon nanotube composite electrocatalyst for oxygen reduction and evolution reactions. *Journal of Materials Science*, 53(5), 3624–3639. <https://doi.org/10.1007/s10853-017-1768-0>

59. Wang, X., Zhang, X., Zhou, W., Liu, L., Ye, J., & Wang, D. (2019). An ultrathin porphyrin-based metal-organic framework for efficient photocatalytic hydrogen evolution under visible light. *Nano Energy*, 62, 250–258. <https://doi.org/10.1016/j.nanoen.2019.05.023>
60. Wang, P., Wu, Y.-Y., Wu, J., Wang, S., Yu, L., Zhu, Q.-Y., et al. (2013). Perylene carboxylate-modified titanium–oxide gel, a functional material with photoswitchable fluorescence properties. *Journal of Materials Chemistry C*, 1(47), 7973–7978. <https://doi.org/10.1039/c3tc31607f>
61. Dong, B.-X., Qian, S.-L., Bu, F.-Y., Wu, Y.-C., Feng, L.-G., Teng, Y.-L., et al. (2018). Electrochemical reduction of CO₂ to CO by a heterogeneous catalyst of Fe–porphyrin-based metal-organic framework. *ACS Applied Energy Materials*, 1(9), 4662–4669. <https://doi.org/10.1021/acsaem.8b00797>
62. Zheng, C., Qiu, X., Han, J., Wu, Y., & Liu, S. (2019). Zero-dimensional-g-CNQD-coordinated two-dimensional porphyrin MOF hybrids for boosting photocatalytic CO₂ reduction. *ACS Applied Materials & Interfaces*, 11(45), 42243–42249. <https://doi.org/10.1021/acsami.9b15306>
63. Wang, Y.-R., Huang, Q., He, C.-T., Chen, Y., Liu, J., Shen, F.-C., et al. (2018). Oriented electron transmission in polyoxometalate-metalloporphyrin organic framework for highly selective electroreduction of CO₂. *Nature Communications*, 9(1), 1–8.
64. Yuan, Y.-J., Tu, J.-R., Ye, Z.-J., Lu, H.-W., Ji, Z.-G., Hu, B., et al. (2015). Visible-light-driven hydrogen production from water in a noble-metal-free system catalyzed by zinc porphyrin sensitized MoS₂/ZnO. *Dyes and Pigments*, 123, 285–292. <https://doi.org/10.1016/j.dyepig.2015.08.014>
65. Fateeva, A., Chater, P. A., Ireland, C. P., Tahir, A. A., Khimyak, Y. Z., Wiper, P. V., et al. (2012). A water-stable porphyrin-based metal-organic framework active for visible-light photocatalysis. *Angewandte Chemie International Edition*, 51(30), 7440–7444. <https://doi.org/10.1002/anie.201202471>
66. Zhao, Y., Cai, X., Zhang, Y., Chen, C., Wang, J., & Pei, R. (2019). Porphyrin-based metal–organic frameworks: protonation induced Q band absorption. *Nanoscale*, 11(25), 12250–12258. <https://doi.org/10.1039/c9nr02463h>
67. Hou, J., Cao, S., Wu, Y., Liang, F., Ye, L., Lin, Z., et al. (2016). Perovskite-based nanocubes with simultaneously improved visible-light absorption and charge separation enabling efficient photocatalytic CO₂ reduction. *Nano Energy*, 30, 59–68. <https://doi.org/10.1016/j.nanoen.2016.09.033>
68. Liu, J., Fan, Y.-Z., Li, X., Wei, Z., Xu, Y.-W., Zhang, L., et al. (2018). A porous rhodium(III)-porphyrin metal-organic framework as an efficient and selective photocatalyst for CO₂ reduction. *Applied Catalysis, B: Environmental*, 231, 173–181. <https://doi.org/10.1016/j.apcatb.2018.02.055>
69. Ye, L., Gao, Y., Cao, S., Chen, H., Yao, Y., Hou, J., et al. (2018). Assembly of highly efficient photocatalytic CO₂ conversion systems with ultrathin two-dimensional metal–organic framework nanosheets. *Applied Catalysis, B: Environmental*, 227, 54–60. <https://doi.org/10.1016/j.apcatb.2018.01.028>
70. Shaikh, S. M., Chakraborty, A., Alatis, J., Cai, M., Danilov, E., & Morris, A. J. (2019). Light harvesting and energy transfer in a porphyrin-based metal organic framework. *Faraday Discussion*, 216, 174–190. <https://doi.org/10.1039/c8fd00194d>
71. Rahimi, R., Moghaddas, M. M., & Zargari, S. (2013). Investigation of the anchoring silane coupling reagent effect in porphyrin sensitized mesoporous V-TiO₂ on the photodegradation efficiency of methyl orange under visible light irradiation. *Journal of Sol-Gel Science and Technology*, 65(3), 420–429.
72. Abe, R., Hara, K., Sayama, K., Domen, K., & Arakawa, H. (2000). Steady hydrogen evolution from water on Eosin Y-fixed TiO₂ photocatalyst using a silane-coupling reagent under visible light irradiation. *Journal of Photochemistry and Photobiology A*, 137(1), 63–69.
73. Bae, E., & Choi, W. (2006). Effect of the anchoring group (carboxylate vs phosphonate) in Ru-complex-sensitized TiO₂ on hydrogen production under visible light. *The Journal of Physical Chemistry B*, 110(30), 14792–14799.
74. Johnson, J. A., Zhang, X., Reeson, T. C., Chen, Y.-S., & Zhang, J. (2014). Facile control of the charge density and photocatalytic activity of an anionic indium porphyrin framework via in situ metalation. *Journal of the American Chemical Society*, 136(45), 15881–15884. <https://doi.org/10.1021/ja5092672>
75. Allison, J. B., & Becker, R. S. (1960). Effect of metal atom perturbations on the luminescent spectra of porphyrins. *The Journal of Chemical Physics*, 32(5), 1410–1417.
76. Fidalgo-Marijuan, A., Barandika, G., Bazán, B., Urriaga, M.-K., & Arriortua, M. I. (2013). Thermal stability and crystallochemical analysis for CoII-based coordination polymers with TPP and TPPS porphyrins. *CrystEngComm*, 15(20), 4181–4188. <https://doi.org/10.1039/c3ce40161h>
77. Lu, H., & Zhang, X. P. (2011). Catalytic C–H functionalization by metalloporphyrins: recent developments and future directions. *Chemical Society Reviews*, 40(4), 1899–1909. <https://doi.org/10.1039/c0cs00070a>
78. Yan, Z.-H., Du, M.-H., Liu, J., Jin, S., Wang, C., Zhuang, G.-L., et al. (2018). Photo-generated dinuclear {Eu(II)}₂ active sites for selective CO₂ reduction in a photosensitizing metal-organic framework. *Nature Communication*, 9(1), 3353. <https://doi.org/10.1038/s41467-018-05659-7>
79. Qin, J., Wang, S., Ren, H., Hou, Y., & Wang, X. (2015). Photocatalytic reduction of CO₂ by graphitic carbon nitride polymers derived from urea and barbituric acid. *Applied Catalysis, B: Environmental*, 179, 1–8. <https://doi.org/10.1016/j.apcatb.2015.05.005>
80. Nai, J., Wang, S., & Lou, X. W. (2019). Ordered colloidal clusters constructed by nanocrystals with valence for efficient CO₂ photoreduction. *Science Advance*. <https://doi.org/10.1126/sciadv.aax5095>
81. Xia, X.-H., Jia, Z.-J., Yu, Y., Liang, Y., Wang, Z., & Ma, L.-L. (2007). Preparation of multi-walled carbon nanotube supported TiO₂ and its photocatalytic activity in the reduction of CO₂ with H₂O. *Carbon*, 45(4), 717–721.
82. Indrakanti, V. P., Kubicki, J. D., & Schobert, H. H. (2009). Photoinduced activation of CO₂ on Ti-based heterogeneous catalysts: Current state, chemical physics-based insights and outlook. *Energy & Environmental Science*, 2(7), 745–758.
83. Asi, M. A., He, C., Su, M., Xia, D., Lin, L., Deng, H., et al. (2011). Photocatalytic reduction of CO₂ to hydrocarbons using AgBr/TiO₂ nanocomposites under visible light. *Catalysis Today*, 175(1), 256–263.
84. Tseng, I.-H., Chang, W.-C., & Wu, J. C. (2002). Photoreduction of CO₂ using sol–gel derived titania and titania-supported copper catalysts. *Applied Catalysis, B: Environmental*, 37(1), 37–48.
85. Kaneco, S., Kurimoto, H., Shimizu, Y., Ohta, K., & Mizuno, T. (1999). Photocatalytic reduction of CO₂ using TiO₂ powders in supercritical fluid CO₂. *Energy*, 24(1), 21–30.
86. Izumi, Y. (2017). Recent advances in the photocatalytic conversion of carbon dioxide to fuels with water and/or hydrogen using solar energy and beyond. *Coordination Chemistry Reviews*, 257(1), 171–186. <https://doi.org/10.1016/j.ccr.2012.04.018>
87. Wang, D., Huang, R., Liu, W., Sun, D., & Li, Z. (2014). Fe-based MOFs for photocatalytic CO₂ reduction: role of coordination unsaturated sites and dual excitation pathways. *ACS Catalysis*, 4(12), 4254–4260. <https://doi.org/10.1021/cs501169t>