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CO_2 Reduction

Anchoring Co(II) Ions into a Thiol-Laced Metal-Organic Framework for Efficient Visible-Light-Driven CO_2-to-CO Conversion

Dong-Cheng Liu,† Ting Ouyang,† Ran Xiao,† Wen-Ju Liu, Di-Chang Zhong,* Zhengtao Xu* and Tong-Bu Lu*

***Abstract**: Using solar energy to convert CO_2 into valuable fuels or chemicals offers a powerful solution to the urgent energy and environment problems. However, the development of efficient and selective catalysts remains a considerable scientific challenge. Herein, we report a versatile strategy for anchoring catalytically active Co(II) centers into the porous matrix of metal-organic frameworks (MOFs), by utilizing a robust Zr-based MOF (Zr-DMBD) functionalized with self-standing thiol (−SH) groups to enable efficient post-synthetic metal insertion. The Zr-DMBD-Co MOF solids thus prepared are modified by well-defined Co-thiolate units and possess the capability of photocatalytically converting CO_2 to CO with high efficiency and selectivity under visible-light irradiation in a water-containing system. The turnover number (TON) and CO selectivity reach as high as 97941 and 98%, respectively.*

The utilization of solar energy to convert CO_2 into valuable chemical feedstocks is one of the most promising ways to solve the problems of global warming and renewable solar fuel production. [1] The key is to develop artificial photosynthetic systems from which solar fuels can be produced from CO_2 and H_2O.[2] The ideal artificial photosynthetic systems for CO_2 reduction, just as the chloroplasts of natural green plants, should be highly-efficient, highly-selective and highly-stable. Over the past several decades, tremendous efforts have been devoted to addressing one or more of these challenges. A large number of homogeneous molecular catalysts[3] and heterogeneous catalysts[4] for photocatalytic CO_2 reduction have been reported. Homogeneous catalysts possess advantages of definite structures and thus easier mechanism investigation.[5] However, they often entail expensive precious metal catalysts, and show low efficiency and stability in aqueous-containing catalytic systems.[6] Water participation also tends to cause competitive proton reduction in the photocatalytic process and thus decease the activity and selectivity of catalysts.[7] Heterogeneous catalysts used in photocatalytic CO_2 reduction mainly include semiconductor materials[8] and metal-incorporated zeolites[9]. They show better durability and can be employed in water-containing systems, but most of them are active only in the UV region and their efficiency for photocatalytic CO_2 reduction needs to be further enhanced.[10] Therefore, it is still a challenge to develop highly efficient and selective catalysts composed of earth-abundant transition metals and capable of reducing CO_2 under visible-light irradiation in a water-containing system.

Metal-organic frameworks (MOFs), constructed from metals or metal clusters interconnected by multidentate organic linkers, are a new class of three-dimensional crystalline porous materials.[11] Their inherent large surface areas, uniform but tunable cavities, and tailorable chemistry impart notable properties[12] including gas adsorption,[13] chemical sensing,[14] heterogeneous catalysis,[15] proton conduction,[16] and drug delivery.[17] Recently, MOFs have also been explored for electrochemical[18] and photochemical[19] CO_2 reduction. Their excellent CO_2 adsorption capacities, high-density catalytically active sites, and tailorable light-absorption abilities contribute to accelerate photocatalytic CO_2 reduction. [19a, 20] In these studies, the MOF systems comprise robust metal clusters such as $Zr_6O_4(OH)_4$ (e.g. NH_2-UiO-66(Zr))[21] and Fe_3O/Ti_3O (e.g. MIL-101(Fe), MIL-125 (Ti))[22]; moreover, they incorporate ligands functionalized with photosensitive groups to enhance light harvesting and expedite charge separation,[19a] as showcased in $Re(CO)_3(dcbpy)Cl$-UiO-67,[23] PCN-222,[24] and NH_2-MIL-125(Ti) [25]. MOFs can also be composited with metal nanoparticles (e.g. $Ag\subset Re_3$-MOF),[26] semiconductors (e.g. $Cu_3(BTC)_2@TiO_2$),[27] and photosensitizers (e.g. $[Ru(bpy)_3]Cl_2$)[28] to boost the photocatalytic efficiency for CO_2 reduction.

Several issues, however, still need to be addressed in the development of MOF-based catalysts for photochemical CO_2 reduction. Firstly, a universal approach to catalyst preparation is needed for conveniently and systematically modifying the composition and other features, so as to optimize the catalytic performances. Such a need is more stark in view of the poor stability and efficiency/selectivity in most MOF-based catalysts, especially in water-containing conditions (Table S1). Also, the active sites of the MOF catalysts, like in other heterogeneous catalysts, are often not well defined. In this connection, anchoring catalytically active metal centers into the porous MOF matrix is advantageous: one can easily insert variable amounts/types of metal guests; and the crystalline MOF structure can also offer well-defined anchoring sites to generate the active centers, and to help elucidate the catalytic mechanisms. Herein, we anchored the catalytically active Co(II) into the MOF matrix of Zr-DMBD[29] through the coordination of self-standing thiol (−SH) groups, to form a Co(II)-modified MOF Zr-DMBD-Co (Figure 1). Zr-DMBD was chosen as a support on the

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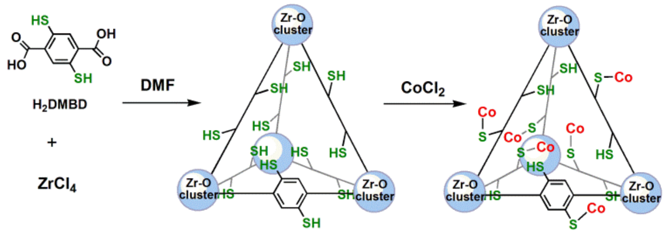

Figure 1. Synthetic scheme for the Zr-DMBD-Co network.

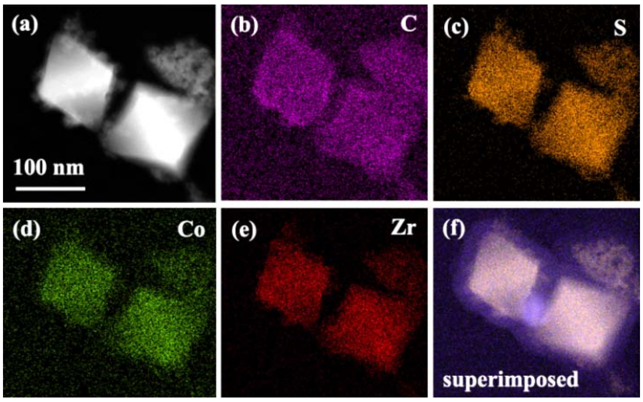

Figure 2. (a) TEM image and (b-f) EDS elemental mapping images of Zr-DMBD-Co-0.002%.

basis of the following reasons: (1) the framework of Zr-DMBD has good stability toward water and common organic solvent, even under mild acid/base conditions.[21c, 30] (2) Zr-DMBD possesses suitable pores capable of CO_2 adsorption. (3) the free-standing −SH groups of Zr-DMBD strongly bind guests of metal ions to create highly active metal-thiolate units on its extensive pore surface to boost catalytic efficiency.[31] As expected, the resulting Zr-DMBD-Co exhibits high activity and stability for visible-light-driven CO_2-to-CO conversion in a water-containing catalytic system (CH_3CN/H_2O, $v/v = 4{:}1$). The TON and TOF values reach as high as 97941 and 2.72 s^{-1}, respectively, and the selectivity to CO reaches 98%.

Zr-DMBD was synthesized according to the literature procedure.[29] To investigate the influence of the loaded amounts of Co(II) on the catalytic activity, a series of Zr-DMBD-Co with Co(II) contents of 0.002, 0.02, 0.3, 1, 3.11, 8.69%, designated as Zr-DMBD-Co-*x* (*x* is the weight percentages of Co(II) ions, Figure S1), were prepared by three methods (see the synthetic details in the Supporting Information). Zr-DMBD and Zr-DMBD-Co-*x* revealed by the distinct powder X-ray diffraction (PXRD) studies showed that the patterns of Zr-DMBD-Co-*x* are the same as those of Zr-DMBD, demonstrating that the framework of Zr-DMBD keeps stable after anchoring Co(II) (Figure S2). Scanning electron microscopy (SEM) results show that after uptake of Co(II) ions, Zr-DMBD-Co-*x* retains homogenous sizes as that of Zr-DMBD (Figures S3). The elemental mapping of Zr-DMBD-Co-0.002% further reveals the homogeneous distribution of C, S, Co, and Zr elements in the bulky crystals (Figure 2). The permanent porosity of Zr-DMBD-Co-0.002% was confirmed by the N_2 and CO_2 adsorption/desorption. At 77 K, the N_2 adsorption isotherm of the activated Zr-DMBD-Co-0.002% exhibits a typical type-I curve, with a BET surface area of 428 m^2/g (Figure S4). This value is slightly smaller than that of the Zr-DMBD (*ca.*500 m^2/g),[29] indicating that a little amount of Co(II) loading occupies a tiny pore cavity of the framework. Zr-DMBD-Co-0.002% exhibits good CO_2 adsorption capacity at 273 K, with the adsorption amount of 40 cm^3/g at 1 atm (Figure S5), which is similar to that of Zr-DMBD (49 cm^3/g).[29] The capacity of CO_2 adsorption of Zr-DMBD-Co may improve its catalytic performance for CO_2 reduction.

IR, Raman and X-ray photoelectron (XPS) spectra verify the successful immobilization of Co(II) into the pores of Zr-DMBD, i.e., *via* S−H bond cleavage and S−Co bond formation. The IR and Raman spectra of the as-prepared Zr-DMBD-Co-*x* samples demonstrate that the intensity of the characteristic S−H stretching vibration at 2563 cm^{-1} steadily diminishes and even disappears with the weight percentages of Co(II) increasing from 0 to 8.69% (Figure S6 and S7).[29, 32] In addition, a new peak at 362 cm^{-1} corresponding to S−Co stretching vibration emerges in Zr-DMBD-Co-8.69%, which is consistent with its highest Co(II) loading (Figure S7g).[29, 31, 33] These marked changes indicate that the disappearance of the S−H signal in the Zr-DMBD-Co-*x* samples is directly correlated to the formation of the S−Co bonds. This observation was further confirmed by XPS studies. The S2p spectrum of Zr-DMBD shows two main peaks at 163.5 and 164.6 eV indicative of the unbound thiols (−SH),[34] and one small peak at 168.1 eV pointing to trace amount of oxidized sulfur centers (Figure S8).[35] No cobalt species was detected by XPS in Zr-DMBD-Co-0.002% (Figure S9a), as the very low Co(II) loading was likely beyond the detection limit of XPS. For Zr-DMBD-Co-3.11% and Zr-DMBD-Co-8.96% (Figure S9b and S9c), the high resolution Co 2p XPS spectra show the main peaks of Co $2p_{3/2}$ and Co $2p_{1/2}$ at 781.0 and 796.9 eV, respectively, indicating the presence of Co(II) in the metalated Zr-DMBD.[36] A new peak is also noted at 162.5 eV in the S2p spectra of Zr-DMBD-Co-3.11% and Zr-DMBD-Co-8.96%, which can be attributed to the thiol groups coordinating with Co(II).[35b, 37] The S2p peaks of the −SH groups monotonically weakened and the Co2p peaks correspondingly intensified with the increasing weight percentages of Co(II) in the Zr-DMBD-Co-*x* samples (Figure S9), indicating the steady conversion of S−H bonds into S−Co units. These results thus corroborate that the Co(II) ions are immobilized on the pore surface of Zr-DMBD by the strongly-binding thiol groups.

The CO_2 reduction reactions were conducted in a visible-light-driven catalytic system, by using Zr-DMBD-Co-*x* as a catalyst, $[Ru(phen)_3](PF_6)_2$ as a photosensitizer, and triethanolamine (TEOA) as a sacrificial reductant.[7a, 38] Typically, a glass reactor containing a mixture of 5 mL CO_2-saturated CH_3CN/H_2O ($v/v = 4{:}1$), Zr-DMBD-Co-*x*, $[Ru(phen)_3](PF_6)_2$ and TEOA, was irradiated by a 450 nm LED light with an intensity of 100 $mW\cdot cm^{-2}$. The generated gases were analyzed by a gas chromatography (GC). The results show that the visible-light photoredox cycle produced a significant amount of CO and a small amount of H_2 (Table 1, Table S2, and Figure S10), along with a trace amount of formate detected in the liquid phase by ion chromatograph (IC). Under the same conditions, Zr-DMBD-Co-*x* with different Co(II) contents exhibit impressive photocatalytic CO_2 reduction activity and CO selectivity. Notice that even the catalyst content is as low as 0.002%, CO generated by photochemical CO_2 reduction is substantial and can be readily quantified. This result further confirms that Zr-DMBD-Co-*x* clearly possess good catalytic activity for photocatalytic CO_2 reduction. For example, by using 0.1 mg of Zr-DMBD-Co-0.002%, 3.33 μmol of CO and 0.041 μmol of H_2 were produced within 10 h, corresponding to the TON and TOF values of 97941 and 2.72 s^{-1}, respectively, and

Table 1. The results of photochemical CO_2-to-CO conversion catalyzed by Zr-DMBD-Co-*x*.[a]

Entry	Co(II)/%	Co(II)/μmol	Zr-DMBD /μM	CO/μmol	H_2/μmol	CO/%	TON	TOF/s^{-1}
1	8.96	0.15	7.51	8.59	0.33	96	57	0.0016
2	3.11	5.3×10^{-2}	7.99	10.08	0.28	97	190	0.0053
3	1	1.7×10^{-2}	8.16	9.45	0.16	98	556	0.0154
4	0.3	5.0×10^{-3}	8.22	6.75	0.11	98	1350	0.038
5	0.02	3.4×10^{-4}	8.245	3.69	0.10	97	10853	0.30
6	0.002	3.4×10^{-5}	8.247	3.33	0.041	98	97941	2.72

[a] Reaction conditions: LED light (λ = 450 nm), catalyst (0.1 mg), $[Ru(phen)_3](PF_6)_2$ (0.4 mM), TEOA (0.3 M), 1 atm CO_2 atmosphere. All the reactions were performed at room temperature (25 °C). TON values of CO for Zr-DMBD-Co-*x* were calculated based on per cobalt ion. To confirm the reliability of the data, each photocatalytic reaction was repeated at least three times. The TON value presented is the average one of three repeated experiments; all the data with deviations below 4.5%.

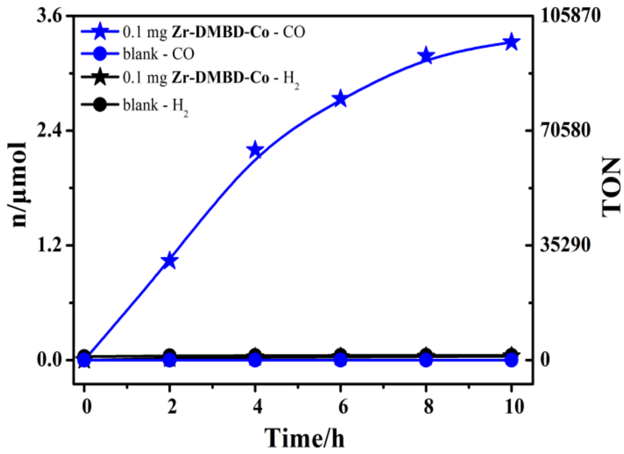

Figure 3. Photocatalytic evolution of CO (blue) and H_2 (black) catalyzed by Zr-DMBD-Co-0.002% (★, 0.1 mg) and blank (●) under irradiation of a LED light (450 nm, 100 mW·cm^{-2}, irradiation area, 0.8 cm^2) in the presence of $[Ru(phen)_3](PF_6)_2$ (0.4 mM) and TEOA (0.3 M) in 5 mL CO_2-saturated CH_3CN/H_2O (*v*/*v* = 4:1) solution at 25 ºC.

Table 2. Control experiments for the photocatalytic CO_2-to-CO conversion.[a]

Entry	Cat	CO /μmol	H_2/μmol	CO%	TON	TOF/ s^{-1}
1	Zr-DMBD-Co-0.002%	3.33	0.041	98%	97941	2.72
2	blank	0	0.049	0	0	0
3	Zr-DMBD-Co-0.002%	0	0	0	0	0
4	Zr-DMBD-Co-0.002%	0	0.16	0	0	0
5	Zr-DMBD-Co-0.002%	0	0	0	0	0
6	Zr-DMBD-Co-0.002%	0	0.21	0	0	0
7	Zr-DMBD	0	0.11	0	0	0
8	$CoCl_2$ + H_2DMBD	0.22	0.062	78%	6470	0.18
9	Zr-DMBD-Co-0.002%	3.15	0.072	98%	92647	2.57

[a] Reaction conditions: LED light (λ = 450 nm), $[Ru(phen)_3](PF_6)_2$ (0.4 mM), TEOA (0.3 M), Zr-DMBD-Co-0.002% (0.1 mg), 1 atm CO_2 atmosphere. All the reactions were performed at 25 °C. 2: without catalyst; 3: without $[Ru(phen)_3](PF_6)_2$; 4: without TEOA; 5: without light; 6: with Zr-DMBD-Co-0.002% in Ar; 7: with Zr-DMBD (0.1 mg) as catalyst; 8: with $CoCl_2$ (3.4×10^{-5} μmol) and ligand H_2DMBD as catalysts; 9: with Hg(0) (0.2 mL).

the selectivity to CO of 98%, as well as the quantum yield of 0.06% (see more details in the Supporting Information). Compared with the reported MOF-based catalysts for photochemical CO_2 reduction (Table S1), Zr-DMBD-Co-0.002% exhibits the highest efficiency and activity, as well as the highest atomic economy. This suggests that the Zr-DMBD-Co-0.002% solid may likely enable highly efficient single-site catalysis in photochemical CO_2 reduction.

A series of control experiments were performed to thoroughly investigate the photochemical CO_2-to-CO conversion catalyzed by Zr-DMBD-Co-0.002%. Firstly, the photocatalytic reaction was carried out in the absence of Zr-DMBD-Co-0.002% (Figure 3, and Table 2, entry 2). The result shows that no CO was detected, and 0.049 μmol H_2 was recorded, indicating that the production of CO originates from the catalytic reduction of CO_2 by Zr-DMBD-Co-0.002% rather than by the photosensitizer of $[Ru(phen)_3](PF_6)_2$. Secondly, the photocatalytic reaction was performed without $[Ru(phen)_3](PF_6)_2$, TEOA, or light irradiation (Table 2, entries 3-5). The results show that no CO was detected, suggesting that photosensitizer, sacrificial reductant, and visible-light irradiation are necessary parts in building the photocatalytic CO_2 reduction system. Thirdly, the photocatalytic reaction was performed under an Ar atmosphere (Table 1, entry 6). The result show that no CO was generated, suggesting that the CO formed in entry 1 comes from the reduction of CO_2 rather than the decomposition of Zr-DMBD-Co-0.002% and/or photosensitizer/sacrificial reductant. This result was further confirmed by an isotope tracer experiment. As shown in Figure S11, using $^{13}CO_2$ instead of CO_2, the generated gas is ^{13}CO rather than CO, strongly evidencing that the generated CO originates from the reduction of CO_2 by Zr-DMBD-Co-0.002%. Fourthly, the photocatalytic reaction was operated using Zr-DMBD as catalyst (Table 2, entry 7). There was no CO detected in the reaction system, indicating the Zr-DMBD support has no photocatalytic activity for CO_2-to-CO conversion. We also performed the photocatalytic reaction by using the mixture of H_2DMBD and Co(II) ions as catalyst. The result shows that the mixture also exhibits the ability to catalyze CO_2 reduction to CO (Table 2, entry 8), but only 0.22 μmol of CO was determined, corresponding a relatively lower TON value (6470) and CO selectivity (78%). Besides, experiment carried out in the presence of Hg(0) gave the lack of change in catalytic activity (Table 2, entry 9), indicating that the formation of CO was due to the molecular catalyst. These observations clearly demonstrate that the anchoring of Co(II) in Zr-DMBD greatly enhances the catalytic activity of the Co(II) catalytic centres, and Zr-DMBD is an ideal support for preparation of Zr-DMBD-Co-*x* heterogeneous catalysts that may low the reduction potential of Co^{II}/Co^{I}, stabilize the low-valent Co species, or improve the charge-separation efficiency to dramatically boost the photocatalytic CO_2-to-CO conversion .

The stability of Zr-DMBD-Co-0.002% was examined by repeated photocatalytic reactions. As shown in Figure S12, the amount of CO generated from the photocatalytic system in the second/third run was almost the same as that in the first run, demonstrating that Zr-DMBD-Co-0.002% possesses good durability. This result is further evidenced by the powder X-ray diffraction profile of Zr-DMBD-Co-0.002% after the CO_2 photoreduction reactions. As shown in Figure S13, the PXRD patterns of Zr-DMBD-Co-0.002% after the photocatalytic tests closely match that of the as-made Zr-DMBD sample. Besides, the result of ICP-MS experiment shows that no Co(II) ions was detected in the reaction solution after the photocatalytic CO_2 reduction by Zr-DMBD-Co-0.002%. Based on the above observations, we conclude that Zr-DMBD-Co-0.002% can serve as a stable heterogenous catalyst for photocatalytic CO_2 reduction.

In summary, we have used a versatile post-synthetic metalation method to prepare a series of MOF solids (Zr-DMBD-Co) functionalized by Co-thiolate interactions. These MOF materials show high photocatalytic activity and selectivity for visible-light-driven CO_2-to-CO conversion in a water-containing system in the presence of $[Ru(phen)_3](PF_6)_2$ as a photosensitizer, and TEOA as a sacrificial agent. The high catalytic efficiency originates from the strong-binding thiol groups (−SH) that effectively anchor Co(II) guest ions into the pore surface of Zr-DMBD to create the catalytic-active sites. The experimental results presented here point to a new direction of using thiol-equipped MOF materials to anchor various metal ions, so as to generate versatile and economical catalysts for photochemical applications (e.g., reduction of CO_2 to CO). We will also explore various spatial configurations of the mercaptan groups within the MOF matrix, in order to further elucidate the catalytic processes, and to optimize the metal-sulfur interaction for better photocatalytic performances.

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[1] a) H. Rao, L. C. Schmidt, J. Bonin, M. Robert, *Nature* **2017**, *548*, 74-77; b) A. J. Morris, G. J. Meyer, E. Fujita, *Acc. Chem. Res.* **2009**, *42*, 1983-1994.

[2] a) Y. Yu, Y. Shi, B. Zhang, *Acc. Chem. Res.* **2018**, *51*, 1711-1721; b) S. Berardi, S. Drouet, L. Francas, C. Gimbert-Surinach, M. Guttentag, C. Richmond, T. Stoll, A. Llobet, *Chem. Soc. Rev.* **2014**, *43*, 7501-7519; c) X. Du, J. Zhao, J. Mi, Y. Ding, P. Zhou, B. Ma, J. Zhao, J. Song, *Nano Energy* **2015**, *16*, 247-255; d) X. Fang, Q. Shang, Y. Wang, L. Jiao, T. Yao, Y. Li, Q. Zhang, Y. Luo, H.-L. Jiang, *Adv. Mater.* **2018**, *30*, 1705112.

[3] a) N. Elgrishi, M. B. Chambers, X. Wang, M. Fontecave, *Chem. Soc. Rev.* **2017**, *46*, 761-796; b) Y. Yamazaki, H. Takeda, O. Ishitani, *J. Photochem. Photobiol. C* **2015**, *25*, 106-137; c) L. Chen, Z. Guo, X. G. Wei, C. Gallenkamp, J. Bonin, E. Anxolabehere-Mallart, K. C. Lau, T. C. Lau, M. Robert, *J. Am. Chem. Soc.* **2015**, *137*, 10918-10921; d) S. Fukuzumi, Y.-M. Lee, H. S. Ahn, W. Nam, *Chem. Sci.* **2018**, *9*, 6017-6034.

[4] a) J. Liu, C. Woll, *Chem. Soc. Rev.* **2017**, *46*, 5730-5770; b) C. A. Trickett, A. Helal, B. A. Al-Maythalony, Z. H. Yamani, K. E. Cordova, O. M. Yaghi, *Nat. Rev. Mater.* **2017**, *2*, 17045; c) D. Voiry, H. S. Shin, K. P. Loh, M. Chhowalla, *Nat. Rev. Chem.* **2018**, *2*, 0105; d) J. Ran, M. Jaroniec, S. Z. Qiao, *Adv. Mater.* **2018**, *30*, 1704649 ; e) J. K. Stolarczyk, S. Bhattacharyya, L. Polavarapu, J. Feldmann, *ACS Catal.* **2018**, *8*, 3602-3635; f) K. Zhao, S. Zhao, C. Gao, J. Qi, H. Yin, D. Wei, M. F. Mideksa, X. Wang, Y. Gao, Z. Tang, R. Yu, *Small* **2018**, *14*, 1800762

[5] a) V. S. Thoi, N. Kornienko, C. G. Margarit, P. Yang, C. J. Chang, *J. Am. Chem. Soc.* **2013**, *135*, 14413-14424; b) D. Hong, Y. Tsukakoshi, H. Kotani, T. Ishizuka, T. Kojima, *J. Am. Chem. Soc.* **2017**, *139*, 6538-6541.

[6] H. Takeda, C. Cometto, O. Ishitani, M. Robert, *ACS Catal.* **2017**, *7*, 70-88.

[7] a) T. Ouyang, H. H. Huang, J. W. Wang, D. C. Zhong, T. B. Lu, *Angew. Chem. Int. Ed.* **2017**, *56*, 738-743; b) E. Fujita, *Coord. Chem. Rev.* **1999**, *185-186*, 373-384.

[8] a) J. L. White, M. F. Baruch, J. E. Pander Iii, Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T. W. Shaw, E. Abelev, A. B. Bocarsly, *Chem. Rev.* **2015**, *115*, 12888-12935; b) C. Gao, S. Chen, Y. Wang, J. Wang, X. Zheng, J. Zhu, L. Song, W. Zhang, Y. Xiong, *Adv. Mater.* **2018**, *30*, 1704624; c) J. Hou, S. Cao, Y. Wu, Z. Gao, F. Liang, Y. Sun, Z. Lin, L. Sun, *Chem. Eur.J.* **2017**, *23*, 9481-9485; d) S. N. Habisreutinger, L. Schmidt-Mende, J. K. Stolarczyk, *Angew. Chem. Int. Ed.* **2013**, *52*, 7372-7408.

[9] a) N. M. Dimitrijevic, B. K. Vijayan, O. G. Poluektov, T. Rajh, K. A. Gray, H. He, P. Zapol, *J. Am. Chem. Soc.* **2011**, *133*, 3964-3971; b) A. Dhakshinamoorthy, S. Navalon, A. Corma, H. Garcia, *Energy Environ. Sci.* **2012**, *5*, 9217-9233.

[10] J. Wu, X. Li, W. Shi, P. Ling, Y. Sun, X. Jiao, S. Gao, L. Liang, J. Xu, W. Yan, C. Wang, Y. Xie, *Angew. Chem. Int. Ed.* **2018**, *57*, 8719-8723.

[11] a) K. K. Tanabe, S. M. Cohen, *Chem. Soc. Rev.* **2011**, *40*, 498-519; b) B. Chen, S. Xiang, G. Qian, *Acc. Chem. Res.* **2010**, *43*, 1115-1124; c) N. Huang, H. Drake, J. Li, J. Pang, Y. Wang, S. Yuan, Q. Wang, P. Cai, J. Qin, H.-C. Zhou, *Angew. Chem. Int. Ed.* **2018**, *57*, 8916-8920.

[12] a) N. Huang, K. Wang, H. Drake, P. Cai, J. Pang, J. Li, S. Che, L. Huang, Q. Wang, H. C. Zhou, *J. Am. Chem. Soc.* **2018**, *140*, 6383-6390; b) T. Y. Ma, S. Dai, M. Jaroniec, S. Z. Qiao, *J. Am. Chem. Soc.* **2014**, *136*, 13925-13931; c) M. Usman, S. Mendiratta, K. L. Lu, *Adv. Mater.* **2017**, *29*, 1605071.

[13] a) K. Tan, S. Zuluaga, E. Fuentes, E. C. Mattson, J. F. Veyan, H. Wang, J. Li, T. Thonhauser, Y. J. Chabal, *Nat. Commun.* **2016**, *7*, 13871; b) J. R. Li, R. J. Kuppler, H. C. Zhou, *Chem. Soc. Rev.* **2009**, *38*, 1477-1504.

[14] a) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, *Chem. Rev.* **2012**, *112*, 1105-1125; b) J. J. Gassensmith, J. Y. Kim, J. M. Holcroft, O. K. Farha, J. F. Stoddart, J. T. Hupp, N. C. Jeong, *J. Am. Chem. Soc.* **2014**, *136*, 8277-8282.

[15] a) Y. B. Huang, J. Liang, X. S. Wang, R. Cao, *Chem. Soc. Rev.* **2017**, *46*, 126-157; b) L. Zhu, X. Q. Liu, H. L. Jiang, L. B. Sun, *Chem. Rev.* **2017**, *117*, 8129-8176; c) L. Ye, J. Liu, Y. Gao, C. Gong, M. Addicoat, T. Heine, C. Woll, L. Sun, *J. Mater. Chem. A* **2016**, *4*, 15320-15326; d) L. Shen, M. Luo, L. Huang, P. Feng, L. Wu, *Inorg. Chem.* **2015**, *54*, 1191-1193; e) Y. Fang, Y. Ma, M. Zheng, P. Yang, A. M. Asiri, X. Wang, *Coord. Chem. Rev.* **2018**, *373*, 83-115.

[16] a) G. K. Shimizu, J. M. Taylor, S. Kim, *Science* **2013**, *341*, 354-355; b) M. Sadakiyo, T. Yamada, H. Kitagawa, *ChemPlusChem* **2016**, *81*, 691-701.

[17] a) M. X. Wu, Y. W. Yang, *Adv. Mater.* **2017**, *29*, 1606134; b) L. Wang, M. Zheng, Z. Xie, *J. Mater. Chem. B* **2018**, *6*, 707-717.

[18] a) Z. Liang, C. Qu, W. Guo, R. Zou, Q. Xu, *Adv. Mater.* **2018**, *30*, 1702891; b) B. A. Rosen, I. Hod, *Adv. Mater.* **2018**, *30*, 1706238 ; c) N. Kornienko, Y. Zhao, C. S. Kley, C. Zhu, D. Kim, S. Lin, C. J. Chang, O. M. Yaghi, P. Yang, *J. Am. Chem. Soc.* **2015**, *137*, 14129-14135.

[19] a) R. Li, W. Zhang, K. Zhou, *Adv. Mater.* **2018**, *30*, 1705512; b) L. Jiao, Y. Wang, H. L. Jiang, Q. Xu, *Adv. Mater.* **2018**, *30*, 1703663; c) A. Dhakshinamoorthy, A. M. Asiri, H. Garcia, *Angew. Chem. Int. Ed.* **2016**, *55*, 5414-5445.

[20] W. Tu, Y. Zhou, Z. Zou, *Adv. Mater.* **2014**, *26*, 4607-4626.

[21] a) C. Wang, Z. Xie, K. E. de Krafft, W. Lin, *J. Am. Chem. Soc.* **2011**, *133*, 13445-13454; b) M. B. Chambers, X. Wang, N. Elgrishi, C. H. Hendon, A. Walsh, J. Bonnefoy, J. Canivet, E. A. Quadrelli, D. Farrusseng, C. Mellot-Draznieks, M. Fontecave, *ChemSusChem* **2015**, *8*, 603-608; c) D. Sun, Y. Fu, W. Liu, L. Ye, D. Wang, L. Yang, X. Fu, Z. Li, *Chem. Eur. J.* **2013**, *19*, 14279-14285; d) Y. Lee, S. Kim, H. Fei, J. K. Kang, S. M. Cohen, *Chem. Commun.* **2015**, *51*, 16549-16552.

[22] a) D. Wang, R. Huang, W. Liu, D. Sun, Z. Li, *ACS Catal.* **2014**, *4*, 4254-4260; b) Y. Fu, D. Sun, Y. Chen, R. Huang, Z. Ding, X. Fu, Z. Li, *Angew. Chem. Int. Ed.* **2012**, *51*, 3364-3367; c) S. A. Matthew W. Logan, Jeremy D. Adamson,Tristan Dilbeck,, a. F. J. U.-R. Kenneth Hanson, *J. Mater. Chem. A,* **2017**, *5*, 11854-11863.

[23] a) Z. H. Yan, M. H. Du, J. Liu, S. Jin, C. Wang, G. L. Zhuang, X. J. Kong, L. S. Long, L. S. Zheng, *Nat. Commun.* **2018**, *9*, 3353; b) T. Kajiwara, M. Fujii, M. Tsujimoto, K. Kobayashi, M. Higuchi, K. Tanaka, S. Kitagawa, *Angew. Chem. Int. Ed.* **2016**, *55*, 2697-2700; c) L. Li, S. Zhang, L. Xu, J. Wang, L.-X. Shi, Z.-N. Chen, M. Hong, J. Luo, *Chem. Sci.* **2014**, *5*, 3808-3813; d) S. Zhang, L. Li, S. Zhao, Z. Sun, M. Hong, J. Luo, *J. Mater. Chem. A* **2015**, *3*, 15764-15768.

[24] a) H. Zhang, J. Wei, J. Dong, G. Liu, L. Shi, P. An, G. Zhao, J. Kong, X. Wang, X. Meng, J. Zhang, J. Ye, *Angew. Chem. Int. Ed.* **2016**, *55*, 14310-14314; b) H. Q. Xu, J. Hu, D. Wang, Z. Li, Q. Zhang, Y. Luo, S. H. Yu, H. L. Jiang, *J. Am. Chem. Soc.* **2015**, *137*, 13440-13443; c) J. Liu, Y.-Z. Fan, X. Li, Z. Wei, Y.-W. Xu, L. Zhang, C.-Y. Su, *Appl. Catal. B: Environ.* **2018**, *231*, 173-181; d) D. Chen, H. Xing, C. Wang, Z. Su, *J. Mater. Chem. A* **2016**, *4*, 2657-2662.

[25] a) Y. Lee, S. Kim, J. K. Kang, S. M. Cohen, *Chem. Commun.* **2015**, *51*, 5735-5738; b) W.-M. Liao, J.-H. Zhang, Z. Wang, Y.-L. Lu, S.-Y. Yin, H.-P. Wang, Y.-N. Fan, M. Pan, C.-Y. Su, *Inorg. Chem.* **2018**, *57*, 11436-11442; c) D. Sun, W. Liu, Y. Fu, Z. Fang, F. Sun, X. Fu, Y. Zhang, Z. Li, *Chem. Eur. J.* **2014**, *20*, 4780-4788.

[26] a) K. M. Choi, D. Kim, B. Rungtaweevoranit, C. A. Trickett, J. T. D. Barmanbek, A. S. Alshammari, P. Yang, O. M. Yaghi, *J. Am. Chem. Soc.* **2017**, *139*, 356-362; b) K. Khaletskaya, A. Pougin, R. Medishetty, C. Roesler, C. Wiktor, J. Strunk, R. A. Fischer, *Chem. Mater.* **2015**, *27*, 7248-7257.

[27] a) R. Li, J. Hu, M. Deng, H. Wang, X. Wang, Y. Hu, H. L. Jiang, J. Jiang, Q. Zhang, Y. Xie, Y. Xiong, *Adv. Mater.* **2014**, *26*, 4783-4788; b) Z.-C. Kong, J.-F. Liao, Y.-J. Dong, Y.-F. Xu, H.-Y. Chen, D.-B. Kuang, C.-Y. Su, *ACS Energy Lett.* **2018**, *3*, 2656-2662; c) L. Shi, T. Wang, H. Zhang, K. Chang, J. Ye, *Adv. Funct. Mater.* **2015**, *25*, 5360-5367; d) A. Crake, K. C. Christoforidis, A. Kafizas, S. Zafeiratos, C. Petit, *Appl. Catal. B: Environ.* **2017**, *210*, 131-140.

[28] a) Y. Wang, N. Y. Huang, J. Q. Shen, P. Q. Liao, X. M. Chen, J. P. Zhang, *J. Am. Chem. Soc.* **2018**, *140*, 38-41; b) S. Wang, W. Yao, J. Lin, Z. Ding, X. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 1034-1038; c) J. Zhao, Q. Wang, C. Sun, T. Zheng, L. Yan, M. Li, K. Shao, X. Wang, Z. Su, *J. Mater. Chem. A* **2017**, *5*, 12498-12505.

[29] K. K. Yee, N. Reimer, J. Liu, S. Y. Cheng, S. M. Yiu, J. Weber, N. Stock, Z. Xu, *J. Am. Chem. Soc.* **2013**, *135*, 7795-7798.

[30] M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino, K. P. Lillerud, *Chem. Mater.* **2010**, *22*, 6632-6640.

[31] B. Gui, K. K. Yee, Y. L. Wong, S. M. Yiu, M. Zeller, C. Wang, Z. Xu, *Chem. Commun.* **2015**, *51*, 6917-6920.

[32] J. S. Kachian, S. F. Bent, *J. Phys. Chem. C* **2010**, *114*, 22230-22236.

[33] T. C. Higgs, D. Ji, R. S. Czernuszewicz, B. F. Matzanke, V. Schunemann, A. X. Trautwein, M. Helliwell, W. Ramirez, C. J. Carrano, *Inorg. Chem.* **1998**, *37*, 2383-2392.

[34] a) Z. Danyıldız, D. Uzun, T. T. Calam, E. Hasdemir, *J. Electroanal. Chem.* **2017**, *805*, 177-183; b) Z. Niu, Y. Zhao, W. Sun, S. Shi, Y. Gong, *Appl. Surf. Sci.* **2016**, *386*, 41-50; c) F. Blobner, P. N. Abufager, R. Han, J. Bauer, D. A. Duncan, R. J. Maurer, K. Reuter, P. Feulner, F. Allegretti, *J. Phys. Chem. C* **2015**, *119*, 15455-15468.

[35] a) C. Z. Yuan, Z. T. Sun, Y. F. Jiang, Z. K. Yang, N. Jiang, Z. W. Zhao, U. Y. Qazi, W. H. Zhang, A. W. Xu, *Small* **2017**, *13*, 1604161; b) J. C. Love, D. B. Wolfe, R. Haasch, M. L. Chabinyc, K. E. Paul, G. M. Whitesides, R. G. Nuzzo, *J. Am. Chem. Soc.* **2003**, *125*, 2597-2609.

[36] T. Zhou, Y. Du, S. Yin, X. Tian, H. Yang, X. Wang, B. Liu, H. Zheng, S. Qiao, R. Xu, *Energy Environ. Sci.* **2016**, *9*, 2563-2570.

[37] B. Zhang, J. Liu, J. Wang, Y. Ruan, X. Ji, K. Xu, C. Chen, H. Wan, L. Miao, J. Jiang, *Nano Energy* **2017**, *37*, 74-80.

[38] D. C. Liu, H. J. Wang, J. W. Wang, D. C. Zhong, L. Jiang, T. B. Lu, *Chem. Commun.* **2018**, *54*, 11308-11311.

CO_2 Reduction

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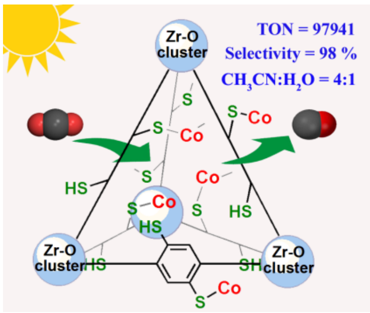
Anchoring Co(II) Ions into a Thiol-Laced Metal-Organic Framework for Efficient Visible-Light-Driven CO_2-to-CO Conversion



Using solar energy to convert CO_2 into valuable fuels or chemicals offers a powerful solution to the urgent energy and environment problems. However, the development of efficient and selective catalysts remains a considerable scientific challenge. Herein, we report a versatile strategy for anchoring catalytically active Co(II) centers into the porous matrix of metal-organic frameworks (MOFs), by utilizing a robust Zr-based MOF (Zr-DMBD) functionalized with self-standing thiol (−SH) groups to enable efficient post-synthetic metal insertion. The Zr-DMBD-Co MOF solids thus prepared are modified by well-defined Co-thiolate units and possess the capability of photocatalytically converting CO_2 to CO with high efficiency and selectivity under visible-light irradiation in a water-containing system. The turnover numbers (TON) and CO selectivity reach as high as 97941 and 98%, respectively.