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Encapsulation of cobalt oxide into metal-organic frameworks for an improved photocatalytic CO₂ reduction

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Abstract: The increased emission of CO₂ has negative impacts on environment. Among the strategies, photocatalytic reduction is promising to convert the CO₂ into chemicals. In this report, CoO_x nanoparticles are loaded in the channels of MIL-101(Cr), a kind of metal organic frameworks (MOF), to construct a novel CoO_x/MIL-101(Cr) system to facilitate CO₂ photoreduction. Under the optimal conditions, the CoO_x/MIL-101(Cr) has showed a significantly enhanced performance for photocatalytic CO₂ reduction compared with bare CoO_x and MIL-101(Cr). Our findings provide a pathway for a rational design of efficient MOF system for the photocatalytic reduction of CO₂.

Introduction

The increasing emission of the CO₂ is considered as one of the main factors for global warming, and resulting an irreversible damage of the environment by climate change.^[1] In the past years, numbers of strategies have been developed to reduce the atmospheric concentration of CO₂, and they mainly include physical absorbing CO₂ for storage and chemical conversing CO₂ to other chemicals.^[2] Among them, photocatalytic conversion of CO₂ by primarily sunlight energy is an ideal approach to immobilize and recycle CO2.[3] However, the efficiency is still faraway to the state-of-the-art. This phenomenon can be attributed to a few key factors in photocatalytic system, such as light harvesting, charge separation and catalytic surface reaction.^[4] Among them, catalytic surface-reaction is particularly important for CO₂ reduction reaction because of the chemical inertness of CO₂ with the energy, ca. 750 kJ·mol⁻¹, for the C=O cleavage.^[5] While, most of the photocatalysts present poor capability of physical adsorbing and chemical activate CO₂, therefore a rational design of the co-catalyst for CO₂ reduction reaction has received increasing attention.^[6]

Metal-organic frameworks (MOFs) have emerged as a mediate for the activate CO₂ gas and selective photo-reduce CO₂ gas due to their large capacity and functional tenability of its surface.^[7] As a noble example, MIL-101(Cr) can stably uptake CO₂ gas by dispersion-dominated interaction through delocalize π electrons of the benzene ring for the quadrupole of CO₂ molecules.^[8] Meanwhile, Cr(III) functionalizes as Lewis acid sites that coordinate with CO₂ molecules via O=C=O····Cr³⁺ to active CO₂.^[9] In addition to the surface adsorption and CO₂ activation, reducing the over-potential for the reduction reaction is the subsequent step, and it relies on the activity of the co-catalytic species.^[10]

Cobalt oxide species (CoO_x) is a typical one that has been widely investigated for CO₂ to CO conversion, and its low cost and high stability have generated broad scientific interesting.^[11] It is therefore promising to encapsule CoO_x nanoparticles homogeneously in the channels of the MOF as a co-catalytic system for surface CO₂ reduction reaction, and sufficiently promote the efficiency of photocatalytic CO₂ conversion.^[12]

In this study, MIL-101(Cr) is acquired with encapsulated CoO_x nanoparticles as a co-catalytic system for photocatalytic CO_2 reduction. The chemical absorption of MIL-101(Cr) is investigated, and strong adsorption property is presented to uptake CO_2 . Simultaneously, homogeneously dispersed CoO_x nanoparticles presented an improved performance for photocatalytic CO_2 conversion. As a result, this system presented a significant improvement for photocatalytic CO_2 reduction with respect to the pristine MIL-101(Cr) and CoO_x . Our findings provide pathway for a rational design of an efficient MOF system for the photocatalytic reduction of CO_2 .

Results and Discussion

MIL-101(Cr) was synthesized according to the reported procedures and the CoO_x nanoparticles were loaded by in-situ double solvent method.^[13] By this approach, Co2+ ions were incorporated into the pores of MIL-101(Cr) driving by capillary force. Subsequently, the thermal oxidization was carried out to convert Co^{2+} ions into CoO_x nanoparticle. The crystallinities of the as-prepared samples were characterized by powder X-ray diffraction (PXRD). As shown in Figure 1a, the diffraction patterns of MIL-101(Cr) loading with 1.4 wt% and 2.6 wt% CoO_x were nearly the same as the pure MIL-101(Cr), indicating the crystal structure of MIL-101(Cr) was retained after loading CoO_x. When the concentration of the CoO_{x} becomes 3.9 wt%, the crystallization of MIL-101 (Cr) reduces, which is reflected by the reduced intensities of the PXRD peaks. This phenomenon can be attributed to the formation of disordered crystal structure with increasing the particle size of CoO_x into MIL-101(Cr) channels. The diffraction peaks of MIL-101(Cr) cannot be clearly observed when CoO_x is 4.9 wt%. However, we cannot detect any signal of CoO_x from PXRD. Therefore, X-ray photoelectron spectroscopy (XPS) was further carried out to understand the chemical composition of the samples (Figure S1-S3). The Co 2p spectrum is shown in Figure 2a when 2.6 wt% of CoO_x is loaded into MIL-101(Cr). The CoO_x can be deconvoluted into four peaks,

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corresponding to the mixed divalent and trivalent Co element, $^{[14]}$ indicating it is a mixture of CoO and Co₃O₄ to encapsulate into the MIL-101(Cr).



Figure 1. (a) PXRD patterns of MIL-101(Cr), CoO_x and $CoO_x/MIL-101$ with different loading concentration of the CoO_x . (b) The diameter distribution of the CoO_x in MIL-101(Cr). (c) TEM and (d) HRTEM of 2.6 wt% $CoO_x/MIL-101(Cr)$. (e, f) EDX elemental mapping results of Co.

The samples were studied by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) (Figure S4a and S4b). As shown in Figure 1c, the structure of MIL-101(Cr) can be clearly observed. Figure 1d presents the high-resolution TEM (HR-TEM) image of the compound, in which, CoO_x nanoparticles were found to be homogeneously loaded into the channel of MIL-101(Cr). The particle size of CoO_x obtained from statistical analysis ranges from 1.7 to 3.1 nm (Figure 1b), and a dominant peak locates at 2.3 nm, which is smaller than the pore size of MIL-101(Cr) (2.9 to 3.4 nm).^[15] In addition, the pore windows of MIL-101(Cr) is around 1.2 to 1.6 nm in diameters, and this size is appropriate to diffuse Co2+ into the channel. The energydispersive X-ray spectroscopy (EDX) elemental mapping was further conducted to identify the chemical composition (Figure 1e and 1f), and C, O and Cr can be clearly observed from the EDX (Figure S5). Meanwhile, we can confirm that the CoO_x nanoparticles are homogeneous distributing along the MOF channels.

Photocatalytic CO₂ reduction is conducted subsequently to study the performance of CoO_x/MIL-101(Cr) co-catalytic system by using [Ru(bpy)₃]Cl₂ as photosensitizer. The quantity of the CoO_x that loading in MIL-101(Cr) was studied as shown in Figure 3. The rate of CO evolution was 21.5 µmol·h⁻¹ by loading 1.4 wt% CoO_x in MIL-101(Cr). The performance improves to 28.7 µmol·h⁻¹ for CO production when the loading amount of CoO_x is increased to 2.6 wt%. However, further increasing the loading amount of CoO_x decreases CO evolution rate. It is most likely that high loading content of CoO_x would lead to the aggregation of nanoparticles, which decreased the porosity of support and number of active sites, and thus reduced the CO evolution rate. The observation reveals that it is important to homogeneous distribute CoO_x with trace amount of the quantity to ensure the exposed active site for CO₂ photoreduction.

Table 1. The research of reaction conditions and reference experiments.			
Entry	CO [µmol]	H2 [µmol]	Sel. CO [%] ^[b]
1	28.7	12.1	70.3
2 ^[c]	13.6	6.8	66.7
3 ^[d]	0.7	0.2	77.8
4 ^[e]	n.d.	0.2	-
5 ^[f]	n.d.	21.5	-
6 ^[g]	n.d.	n.d.	-

[a] Reaction conditions: $[Ru(bpy)_3]Cl_2 H_2O$ (10 µmol), CoO_x/MIL-101 (1 mg), solvent (5 mL, acetonitrile:H₂O=3:2), triethanolamine (TEOA, 1 mL), CO₂ (1 atm), λ >420 nm. [b] Sel. CO=mol CO/mol (H₂+CO). [c] Using CoO_x/MIL-101 instead of CoO_x. [d] Using CoO_x/MIL-101 instead of MIL-101. [e] Without using any co-catalyst. [f] Using Ar instead of CO₂. [g] Experiment conducted in dark condition.

We also conducted a series of control experiment as shown in Table 1. Compared with the optimal performance (entry 1, Table 1), it was not able to detect any CO, but trace amount of H₂ was detected in the absence of 2.6 wt% CoOx /MIL-101(Cr) (entry 4, Table 1). When 2.6 wt% CoO_x/MIL-101(Cr) was used, the CO evolution rate decreased to 13.6 µmol·h⁻¹ (entry 2, Table 1). In addition, negligible CO and H₂ were found when MIL-101(Cr) was used (entry 3, Table 1). The results indicate that MIL-101 acts as a mediate to chemisorb CO2 gas for activation, but charge must be injected in CoO_x as active sites for the reduction reaction. We have also conducted the experiment by replacing CO2 gas with Ar gas (entry 5, Table 1), but no CO was detected and only H₂ gas, confirming the produced CO come from induced CO₂ gas, but not by decomposing acetonitrile or other substrates. Without light illumination, neither H₂ nor CO are detected (entry 6, Table 1), and the result also confirm that the reduction reaction is driven by light by photoredox catalysis.



Figure 2. (a) XPS Co 2p spectrum of 2.6 wt% CoO_x/MIL-101(Cr). (b) CO₂ adsorption isotherms (273 K) of MIL-101(Cr) and 2.6 wt% CoO_x/MIL-101(Cr).

The co-catalytic system was studied by the N₂ and CO₂ adsorption-desorption isotherms. The BET surface area of MIL-101(Cr) was 3255 cm³·g⁻¹ (Figure S6 in the Supporting Information), which provides sufficient space to load CoO_x nanoparticles. After loading CoO_x, the BET surface area decreased to 2408 cm³·g⁻¹. In addition, CO₂ absorption was also measured as it is one of the key steps to determine the activity in CO₂ photoreduction reaction. As shown in Figure 2b, the maximum CO₂ uptake of MIL-101(Cr) is 105 cm³·g⁻¹ and 2.6 wt%

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 $CoO_x/MIL-101(Cr)$ is 78 cm³·g⁻¹ at 1 atm and 273 K. This performance is better than many reported materials,^[16] and confirmed the intrinsic properties of MIL-101(Cr) for chemisorb and activate CO_2 gas.^[17]



Figure 3. Productions of CO and H_2 by different amounts of CoO_x loaded into MIL-101(Cr) under visible light illumination.

To understand the working mechanism of this photocatalytic CO2 reduction, cyclic voltammetry (CV) was also acquired. The CV curves of CoO_x, MIL-101(Cr) and 2.6 wt% CoO_x/MIL-101(Cr) in CO₂-saturated MeCN electrolyte were shown in Figure 4a. The CV of CoO_x showed two irreversible reduction peaks at -0.9 V and -1.3 V, which can be assigned to the reduction of Co ions from Co^{III} to Co^{II} and Co^{II} to Co⁰. The third reduction peak after the Co^{II} to Co⁰ was the reduction of CO₂ and located at around -2.0 V. As for the support MIL-101(Cr), its CV curve showed a weak CO2 reduction peak located at the more negative -2.3 V, indicating its weak CO₂ activation and reduction ability. Furthermore, the cocatalyst system 2.6 wt% CoOx/MIL-101(Cr) possessed a CO2 reduction peak at -2.1 V and the catalytic current was much higher than that of the other two samples, which illustrated that overpotential of 2.6 wt% CoO_x/MIL-101(Cr) system is lower than CoO_x. The absence of the first two reduction peaks was due to the very low loading of CoOx. The 2.6 wt% CoOx/MIL-101(Cr) was also performed under Ar conditions as shown in Figure 4b. This observation reveals that the reduction peak is owing to the interaction between CO2 and CoOx/MIL-101(Cr). Electrochemical impedance spectrscopy (EIS) was also acquired for MIL-101(Cr) and 2.6 wt% CoO_x/MIL-101(Cr), as shown in Figure S7. The electron transmission capacity is enhanced after MIL-101 is loaded with CoO_x, indicating the improved intraction between 2.6 wt% CoO_x/MIL-101(Cr) and CO₂, and thus increased performance for photocatalytic CO₂ reduction.

The influences of the reaction conditions on the photocatalytic performance was further studied.^[18] Generally, solvent plays an important role in the reaction, especially when it contains nitrogen or oxygen, it would be favor to interact with CO₂ by Lewis acid-base interactions.^[19] In this study, solvents including MeCN, DMF and THF, were investigated for CO₂ photoreduction reaction as

shown in Figure S8. When aprotic hybrid-atom-containing used, an improved performance for photoreduction of CO₂ can be received. On the contrary, when the reactions were performed in TCM as solvent, only trace amount of CO and H₂ can be observed since this solvent possesses weak chemical affinity toward uptake CO2. The studies demonstrated that selecting appropriate reaction medium is important for photocatalytic CO₂ conversion. The effects of H₂O additive on the catalytic performance were also studied. As listed in Table S1, there is only small amount of CO and H₂ can be received when using pure MeCN as solvent (entry 1, Table S1). Adding H₂O into the reaction solution can significantly improve the photocatalytic activity and the selectivity of CO (entries 2, Table S1). Further increasing volume ratio of MeCN/H₂O to 4/1, the maximum evolution rate of the CO₂ and H₂ were obtained, while the CO selectivity was 54.1%. However, excess H₂O led to decreased evolution rates of CO and H₂ (entries 3, 4 and 5, Table S1). There was no CO but only a small amount H₂ produced when using pure water as solvent (entry 6, Table S1). Therefore, appropriate water is indispensable to promote the performance in this photoreduction system. Water may induce a small amount of dissociation for Ru(bpy)32+ and produced the ligand bpy, which is also benefit for CO2 reduction.[20]



Figure 4. (a) Cyclic voltammograms of CoO_x , MIL-101(Cr) and $CoO_x/MIL-101(Cr)$ in CO_2 atmosphere. (b) Cyclic voltammograms of $CoO_x/MIL-101(Cr)$ in CO_2 and Ar atmosphere.

The temperature is also important to affect the reaction rate. Figure S9 presents the evolution rate of CO and H₂ at different reaction temperatures. The evolution rate of CO and H₂ increases by increasing the reaction temperature from 10°C to 30°C. The increased temperature is favorable to active CO2 and therefore an improved performance. Further increasing the temperature to 50°C led to the reduction of CO yield, which is probability due to the decreased solubility of CO2 in the solvent.^[21] Therefore, the reaction temperature at 30°C is the optimal temperature to balance between CO₂ adsorption and thermodynamic equilibrium. The thermal stability of the 2.6 wt% CoO_x/MIL-101(Cr) was also studied by thermal gravimetric analysis (TGA, Figure 5a). A rapid weight-loss up to 100°C is owing to the leaving of the guest molecules. A weak structure response was observed from 100°C to 270°C, and seriously structural damage was presented up to 350°C. Therefore, the CoO_x/MIL-101(Cr) is stable for the photoreduction reaction. The weight-dependent performance of CoO_x/MIL-101(Cr) was also carried out for the photocatalytic reaction, and the result is shown in Figure S10. The relatively high evolution rate of CO and H₂ were achieved with 0.5 mg of 2.6 wt% CoO_x/MIL-101(Cr). When the amount of 2.6 wt% CoO_x/MIL-101(Cr) increases to 1.0 mg, the maximum production rate of CO

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was obtained with the selective ca. 70.3%. Further increasing the amount to 3.0 mg resulted the increased H₂ evolution rate but decreased the yield of CO₂ reduction and selectively conversion of CO production. Generally, the high amount of the 2.6 wt% CoO_x/MIL-101(Cr) would reduce illumination on the catalyst, and thus a non-liner relationship between the activity and the weight



of the co-catalyst system.

Figure 5. (a) Thermal gravimetrical analysis of the as-prepared 2.6 wt% CoO_x/MIL-101(Cr). (b) Four-hour measurement of 2.6 wt% CoO_x/MIL-101(Cr) for photocatalytic CO2 reduction.

The prolong-time experiment was carried out to verify the stability of 2.6 wt% CoOx/MIL-101(Cr), and the CO and H₂ evolutions of every hour is shown in Figure S11. In the first half hour, the produced CO and H₂ were sharply increased. After that, the evolution rates were gradually decreased. This observation is likely due to the photo-blenching dye of [Ru(bpy)₃]Cl₂.^[22] Therefore, the dye was added every hour for this four-hour experiment. Results are shown in Figure 5b, and in this test, the co-catalyst system is preserved. The production rate of CO was nearly the same as the first hour, suggesting the deactivation was resulted from the photobleaching of [Ru(bpy)₃]Cl₂ rather than the degeneration of CoO_x/MIL-101(Cr). Furthermore, the used sample was characterized by PXRD (Figure S12), Fourier transformed infrared (FTIR, Figure S13), UV-Vis diffuse reflectance spectra (UV-Vis DRS, Figure S14), and XPS Co 2p (Figure S15), C 1s (Figure S16), O 1s (Figure S17) and Cr 2p (Figure S18). Negligible differences are observed from those experiments and confirmed the stability of the 2.6 wt% CoO_x/MIL-101(Cr) for this CO₂ photoreduction reaction.



Figure 6. A plausible mechanism of the CO₂ photoreduction by this system.

The plausible mechanism of the CO₂ photoreduction by this photocatalytic system was illustrated in Figure 6. With pumping CO₂ gas into the system, it could be chemisorbed by the MOF part in CoO_x/MIL-101(Cr). Meanwhile, under light illumination, the photosensitizer, Ru(bpy)32+, is excited to generate electrons by forming Ru(bpy)₃³⁺. Electrons migrate from the excited dye to CoO_x/MIL-101(Cr), and CoO_x in CoO_x/MIL-101(Cr) acts as electron acceptor and meanwhile as active sites to convert the activated CO₂. Finally, TEOA acts as the sacrificial electron donor to quench $Ru(bpy)_3^{3+}$, and re-produce $[Ru(bpy)_3]^{2+}$.

Conclusion

In summary, photocatalytic CO evolution by reduction of CO₂ was achieved using CoO_x/MIL-101(Cr) system with a photosensitizer. The MIL-101(Cr) presented superior capability for CO2 chemisorbing. In addition, we had encapsuled CoOx nanoparticles in the channels of MIL-101(Cr) to reduce the overpotentials of the photoreduction of CO2. As a result, the CoOx/MIL-101(Cr) system had presented an improved performance for photocatalytic CO₂ reduction compared with bare CoO_x and MIL-101(Cr). This work demonstrates the MIL-101(Cr), a chemically stable MOFs, is a promising support to uptake CO₂, and with encapsulation of a proper photocatalyst, the system offers opportunities for CO₂ photocatalytic reduction.^[23]

Experimental Section

Materials. Cr(NO₃)₃·9H₂O, HF, NH₄F, Co(NO₃)₂·6H₂O were purchased from Alfa Aesar. [Ru(bpy)₃]Cl₂·6H₂O was purchased from Tokyo Chemical Industry (TCI, Shanghai). The organic solvents, including acetonitrile, N,Ndimethylformamide, triethanolamine, trichloromethane (TCM) and tetrahydrofuran (THF) were purchased from China Sinopharm Chemical reagent Co., Ltd. All the chemicals were used without further purification.

Synthesis of MIL-101(Cr). Typically, terephthalic acid (1.6 g, 10.0 mmol), Cr(NO₃)₃·9H₂O (4.0 g, 10.0 mmol), HF solution (0.5 mL, 46 wt%) and deionized water (70 mL) were mixed in a 100 mL Teflon-liner autoclave and heated at 220°C for 8 h. After cooling down to the room temperature, the as-prepared solid was separated by filtration and washed with DMF (150 ml) to remove the unreacted chemicals. The powder was further purified by using ethanol at 100°C for 24 h. Ion exchange was carried out by dispersing the solid in 37.5 mmol of NH₄F aqueous solution with stirring at 70°C for 10 h. The green powder was collected by filtration and then washed with hot water (80°C) for several times. The products were dried in vacuum oven. As a result, 1.6 g terephthalic acid and 4.0 g Cr(NO₃)₃·9H₂O yields 0.8 g MIL-101(Cr).

Load CoO_x in MIL-101(Cr). A double solvent approach was used to load Co2+ cations into the channel of MIL-101(Cr). Normally, the as-prepared MIL-101(Cr) (150 mg, 0.13 mmol) was dispersed in 30 mL anhydrous hexane. The solution was sonicated and stirred vigorously for 30 min. 200 µL Co(NO₃)₂ aqueous solutions with different concentration (0.2 M, 0.4 M, 0.6 M and 0.8 M) was slowly added to the prepared solution by syringe pump, and the mixture was stirred for 2 h. The production was collected by filtration and then washed with hexane for several times. The obtained product was dried in vacuum. The sample was calcined at 250°C for 3 h in argon atmosphere followed by heating at 150°C for 2 h. The as-obtained sample was referred to as y wt% CoOx/MIL-101(Cr) (y is the weight percentage of CoO_x, depending on the concentration of the cobalt nitrate aqueous solution). If there were no special instructions, the loading amount of CoO_x on MIL-101(Cr) was 2.6 wt%.

Characterization. Powder X-ray diffraction measurements were performed on Bruker D8 Advance diffractometer with Cu Ka radiation. Xray photoelectron spectroscopy were acquired by a Thermo ESCALAB250 instrument with a monochromatized AI Ka line source (200 W).

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Transmission electron microscopy and energy-dispersive X-ray spectroscopy were performed on the FEI Tencai 20 microscope. HITACHI SU8010 field emission scanning electron microscopy was used to investigate the morphologies of the samples. The UV-vis diffuse reflectance spectra of samples were conducted on a Varian Cary 500 Scan UV-vis spectrophotometer with barium sulfate as the reference. A Netzsch Thermoanalyzer STA 449 F3 was used for thermal gravimetrical analysis with a heating rate of 10°C-min⁻¹ from 20°C to 1000°C under a He atmosphere. N₂ adsorption-desorption isothermal were measured on Micromeritics ASAP3020 equipment and CO₂ adsorption isotherms were measured on Micromeritics ASAP2020 equipment. Fourier transformed infrared (FTIR) spectra were obtained by a Nicolet Magna 670 Fourier transform infrared spectrometer.

Photocatalytic reaction. The photocatalytic reaction was carried out in a 50 mL reactor at 1 atm CO₂ partial pressure and the reaction temperature was maintained at 30°C by water cooling system. The CoO₃/MIL-101(Cr) (1mg) and [Ru(bpy)₃]Cl₂·6H₂O (10 µmol) were added to the reaction solution (5 mL, acetonitrile: H₂O = 3: 2), and 1 ml TEOA was added in the reaction as hole scavenger. The solution was stirred vigorously and irradiated under a 300 W Xe lamp with a 420 nm cut-off filter. An Agilent 7820A gas chromatography, equipping with a thermal conductivity detector (TCD) and a TDX-01 packed column, was employed to analyse the products using Argon as the carried gas.

Electrochemical measurements. The working electrode was prepared by 1 mg CoO_x/MIL-101(Cr) ink, the powder of which was dispersed in 1 ml ethanol followed by bath-sonication. 0.1 mL CoO_x/MIL-101(Cr) ink was dropped on FTO glass and dried at ambient condition. Pt plate was used as counter electrode. For cyclic voltammograms test, Ag/Ag⁺ was used as reference electrode, and the electrolyte is 0.1 M TBAPF₆ in MeCN. For EIS test, Ag/AgCl was used as reference electrode and the electrolyte is 0.5 M KHCO₃ solution.

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In this paper, MIL-101(Cr) is acquired with encapsulated CoO_x nanoparticles as a co-catalytic system for photocatalytic CO_2 reduction. The strong chemical absorption of MIL-101(Cr) is presented to uptake CO_2 , and an improved performance is presented by this system for photocatalytic CO_2 conversion.