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
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A Mixed-Metal Porphyrinic Framework Promoting Gas-Phase CO_2 Photoreduction without Organic Sacrificial Agents

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A photoactive porphyrinic metal–organic framework (MOF) has been prepared by exchanging Ti into a Zr-based MOF precursor. The resultant mixed-metal Ti/Zr porphyrinic MOF demonstrates much-improved efficiency for gas-phase CO_2 photoreduction into CH_4 and CO under visible-light irradiation using water vapor compared to the parent Zr-MOF. Insightful studies have been conducted to probe the photocatalysis processes. This work provides the first example of gas-phase CO_2 photo-reduction into methane without organic sacrificial agents on a MOF platform, thereby paving an avenue for developing MOF-based photocatalysts for application in CO_2 photoreduction and other types of photoreactions.

Carbon dioxide, a primary greenhouse gas, can serve as an abundant and promising C1 building block molecule for a variety of organic reactions.[1] The naturally occurring photosynthesis process is the best example to harness CO_2 from the atmosphere as a C1 source and to utilize solar energy to convert CO_2 and H_2O into carbohydrates and O_2. Inspired by this metabolic process, numerous research efforts have been dedicated to replicating the natural process of photosynthesis using synthetic systems under ambient conditions.[2] These artificial photosynthetic systems thus are expected to produce value-added chemical fuels to replace dwindling fossil fuel reserves while reducing the CO_2 concentration in the atmosphere to mitigate climate change issues. However, the conventional photoactive systems (e.g. TiO_2) typically lack either a suitable band gap to absorb a broad section of the solar spectrum or the appropriate conduction and valence band potentials (band edges) for CO_2 reduction, thereby limiting their efficiencies.[3] Thus, strategies to tailor photocatalysts (e.g. TiO_2) for visible light absorption are critical to advance CO_2 reduction efficiency.[4]

The emerged metal–organic frameworks (MOFs),[5] featuring structural designability and tunability, have been extensively explored for applications in gas storage/separation,[6] catalysis,[7] and many more areas.[8] Recent studies have demonstrated the possibility of utilizing MOFs as photocatalysts for CO_2 conversion in liquid phase (e.g. water or organic solvents) reactions.[9] Furthermore, these liquid phase reactions often require organic sacrificial agents, such as triethanolamine and triethylamine, making CO_2 reduction process costly.[10] The gas-phase CO_2 photoreduction using water vapor as the sacrificial agent remains promising but challenging, while the reaction medium affects the reaction pathway and selectivity.[11] Employing designer MOFs as photocatalysts has been rarely investigated in gas-phase CO_2 photoreduction. Herein, we report that a MOF photocatalyst enables gas-phase CO_2 photoreduction into CH_4 and CO under visible-light irradiation in presence of water vapor without using any sacrificial agents.

A highly desired photocatalytic system needs to address the aforementioned critical issues: 1) appropriate band gap to absorb visible light; 2) using water, instead of organic sacrificial agents, as electron donor. To illustrate the proof-of-concept, we choose a porphyrin-based MOF as the photocatalyst for gas-phase CO_2 reduction. The proposed photoactive MOF uses a porphyrinic ligand as a visible light harvesting antenna and metal-containing nodes or cluster as the catalytically active sites for CO_2 reduction. Meanwhile, inspired by the well-established

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studies of TiO_2 as photocatalysts for CO_2 reduction,[12] incorporation of active TiO_2 sites can be envisioned by post-synthetic metal metathesis with Ti species.

Considering its well-known remarkable water/chemical stability, the zirconium-based MOF-525 (denoted as Zr-MOF-525)[13] was chosen in this work, which is composed of tetrakis (4-carboxyphenyl)porphyrin (H_4TCPP) linkers and zirconium-containing units of $Zr_6O_4(OH)_4$ shown in Figure 1. The desired photoactive catalyst was synthesized by a metal metathesis procedure to replace Zr with Ti in the precursor Zr-MOF-525,[14] resulting into a mix-metal structural isomer denoted as Ti/Zr-MOF-525. The Ti/Zr atomic ratio in Ti/Zr-MOF-525 is 9:1 (see the Supporting Information, Table S1), measured by energy-dispersive X-ray spectroscopy (EDS) and inductively coupled plasma optical emission spectrometry (ICP-OES). Powder X-ray diffraction (PXRD) analysis (Figure S1) confirms that Ti/Zr-MOF-525 retains its structural integrity after metal ion exchange, in good agreement with the calculated PXRD patterns of Zr-MOF-525. N_2 adsorption studies at 77 K on the activated materials (Figure S2) show that both Zr-MOF-525 and Ti/Zr-MOF-525 are highly porous with Brunauer–Emmett–Teller (Langmuir) surface areas of 2492 (3134) $m^2 \cdot g^{-1}$ and 2780 (4202) $m^2 \cdot g^{-1}$, respectively, which are comparable to the reported value of MOF-525.[13]

CO_2 photoreduction experiments were carried out in a home-made batch reactor loaded with water vapor under irradiation using a 150 W Xenon lamp with a visible light long pass filter ($\lambda > 400$ nm). The CO_2 photoreduction results of Zr-

MOF-525 and Ti/Zr-MOF-525 with the generation of CH_4 and CO are shown in Figure 2a and 2b, respectively.

Background experiments (Table S2) include a blank run of Ti/Zr-MOF-525 with only N_2 and H_2O vapor under irradiation, a control run of Ti/Zr-MOF-525 with CO_2 and H_2O under dark conditions, a control experiment of Ti/Zr-MOF-525 with dry CO_2 under irradiation, and a test run of free base porphyrin (H_4TCPP) under the CO_2 photoreduction conditions. No formation of CO or CH_4 was observed for these control experiments, which validates our observed CO and CH_4 formation using Ti/Zr-MOF-525 during CO_2 photoreduction experiments. The reactivity of TiO_2-P25 was also included for comparison due to its wide use as photocatalyst for CO_2 reduction with H_2O. Negligible production of CH_4 occurred over TiO_2-P25. This lack of reactivity was attributed to the large band gap (3.1 eV) of TiO_2-P25.[15] In the initial half hour, the production rate of Ti/Zr-MOF-525 is 1.52 ± 0.23 $\mu mol \cdot h^{-1} \cdot g^{-1}$ CH_4 (2865 ± 427 $ppm \cdot h^{-1} \cdot g^{-1}$) and 0.50 ± 0.17 $\mu mol \cdot h^{-1} \cdot g^{-1}$ CO (947 ± 319 $ppm \cdot h^{-1} \cdot g^{-1}$), meaning a high reduction selectivity toward CH_4 over CO. After six hours under visible-light irradiation, the overall production of CH_4 and CO by Ti/Zr-MOF-525 showed 2.14 ± 0.09 $\mu mol \cdot g^{-1}$ (4042 ± 170 $ppm \cdot g^{-1}$) of CH_4 and 0.79 ± 0.05 $\mu mol \cdot g^{-1}$ (1492 ± 89 $ppm \cdot g^{-1}$) of CO. Meanwhile, a significant amount of O_2 relative to CH_4 and CO was observed during the CO_2 photoreduction process by GC-MS (Figure S3). In contrast, Zr-MOF-525 yielded only 0.116 ± 0.109 $\mu mol \cdot g^{-1}$ (218 ± 205 $ppm \cdot g^{-1}$) of CH_4 and 0.087 ± 0.072 $\mu mol \cdot g^{-1}$ (163 ± 136 $ppm \cdot g^{-1}$) of CO. The overall photocatalytic activity of Ti/Zr-MOF-525 for CH_4 production is ~18 times higher than the parent Zr-MOF-525. Meanwhile, Ti/Zr-MOF-525 also shows much higher selectivity toward CH_4 over CO in comparison with Zr-MOF-525. Since CH_4 is much more energy-valuable than CO, Ti/Zr-MOF-525 presents a beneficial impact forward in the search for better photocatalysts. To track the reaction process, isotope labeled $^{13}CO_2$ was also employed to perform the photoreaction experiments. The signals of $^{13}CH_4$ and ^{13}CO were observed in mass spectrometer (Figure S4), which indicates that the reaction products were generated from $^{13}CO_2$. These results highlight the first example of gas-phase CO_2 photoreduction into high fuel-value compounds under visible-light irradiation without organic sacrificial agents based on a MOF platform. Although the prepared catalyst of Ti/Zr-MOF-525 demonstrates moderate catalytic performance by comparing with previously reported studies (see Table S3 for a comprehensive analysis of CO_2 photoreduction catalysis performances),[16] the strategy of building a photoactive catalyst for selective gaseous CO_2 photoreduction under visible light is beneficial for the development of new catalysts.

Solid-state UV/Vis absorbance studies showed that the optical properties of the two MOFs are highly regulated by their porphyrin ligands (Figure S5). The absorption bands from 400–700 nm implied their ability to absorb light deep in the visible-light wavelength range. Also, observed were the four Q bands from the free-based porphyrin ligands in Zr-MOF-525 and Ti/Zr-MOF-525 at a range from 490–670 nm, which indicate the porphyrin ligand remains nonmetallated during metal metathesis. To estimate the ability of MOF-525 to absorb visible light,
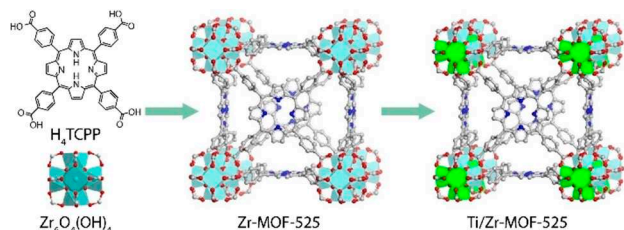

Figure 1. Schematic representation for synthetic processes of a photoactive porphyrin-based MOF, Ti/Zr-MOF-525, which is obtained by metal metathesis with Ti on Zr-MOF-525 assembled by tetrakis(4-carboxyphenyl)porphyrin and $Zr_6O_4(OH)_4$.
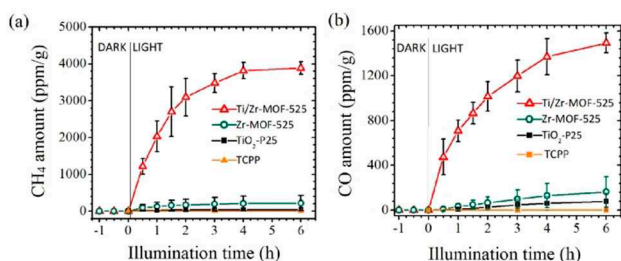

Figure 2. CO_2 photoreduction reactivity of Ti/Zr-MOF-525, Zr-MOF-525, TiO_2-P25, and H_4TCPP: (a) CH_4 and (b) CO production using Zr-MOF-525, Ti/Zr-MOF-525, TiO_2-P25, and H_4TCPP under visible-light illumination ($\lambda > 400$ nm) of a 150 W xenon lamp.

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optical band gaps were calculated from the UV/Vis solid-state absorption spectra of these MOFs by plotting the Kubelka-Munk function versus the energy of incident light in eV (inset of Figure S5). The bandgaps of Zr-MOF-525 and Ti/Zr-MOF-525 are extrapolated to be 1.7 eV (729 nm). The narrow bandgaps in MOFs are influenced strongly by their porphyrinic ligand. In both MOFs, the measured bandgaps (1.7 eV) closely resemble the optical absorbance spectrum of free-base TCPP ligand which has a UV/Vis absorption band (a Q band) at 645 nm or 1.9 eV.[17] The values are red-shifted in respect to the free-base porphyrin ligand, due to the influence from its coordination to metal clusters. This small band gap value thus allows Zr-MOF-525 and Ti/Zr-MOF-525 to be excited in the visible spectrum.

To obtain mechanistic insight into the CO_2 photoreduction process, electron paramagnetic resonance (EPR) spectroscopy was used to probe reactive intermediates. When the pre-activated Ti/Zr-MOF-525 dispersed in water was sealed in a capillary tube, a prominent signal at $g = 1.97$ was observed only after irradiation and assigned to the presence of Ti^{3+} (Figure 3).[18] When air purged into the tube, the Ti^{3+} signal disappeared due to its oxidation back to Ti^{4+}. The EPR spectra were also acquired on the activated Ti/Zr-MOF-525 powder sample with and without irradiation, which demonstrate no generation of Ti^{3+} without H_2O in these two experiments. These results highlight that H_2O plays a critical role of reducing agent to generate Ti^{3+} in the case of Ti/Zr-MOF-525. Another isotope labeled experiment was to employ $H_2^{18}O$ as the reagent for the CO_2 photoreduction experiment. The signal of $^{18}O_2$ ($m/z = 36$;
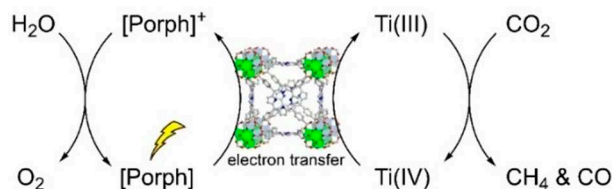
Figure S4f) indicates that H_2O was oxidized into O_2, whereas CO_2 was reduced into CH_4 and CO. In addition, the amount of experimentally observed O_2 is comparable to the amount of O_2 estimated by the amount of the photogenerated CH_4 and CO using reaction stoichiometry (Figure S3). These data confirm that the O_2 is concurrently generated from the oxidation of H_2O vapor while the CO_2 is reduced into CH_4 and CO.

Thus, we propose a tentative mechanism for the Ti-derived porphyrinic MOF catalyzing CO_2 and H_2O conversion into CO and CH_4 (Figure 4). After absorbing visible light, the porphyrinic ligands generate associated excited electrons, which migrate and transfer to the Ti-containing units nearby through an electron transfer process to reduce Ti^{4+} in the Ti–O cluster to Ti^{3+}. This separation process of generated e^-/h^+ pair in MOFs has been proven to benefit the reactivity during photocatalysis.[10e–g,19] Then CO_2 molecules adsorbed in the MOF pores are readily reduced by Ti^{3+} to form adsorbed CO species, which desorb into free CO or further react with more migrated electrons and protons generated from the oxidation of H_2O to form CH_4.[20] Accordingly, the Ti-exchanged MOF has been proven to demonstrate much higher CO_2 affinity than its Zr-based parent MOF.[21] More importantly, in the case of Ti/Zr-MOF-525 each photoactive units containing multiple Ti catalytic centers is connected with twelve TCPP ligands, which is expected to facilitate multiple-electron transfer processes leading to the favored eight-electron reduced product of CH_4. The porphyrinic ligands remain positively charged and oxidize water to generate O_2.[22] Nonetheless, future detailed studies are needed to investigate the mechanism of the CO_2 photoreduction.

In conclusion, our study demonstrates for the first time that the mixed-metal porphyrin-based MOF, prepared by a Ti ion-exchange procedure, is able to selectively reduce CO_2 into CH_4 over CO under visible-light irradiation using water vapor instead of any organic sacrificial agents in the gas phase. Insightful mechanistic studies have been conducted to understand the photocatalysis processes, including EPR, isotopic labeling experiments, and quantitative analysis of O_2 generated from the experiments. Our work opens a new door for developing MOF-based photocatalysts in gas-phase CO_2 reduction without using any organic sacrificial agents. Ongoing work in our laboratory is focused on understanding the mechanism of CO_2 reduction into high-value CH_4 and further improving the efficiency of CO_2 photoreduction catalysts.
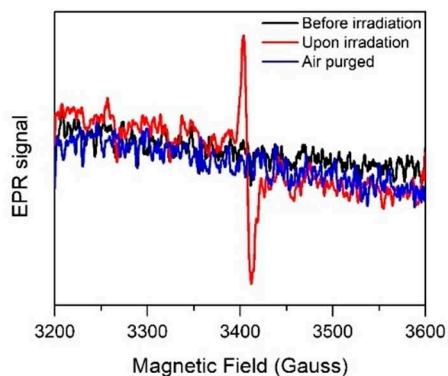

Figure 3. EPR spectra acquired on Ti/Zr-MOF-525 dispersed in H_2O. a prominent signal at $g = 1.97$ was observed only after irradiation and assigned to the presence of Ti^{III}.

Experimental Section

Synthetic procedures

Zr-MOF-525 was prepared using a modified form of the procedure described in the literature.[13] Zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$, 14 mg) was added to N,N-dimethylformamide (DMF, 10 mL) in a 20 mL scintillation vial and sonicated for 15 min. Then, tetrakis(4-carboxylphenyl)porphyrin (H_4TCPP, 29 mg) was added to the solution followed by 10 min of further sonication. Acetic acid (HOAc, 2.5 mL) was added to the solution. The scintillation vial was placed in an oven at 65 °C for 3 days. The dark colored powder was

Figure 4. Proposed mechanism of electron transfer and CO_2 photoreduction processes within Ti/Zr-MOF-525 excited by visible-light illumination based on the observation of Ti^{III} and O_2 generated in the process.

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collected via centrifugation, then washed 5 times with 10 mL of DMF. The DMF solvent was then exchanged 5 times with 30 mL of acetone over three days. The resultant Zr-MOF-525 was activated by heating at 120°C under vacuum for 24 h. The Ti-exchange process of Zr-MOF-525 was carried out according to the work of Cohen and co-workers.[10c] $TiCl_4$ $(THF)_2$ (81 mg, 0.24 mmol) was dissolved in anhydrous DMF (15 mL). Then, the activated Zr-MOF-525 (124 mg) was added. The above steps were finished in a glove box. The mixture was incubated at 85°C in a preheated oven for 5 days. The solids were separated from the solvent via centrifugation and washed with fresh DMF at least 6 times. The washed solids were immersed in methanol for 3 days. The methanol was replaced every 24 h. The solids were activated at 120°C under vacuum overnight.

CO_2 photoreduction experiments

The reaction was carried out in a stainless-steel batch reactor with a quartz window on top. Typically, 50 mg of prepared catalyst was uniformly spread on a 6.5 cm^2 base area of the reactor. Gaseous 99.99% CO_2 was bubbled through distilled water at room temperature before introduction to the reactor. Before the experiment, the reactor was evacuated. Then water saturated CO_2 was flowed through at 2 mL/min for 30 mins to achieve equilibrium before two valves at the inlet and outlet of the reactor were closed for a batch reaction. The reaction was carried out at 20 psi, under irradiation of 150 W Xenon light equipped with a 1.5 AM filter and a visible long pass filter ($\lambda > 400$ nm) for 6 h. The reactor was cooled by flowing water to maintain isothermal reaction temperature at 40°C. Control runs were performed under the following conditions to ensure that the gas products CO and CH_4 are not from non-photo-catalyzed reactions: (1) under dark condition, (2) with N_2 and H_2O vapor under irradiation, (3) control experiments of Ti/Zr-MOF-525 with dry CO_2. To monitor the reaction process, 80 µl gas samples were periodically removed by gastight syringe (Hamilton, 100 µl) for analysis by gas chromatography (GC, Agilent 6970C) with a thermal conductivity detector (TCD), equipped with a HP-Plot column.

Conflict of Interest

The authors declare no conflict of interest.

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