Photocatalysis



# Metallic Cobalt–Carbon Composite as Recyclable and Robust Magnetic Photocatalyst for Efficient CO<sub>2</sub> Reduction

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CO2 conversion into value-added chemical fuels driven by solar energy is an intriguing approach to address the current and future demand of energy supply. Currently, most reported surface-sensitized heterogeneous photocatalysts present poor activity and selectivity under visible light irradiation. Here, photosensitized porous metallic and magnetic 1200 Co-C composites (PMMCoCC-1200) are coupled with a [Ru(bpy)3]Cl2 photosensitizer to efficiently reduce CO<sub>2</sub> under visible-light irradiation in a selective and sustainable way. As a result, the CO production reaches a high yield of 1258.30  $\mu$ L with selectivity of 64.21% in 6 h, superior to most reported heterogeneous photocatalysts. Systematic investigation demonstrates that the central metal cobalt is the active site for activating the adsorbed CO<sub>2</sub> molecules and the surficial graphite carbon coating on cobalt metal is crucial for transferring the electrons from the triplet metal-to-ligand charge transfer of the photosensitizer  $Ru(bpy)_3^{2+}$ , which gives rise to significant enhancement for  $CO_2$ reduction efficiency. The fast electron injection from the excited Ru(bpy)<sub>3</sub><sup>2+</sup> to PMMCoCC-1200 and the slow backward charge recombination result in a long-lived, charge-separated state for CO<sub>2</sub> reduction. More impressively, the long-time stability and easy magnetic recycling ability of this metallic photocatalyst offer more benefits to the photocatalytic field.

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Thanks to the depletion of fossil fuels and the increased daily requirements for energy fuels, large amounts of anthropogenic CO<sub>2</sub> emissions associated with industrial production and daily life have led to global warming and environmental crisis.<sup>[1–3]</sup> Therefore, CO<sub>2</sub> conversion into value-added chemical fuels is an intriguing approach to address the current and future demand of energy supply. The solar light-driven photocatalytic CO2 reduction into chemical fuels is believed to be one of the best methods to address energy and environment problems. Although a number of solar-active catalysts have been reported for CO2 reduction, most of them suffer from low energy conversion efficiency, uncontrollable selectivity, and instability.<sup>[4-6]</sup> Therefore, the design and fabrication of highly active and innovative photocatalytic systems with high conversion efficiency and selectivity of CO<sub>2</sub> reduction remain a great challenge.

Heterogeneous semiconductor catalysts reported to exhibit unsatisfactory

activity and selectivity in photocatalytic CO2 reduction, due to their wide energy band gap nature only allowing for absorption of a small fraction of solar spectrum and kinetically more favorable photocatalytic reduction of H<sup>+</sup>. Simultaneously, homogeneous molecular catalysts also offered an alternative strategy for photocatalytic CO<sub>2</sub> reduction owing to their better light utilization efficiency and low activation requirement for CO<sub>2</sub> reduction.<sup>[6]</sup> However, homogeneous catalysis systems have own shortcomings such as involvement of high cost, timeconsuming synthesis procedure, instability, and nonreusable, which severely impede their practical applications in photocatalysis.<sup>[7]</sup> Indeed, some new systems are being developed to construct molecular combined with semiconductor, to improve the performance of CO<sub>2</sub> converting into chemical fuels. Among different candidates, the cobalt composites have been demonstrated as one of the most promising catalysts.<sup>[8-10]</sup> Cobaltcontaining zeolitic imidazolate framework or Co3O4 metal oxides have been recently reported as novel photocatalytic systems with the assistance of a ruthenium-based photosensitizer for CO<sub>2</sub> reduction.<sup>[11–14]</sup> It is surprising to recognize that heterogeneous photocatalytic photosensitized mechanisms to access excited-stated magnetic recyclable and metallic photocatalysts have never been paid more attentions.<sup>[14,15]</sup>





**Scheme 1.** Schematic illustration of the synthesis procedure for PMMCoCC-1200. a) Synthesis of Co74s with CoCl<sub>2</sub> and 2, 5-dihydroxy-terephthalic acid in a mixture solution. b) Morphology of Co74s and the corresponding crystalline structure. c) Post-treatment of Co74s to produce PMMCoCC for photocatalytic CO<sub>2</sub> reduction by following.

Herein, an artificial photosystem based on photosensitized porous metallic and magnetic Co–C composite is proposed to perform the CO<sub>2</sub> reduction. Interestingly and impressively enough, porous metallic magnetic Co–C composites derived from metal organic frameworks (MOFs) coupled with ruthenium photosensitizer is very rare to apply in photocatalytic CO<sub>2</sub> reduction. We surmise that a breakthrough could be achieved by replacing homogeneous cobalt complexes with surficial photosensitized porous metallic and magnetic 1200 Co–C composite (PMMCoCC-1200), which was used to realize the surface excited-stated electrons superfast transportation, resulting in the CO<sub>2</sub> reduced into CO. It is the first time to propose the recycling metallic and magnetic composites mixed with organic molecule complex to fulfill the high efficiency of CO<sub>2</sub> reduction.

PMMCoCC-1200 was synthesized by calcination of Co-MOF74 sheets (Co74s) precursors which are obtained by mixture of CoCl<sub>2</sub> solution with 2, 5-dihydroxyterephthalic acid in a mixture uniform solution. Schematic illustration of the synthesis procedure for PMMCoCC-1200 is shown by Scheme 1. The scanning electron microscope (SEM) image (Figure 1a) of Co74s shows the sheet-like morphology and typical powder X-ray diffraction (XRD) patterns (Figure 1b) of Co74s is shown by the characteristic diffraction peaks (100) and (300) which are assigned to Co74s. And also the pore size (1.30 nm) distribution and Brunauer-Emmett-Teller (BET) surface area (237.30 m<sup>2</sup> g) image in the Figure S1a,b in the Supporting Information is the similar with the reported Co74s.<sup>[16]</sup> Meanwhile, the thermogravimetric (TG) analysis spectrum of Co74s is shown in Figure S1c in the Supporting Information to claim the H<sub>2</sub>O removing and carbonized process. In addition, the images of SEM and transmission electron microscope (TEM) for the PMMCoCC-1200 derived from Co74s (Figure 1c,d) show well-dispersed sizes distribution of 100-200 nm (Figure S2, Supporting Information). It is noted that there are two types selected area electron diffraction (SAED) patterns of (111) peak from metallic cobalt and (002) peak from graphene (Figure 1d, inset), respectively. Subsequently, the image Figure 1e perfectly matches the face-centered cubic phase of cobalt metal crystalline model pattern (Figure 1e, inset image). Finally, the element mapping images (Figure 1f) show that the cobalt metal and graphite carbon are component of the PMMCoCC-1200, and also the graphite carbon is surrounding outside of cobalt metal.

A detailed description of the sample PMMCoCC-1200 is shown in Figure 2. The specific high-resolution TEM (HRTEM) image (Figure 2a) reveals that the dominant exposed surfaces of PMMCoCC-1200 are (111) facets of cobalt metal, which is corresponding to a lattice space of 0.208 nm. Meanwhile, it is found that the specific structural feature of PMMCoCC-1200 is further presented by selected area fast Fourier transform (SAFFT) image (the inset of Figure 2a) to evidence the metal cobalt existence. Furthermore, the Raman spectrum (Figure 2b) of graphite carbon shows a sharp G2g peak, declaring its better crystallinity with a long-range conjugation structure of sp<sup>2</sup> carbon, rather than that obtained from the modified Hummer's method.<sup>[17-19]</sup> In addition, PMMCoCC-1200 also shows a small D peak near 1325 cm<sup>-1</sup> contributed to defect carbon and sharp G peak (1590 cm<sup>-1</sup>) contributed to graphite carbon.<sup>[17a]</sup> More importantly, the ratio of  $I_D/I_G$  is 0.474, which indicates that PMMCoCC-1200 owns the relatively better crystallinity of graphite. The last point should be figured out that the Raman spectrum (Figure 2b) showed no peak at the 400-600 cm<sup>-1</sup> to give the evidence that PMMCoCC-1200 owns the metallic property instead of cobalt oxide.

After that, the content of PMMCoCC-1200 is obtained from the TG measurement (Figure 2c) including Co metal 90.5 and C 9.5 wt% (graphite carbon, 7.5 wt%; defect carbon, 2.0 wt%). Moreover, the series of post-treatment samples under different calcination temperatures (Figure S3, Supporting Information) show a general regular that the cobalt metal content increases slightly and the carbon content decreases slightly with the temperature increasing. The mainly reason is that the carbon is easy to be removed with the temperature increasing, but at the same time part of defect carbon will transfer into graphite carbon, which is formed due to the metal cobalt catalytic effect, to improve the electron conductivity.<sup>[17b]</sup>

The typical X-ray photoelectron spectroscopy (XPS) analysis reveals that Co2p peak is corresponding to cobalt metal peak derived from carbonized Co74s, which is consistent with the reported literatures.<sup>[18]</sup> And also the peak of absorbed oxygen on the surface of PMMCoCC-1200 is present for XPS analysis of O 2p (Figure 2d), which also give the evidence for PMMCoCC-1200 without the surficial oxidation. In addition, the band gap calculation of PMMCoCC-1200 is confirmed with diffuse reflection spectrum (DRS) and K-M transformation spectrum (Figure 2e). Intriguingly, it is clear that there is largely absorption ranged from 400 to 2000 nm, and the  $E_{\alpha}$  is obtained (~0.5 eV) via the K-M transformation spectroscopy. Besides, the hysteresis loop pattern demonstrates that this type catalyst is magnetic recycling for reusability and more convenient for collection (Figure 2f). Finally, it is given that BET surface areas and pore sizes analysis are shown in Table S1 in the Supporting Information. With the calcination temperature increasing, the pore size becomes large and the BET surface areas show a downtrend. It is worth noting that the samples after HCl aching have the larger BET surface areas and more typical diversity of pore sizes (microporous and nanoporous structure).

In order to illuminate the relationship between material structure and photocatalytic  $CO_2$  reductive property, **Figure 3**a shows the high yield of CO product (1258.30 µL) after 6 h long-time reaction with a high selectivity of 64.21%





**Figure 1.** a) TEM image of Co74s. b) XRD pattern of Co74s. (The inset is the Co74s of crystalline structure.) c) Large areas of SEM image of PMMCoCC-1200 (The inset is the enlarge image of PMMCoCC-1200). d) TEM image and corresponding inserted SAED image of PMMCoCC-1200. e) XRD pattern of PMMCoCC-1200. (Inset is the crystalline structure of metallic cobalt.) f) Element mapping images of PMMCoCC-1200.

over competing H<sub>2</sub> generation by using surface sensitized PMMCoCC-1200. Impressively, with respect to the yield of CO (20  $\mu$ L only sustaining 0.5 h) for the homogeneous [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> photocatalyst which is limited by the stability of the chromophore in aqueous solution (Figure S4, Supporting Information),<sup>[7,8]</sup> PMMCoCC-1200 can continuously generate CO and increase with three orders of magnitude when the reaction time arrives at 6 h. In addition, we further determined the external quantum efficiency (QE) of photocatalytic CO<sub>2</sub> reduction upon PMMCoCC-1200 at a monochromatic

irradiation of  $\lambda = 450$  nm. Very impressively, the external quantum efficiency is estimated to be 0.049%, significantly outperforming the reported high performance photocatalysts for CO<sub>2</sub> reduction (Table S2, Supporting Information). Simultaneously, in order to evidence that the photocatalytic CO<sub>2</sub> reduction is based on the whole system, when any controlled experimental condition is absent, the reaction cannot be approached (Table S3, Supporting Information).

Besides the activity, the recycle usability is another key performance parameter for the photocatalytic system. To evaluate the photocatalytic reusable capacity of PMMCoCC-1200, the used catalysts were recovered and redispersed in a fresh reaction solution with photosensitizer for recycling tests (Figure 3b). It should be noted that the catalysts can be separated by magnet conveniently, due to the magnetic property (Figure S5, Supporting Information), which is evidenced by the Figure 3b inset image. As demonstrated in Figure 3b, even 3 months later, the reused catalysts for the third run still retain ≈90% of their original activity, signifying an excellent stability and reusability of PMMCoCC-1200.

Summarized to further explore the key factors that determine the performance of PMMCoCC-1200, according to Figure 3c, a series of control experiments are given to declare the relationship between Raman spectra (Figure S6, Supporting Information) characterization of carbon  $(I_D/I_G)$  and CO<sub>2</sub> photocatalytic reduction activity of carbonized samples under different calcination temperature (Figure 3c, Supporting Information). 50 mg Co-C composites photocatalytic materials obtained from different calcination temperatures (Figures S7 and S8, Supporting Information) were added into the photocatalytic reaction system, all of samples obtained from 600 to 1600 °C respectively, showed the high performance in photocatalytic CO<sub>2</sub> reduction. The optimal top point is clearly shown that PMMCoCC-1200 reaches at the best performance of CO yield. In order to explain why PMMCoCC-1200 with general

absorption ability of CO<sub>2</sub> (Figure S9, Supporting Information) owns the best photocatalytic performance of CO<sub>2</sub> reduction? As it is shown in Raman spectra, the degree of graphitization of PMMCoCC-1200 has been enhanced tremendously to leading the photoexcited electrons transferring more efficiently. So, it is reasonable to believe that PMMCoCC-1200 has the best graphitized degree ( $I_D/I_G$ , 0.474) with the comparison of other Co–C composites (Figure 3c), as evidenced by the electrochemical impedance spectroscopy (Figure S10 and Table S4, Supporting Information), the higher electrochemical impedance of







**Figure 2.** The basic characteristics of PMMCoCC-1200. a) HRTEM image (inset is the corresponding typical SAFFT pattern). b) Raman spectroscopy (excited wavelength of 514 nm). c) TG analysis spectra. d) XPS spectra for O 1s and Co 2p. e) Absorption spectrum from DRS (inset image is band gap calculation = 0.5 eV). f) Hysteresis loop pattern.

PMMCoCC-1200 is benefit for electron transportation. In addition, based on the analysis of Raman spectra, it is concluded that the detailed information of different samples  $I_D/I_G$  ratio is shown in Table S5 in the Supporting Information. Another important contrast is shown in Figure S11 in the Supporting Information to evident when the Co74s is calcined under the Ar-H<sub>2</sub> mixture gas and finally obtain the cobalt metal particle with less carbon coated, and the performance is worse than that of PMMCoCC-1200. An obvious conclusion can be given that when the conductivity and crystalline graphite carbon composited with metal cobalt was likely to realize the efficient photocatalytic CO<sub>2</sub> reduction.

The photocatalytic active site is the key point for catalytic reaction, so exploration of the active site becomes more and more important. So here, the etching experiments were designed to corrode the metal cobalt under the different condition (Figure 3d). With the increase of the degree for cobalt metal removing, it is found that the photocatalytic performance becomes worse, and even there is no CO product when the cobalt metal nanoparticles cores almost disappear after etching for 5 h (Figure S12, Supporting Information). This phenomenon gives the strong evidence that the cobalt metal is the active site for the photocatalytic  $CO_2$  reduction.

In order to explain the excellent CO<sub>2</sub> reduction property only obtained from Co–C composites combined with Ru complex photosensitizer, a series of contrast experiments were carried out in following test for commercial cobalt metal nanoparticles, Co74s, commercial iron metal nanoparticles, and graphene carbon(Figure 3e). It is expected when commercial cobalt metal powder instead of PMMCoCC-1200 is adopted as catalyst under the same conditions; a relative low CO yield of 405.59  $\mu$ L is obtained (the first column in Figure 3e). Such low catalytic activity should be ascribed to the structural nature

of commercial cobalt metal without the coated layered graphene carbon, hindering the absorption of Ru complexes and the electrons transferring. Meanwhile, compared to the iron powder, a plausible discovery can be concluded that this type system metal composited with graphene carbon is benefit for photocatalytic  $CO_2$  reduction, when the Ru complexes are added in photocatalytic system.

For the innovative photocatalytic system, it is crucial to develop the general materials for that whether this type carbonized MOF derived can be used efficiently for phtocatalytic CO<sub>2</sub> reduction. According to the Figure 3f, because this type structure reflects that the electrons being in direct contact with the metal and graphene carbon support possess active photocatalytic properties, these systems are generally carbonized to enhance the activity toward kinetic favored photocatalytic CO<sub>2</sub> reduction. It has inspired the use of metal organic frameworks (Fe-, Ni-, Mn-, or Co-Fe-MOF74) to take posttreatment for obtaining the metal nanoparticles embedded into the graphene carbon within several layers or inside their channels, to influence the activity of the entire nanoparticle surface while maintaining efficient reactant and product transport owing to the porous nature of the material. Under the same condition, we try to test other kinds of carbonized MOF materials for photocatalytic CO2 reduction. Although other type metal-carbon composites showed low activity for CO<sub>2</sub> reduction, Fe-C composites owned good performance for excellent photocatalytic CO<sub>2</sub> reduction property. In sharp contrast to the reported homogeneous organometallic catalysts that are thermodynamically unstable and subjected to oxidative degradation,<sup>[7]</sup> PMMCoCC-1200 system has advantages of low-cost, ease of synthesis and readily recoverable for reuse. In summarized Table S6 in the Supporting Information, PMMCoCC-1200 system also owns the relatively good







**Figure 3.** a) CO (red square dots) and H<sub>2</sub> (black spherical dots) evolution with reaction prolonging upon irradiation of visible light using PMMCoCC-1200. b) Yields of CO and H<sub>2</sub> in 6 h with PMMCoCC-1200 in recycling tests. (Inset image shows recycling capacity in magnetic absorption method.) c) The relationship between Raman spectrum characterization of carbon  $(I_D/I_g)$  and CO<sub>2</sub> photocatalytic reduction activity of carbonized samples under different calcination temperature. d) PMMCoCC-1200 after etching in 1 mol L<sup>-1</sup> HCl for yields of CO and H<sub>2</sub>. e) Average yields of CO and H<sub>2</sub> in first 6 h for control experiments under the same conditions using commercial cobalt powder, Co74s, iron powder, graphene, respectively. f) Carbonized products derived from Fe-MOF74, Ni-MOF74, Mn-MOF74, and Co-Fe-MOF74 under 1200 °C in Ar atmosphere for photocatalysis. (Test condition: 300 W Xe lamp,  $\lambda > 420$  nm; catalyst: 50 mg; photosensitizer: [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>, 10 mg; reaction solution: water: CH<sub>3</sub>CN: TEOA = 1:3:1, 30 mL solvent under mild reaction conditions (15 °C and 1 atm CO<sub>2</sub>).

selectivity. More importantly, it simultaneously possesses superior activity, selectivity, and highly promising for large-scale photocatalytic CO<sub>2</sub> reduction system.

After quantitatively evaluating the catalytic performance, two additional experiments were carried out to ascertain the photocatalytic products CO from CO<sub>2</sub>. First, the solvent after photocatalytic reaction was analyzed by gas chromatograph and <sup>1</sup>H-NMR spectroscopy. No measurable hydrocarbon products derived from CO<sub>2</sub>, such as CH<sub>3</sub>OH, HCOH, and

HCOOH, were detected (Figure S13a, Supporting Information). Second the isotopic <sup>13</sup>CO<sub>2</sub> was used as the reactant in the photocatalytic reaction and the obtained products were identified by gas chromatography-mass spectrometry (Figure S13b, Supporting Information). The peak appearing at 2.4 min with m/z = 29 can be assigned to the generated <sup>13</sup>CO, while the peak with m/z = 45 is ascribed to the original <sup>13</sup>CO<sub>2</sub>. This confirms that the produced CO is originated from CO<sub>2</sub>.





**Figure 4.** a) Proposed mechanism for the photosensitized catalytic reduction of  $CO_2$  to CO. b) Schematic representation of energy level diagram showing electron transfer from Ru(bpy)<sub>3</sub><sup>2+</sup> to PMMCoCC-1200. *E*<sub>F</sub>: Fermi level; LUMO: lowest unoccupied molecular orbital; HOMO: highest occupied molecular orbital. (See Supporting Information for more details for calculation of *E*<sub>F</sub>, HOMO and LUMO).

On the basis of previous works in homogeneous systems<sup>[1]</sup> and the above results, we propose the following mechanism (Figure 4a). Upon light excitation, the photosensitizer  $Ru(bpy)_{3}^{2+}$  is promoted to the excited state. This excited state is then reductively quenched by a sacrificial electron donor [triethanolamine (TEOA)] to form a reduced photosensitizer. The reduced photosensitizer transfers an electron to PMMCoCC-1200, where CO<sub>2</sub> molecule is absorbed and activated. During above reduction process, it has been evidenced that PMMCoCC-1200 owns a lot of pores on the surface, this porous structure is benefit for small molecule going through, and also the excited photoelectrons can easily transfer between graphite carbon and cobalt metal. Finally, CO<sub>2</sub> is reduced to CO and subsequently released from PMMCoCC-1200 surface. As the catalytic reduction of CO<sub>2</sub> by PMMCoCC-1200 is initiated by the photosensitizer, the electrons transferring from photosensitizer to PMMCoCC-1200 is a prerequisite, which is feasible as demonstrated in the corresponding energy level diagram (Figure 4b). The fermi level  $(E_{\rm F})$  of PMMCoCC-1200 relative to the vacuum level is measured to be 5.04 eV, respectively (Figure S14, Supporting Information). Also, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of Ru(bpy)<sub>3</sub><sup>2+</sup> with respect to the vacuum level are determined as 3.19 and 5.68 eV, respectively (Figure S15, Supporting Information). Since the  $E_{\rm F}$ of PMMCoCC-1200 is lower than the LUMO of Ru(bpy)<sub>3</sub><sup>2+</sup>, the electrons in the LUMO of photosensitizers can be preferentially transferred to the E<sub>F</sub> of PMMCoCC-1200, enabling the subsequent reduction of CO2. The employed PMMCoCC-1200 here play two important roles: 1) hosting the metal cobalt active sites for CO<sub>2</sub> reduction; 2) accepting electrons from the LUMO of [Ru(bpy)<sup>3</sup>]Cl<sub>2</sub> and transferring the received electrons to reactivated CO<sub>2</sub> for reduction at the metal cobalt active sites.<sup>[20,21]</sup>

It is supposed that CO<sub>2</sub> molecular and Ru complexes absorbed on the surface of PMMCoCC-1200 and reactivated, then the visible light excited Ru complex due to the effect of metal–ligand–charge–transferring,<sup>[22–27]</sup> the separated electrons were transferred to PMMCoCC-1200 and the holes take part in the TEOA oxidation. It can be imagined that PMMCoCC-1200 owns the ultraquick transferring function for electrons conduct and gives the  $CO_2$  perfectly reactive condition, leading to the efficient photocatalytic  $CO_2$  reduction.

In summary, tunable structure and contents of PMMCoCC composites are derived from Co74s fabricated by ultrasonication methods. PMMCoCC-1200 with more uniform morphology, high degree of graphitization, and more convenient magnetic recyclability is demonstrated as excellent heterogeneous photocatalyst for CO2 reduction; for instance, highly efficient activity with orders of magnitudes higher than single Ru complexes, outstanding stability with negligible activity decay after three repetitive reactions. Due to the existence of metal cobalt active site and the graphene carbon with superelectronic conductivity, the synergetic effect from metal cobalt and graphene carbon promotes the photocatalytic CO<sub>2</sub> reduction into CO more effectively. It is worth noting that it is the first time to propose porous metallic and magnetic material combined with Ru(bpy)<sub>3</sub><sup>2+</sup>, which is used to obtain an optimized photocatalytic CO<sub>2</sub> reduction. Our understanding for PMMCoCC-1200 will not only provide a guide for the development of efficient and durable magnetic photocatalysts for solar energy conversion, but also offer important insight into the exact identity of active sites in such noble-metal-free composites for photocatalytic CO<sub>2</sub> reduction. This study also gives a new angle through a novel strategy for developing high performance of the surface photosensitized heterogeneous photocatalysts. More impressively, it paves the way to deep insight into understanding the key factors for improving the photocatalytic performance for CO<sub>2</sub> reduction.

#### **Experimental Section**

*Chemicals*: All chemicals used were of analytical grade and were used as received without any further purification.  $MnCl_2 \cdot 4H_2O$ ,  $NiCl_2 \cdot 6H_2O$ , FeCl\_3  $\cdot 6H_2O$ , and  $CoCl_2 \cdot 6H_2O$  was purchased from Sinopharm Chemical Reagent. 2, 5-dihydroxyterephthalic acid and  $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (bpy = 2, 2-bipyridine) were obtained from Sigma-Aldrich. Ethanol, triethylamine (TEA), *N*, *N*-dimethylformamide (DMF), TEOA, and acetonitrile (MeCN) were purchased from Alfa Aesar. Carbon dioxide SCIENCE NEWS \_\_\_\_\_ www.advancedsciencenews.com

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gas, supplied by Beijing Beiwen Gases Company, was of super grade purity (99.999%). The  $^{13}\mathrm{CO}_2$  was 99% enriched providing by Shanghai Wusheng Bio. Company. Ultrapure water (Millipore Milli-Q grade) with a resistivity of 18.2 M\Omega-cm was used in all the experiments.

The Synthesis of Porous Metallic and Magnetic 1200 Co-C Composites (PMMCoCC-1200): First, DMF (30 mL), ethanol (2.5 mL), and water (2.5 mL) were mixed in a 100 mL polytetrafluoroethylene (PE) tube. Next, 0.0775 g 2, 5-dihydroxyterephthalic acid was dissolved into the mixed solution under ultrasonication. Subsequently, 0.375 g  $CoCl_2-6H_2O$  was added and dissolved, then, 0.8 mL TEA was quickly injected into the solution. And then, the solution was stirred for 5 min to obtain a uniform colloidal suspension. Afterward, the colloidal solution was continuously ultrasonicated for 8 h (40 kHz) under airtight condition. Finally, the obtained clay bank precipitates Co-MOF74 sheets (Co74s) were centrifuged and washed with deionized water and DMF for three times, and finally dried by a vacuum oven under 80 °C for 24 h.

The product of Co–C composites were respectively prepared by calcination of the Co74s under 400, 600, 800, 1000, 1200, 1400, and 1600 °C in an  $Al_2O_3$  tube furnace for 3 h with the speed of raising temperature 2 °C min<sup>-1</sup>. The final product Co–C composites were collected. Especially, well-dispersed PMCoCC-1200 was obtained through centrifuging the intermediate mixture ethanol solution with 3000 rmp for 3 min and finally dried by a vacuum oven under 80 °C for 24 h.

The PMCoCC-1200 with Posttreatment for Etching: In a typical procedure, the obtained sample Co–C composites under different calcination temperatures were prepared with 5.0 g, respectively. Subsequently, the former related samples were used HCl solution (the concentration of 1 mol L<sup>-1</sup>) to etching them under different condition with keeping 1, 3, and 5 h, respectively. Then, the obtained products were washed with water and ethanol several times with centrifugating at 14 000 rpm. Finally, all the etching samples dried in the vacuum oven with 80 °C for 24 h, cooled to room temperature in the vacuum environment.

The Porous Metallic 1200 M-C (M = Fe, Ni, Mn, and Co (50 wt%)-Fe) Composites (PMMCC-1200): First, DMF (30 mL), ethanol (2.5 mL), and water (2.5 mL) were mixed in a 100 mL PE tube. Next, 0.0775 g 2,5-dihydroxyterephthalic acid was dissolved into the mixed solution under ultrasonication. Subsequently, 0.375 g M [M = Fe, Ni, Mn, and Co (50 wt.%)-Fe] chloride was added and dissolved, then, 0.8 mL TEA was quickly injected into the solution. And then, the solution was stirred for 5 min to obtain an uniform colloidal suspension. Afterward, the colloidal solution was continuously ultrasonicated for 8 h (40 kHz) under airtight condition. Finally, the obtained clay bank precipitates were centrifuged and washed with deionized water and DMF for three times, and finally dried by a vacuum oven under 80 °C, for 24 h. The product of M-C composites was prepared by calcining the corresponding precursors under 1200 °C in an Al<sub>2</sub>O<sub>3</sub> tube furnace for 3 h with the speed of raising temperature 2  $^\circ\text{C}$  min^-1. The final PMMCC-1200 was collected.

Characterization: Transmission electron microscope (TEM), HRTEM and SAED were performed on a FEI Tecnai G2 F20 electron microscope operated at 200 kV, and the morphology was observed under a Hitachi S4800 scanning electron microscope (SEM). Powder XRD patterns were recorded on a Rigaku D/MAX-TTRIII (CBO) X-ray power diffract meter by using Cu Ka radiation ( $\lambda = 1.5418$  Å). Gas chromatographic analysis was conducted using a gas chromatograph (Tianmei GC-7900) equipped with a TDX-01 packed column, a thermal conductivity detector and a flame ionization detector (FID). The FID detector was fitted with a methanizer to detect CO. The product of the <sup>13</sup>CO<sub>2</sub> isotopic experiment was analyzed by a Trace DSQ GC-MS (Thermo Fisher Scientific, Inc.). The liquid phase of the reaction system was analyzed by a gas chromatograph (Shimadzu GC-2010 Plus) with an Agilent DB-Wax column and <sup>1</sup>H-NMR spectra (Bruker Advance 400 spectrometer, 400 MHz), respectively. CO<sub>2</sub> sorption study was performed in a Micromeritics TriStar II 3020 adsorption apparatus at 288 K up to 1 bar. Prior to sorption measurements, all samples were degassed at 120 °C for 6 h. Electrochemical impedance spectra and

cyclic voltammogram were recorded using a CHI 660C computercontrolled potentiostat (ChenHua Instruments Co., Shanghai, China) in a standard three-electrode system. The measured BET surface area was obtained by ASAP2020 (M+C). Magnetic hysteresis loop patterns were measured by PPMS-9 <sup>1</sup>H-NMR spectra were obtained by AVANCE III HD 400. Fourier transform-infrared spectroscopy was performed using a PerkinElmer Spectrum One spectrometer. Ultraviolet photoelectron spectroscopy (UPS) and XPS were carried out using a UPS/XPS system (Thermo-Fisher, ESCLAB 250, USA). UV–vis diffuse reflection absorption spectra of the samples were recorded by an UV– vis spectrometer (Lambda 950, PE, USA) equipped with an integrating sphere accessory in the diffuse reflectance mode (R) and BaSO<sub>4</sub> as reference material. UV–vis absorption spectra were obtained by a Hitachi U-3010 Spectrophotometer.

*Photocatalytic Test*: The photocatalytic experiments were carried out in a 300 mL pyrex reactor equipped with a Quartz lid under the photoirradiation condition coupled with the gas chromatograph at 15 °C as controlled by cooling water (Figure S16). The reaction system containing [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>·6H<sub>2</sub>O (10 mg), PMM(Co, Fe, Mn, Ni, and Co-Fe)CC-1200 materials (50 mg), solvent [30 mL, MeCN/TEOA/H<sub>2</sub>O = 3:1:1 (Vol. ratio)], by stirring with a magnetic stirrer and irradiated under a 300 W Xenon lamp (Beijing Perfect Light Company) with a 420 nm cutoff filter. The whole reaction setup was vacuum degassed and then the high-purity CO<sub>2</sub> gas was filled into the reaction setup to reach a pressure of 1 bar. Measured by an optical power meter (PM100D, Thorlabs), the optical density of the light source with a 420 nm cutoff filter was 293.61 mW·cm<sup>2</sup> with an illuminated area of 18.08 cm<sup>2</sup> and a distance of 11 cm between the liquid level and light source.

*Quantum Efficiency Values Measurement*: External QE values were calculated using the following equation:

$$QE = \frac{(\text{The number of CO molecules}) \times 2}{(\text{The number of incident photons})} \times 100\%$$
(1)

The external quantum efficiency values for CO generation were determined at 450 nm using a single band pass filter by using the same photochemical experimental setup. The flux of incident photons from the power was measured by a power meter (PM100D, Thorlabs). The lamp intensity at 450 nm was measured to be 37.3 mW·cm<sup>2</sup>, the illuminated area was 18.08 cm<sup>2</sup>, and the incident photon flux was calculated to be  $5.49 \times 1021$  h<sup>-1</sup>. The molecules of CO generated were 6.66 µmol after 3 h photoirradiation.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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## **Conflict of Interest**

The authors declare no conflict of interest.

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### **Keywords**

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