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Synergetic catalysis of a cobalt-based coordination polymer for selective visible-light driven CO_2-to-CO conversion†

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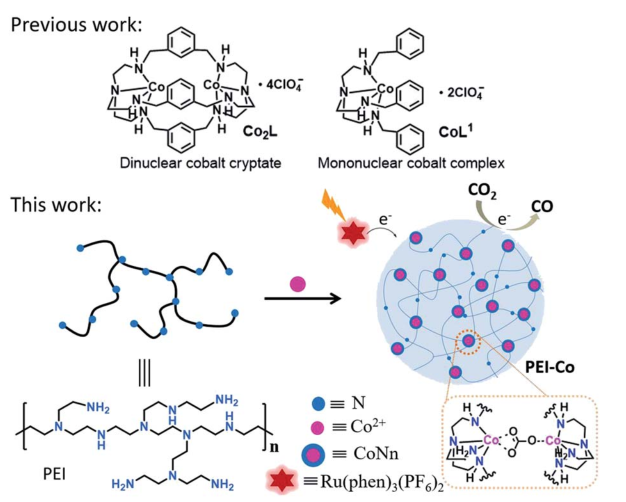
Herein, based on the strategy of synergetic catalysis, we report a cobalt-based coordination polymer PEI_6-Co. As a heterogeneous catalyst, PEI_6-Co shows a selectivity of 95% and a yield of 1170 mmol g^{-1} for visible-light-driven CO_2-to-CO conversion in a water containing system, which is almost 2.8 times that of the mononuclear cobalt catalyst **CoL^1** and is comparable to that of the dinuclear cobalt catalyst **Co$_2$L**.

Energy shortages and greenhouse gas emissions caused by the consumption of fossil fuels have become an indisputable obstacle to the sustainable development of human beings. Solar-driven conversion of CO_2 to carbon fuels is regarded as an ideal strategy to deal with these energy and environmental issues.[1–7] In this context, many researchers have devoted themselves to promote the activity and efficiency of photocatalytic CO_2 conversion.[8–11] Unlike the reduction of H_2O to H_2, the CO_2 reduction reactions are more complicated. Firstly, CO_2 is an inert molecule, it requires high energy to be activated. Secondly, as the carbon atom in CO_2 is the highest valence, various reduction products including CO,[12] formic acid,[13] formaldehyde,[14] methane[15] and some multi-carbon products[16] can be obtained. Besides, due to the competitive reduction of protons, the selectivity of CO_2 reduction is usually low in water containing medium.[17] In this context, the development of a catalyst for the efficient and highly selective reduction of CO_2 to a single valuable product is still challenging, especially in water containing system.

In recent decades, many molecular catalysts for the reduction of CO_2 have been designed elaborately. For example, the catalysts based on Ru,[18,19] Re,[20,21] Ir,[22] Fe,[23,24] Co,[25,26] Ni,[27,28] Mn,[29] *etc.*, have been developed to reduce CO_2 and the mechanisms for the activation and conversion of CO_2 have also been investigated reasonably.[30,31] Notable among them is dinuclear metal synergistic catalysis (DMSC) in which two active centers are involved into the catalytic reaction concurrently and used to decrease the reaction barriers.[32–34] In our previous works,[25] dinuclear cobalt cryptate **Co$_2$L** (Scheme 1) which was composed of aza-cryptand ligand and two adjacent cobalt ions displayed excellent performance in the conversion of CO_2 to CO. Due to the immobilization and synergistic catalysis of two adjacent cobalt active sites to CO_2 molecules, the selectivity and the turnover numbers (TON) of **Co$_2$L** reached as high as 98%, and 16 896, respectively. Although molecular catalysts are significant in the study of catalytic mechanism and optimizing catalyst structure, the synthesis operations of such molecular catalyst are tedious and not conducive to its large-scale practical applications.

Herein, we choose polyethyleneimine (PEI) as the analogue of aza-cryptand and synthesize a cobalt-based coordination polymer (PEI_6-Co) as a heterogeneous catalyst for the photocatalytic reduction of CO_2 (Scheme 1). The reason for choosing PEI as a ligand is that both the structures of aza-cryptand and PEI have secondary amine and tertiary amine groups which can coordinate with Co^{2+}. The formation of the coordination polymer can shorten the distance between cobalt active sites, which



Scheme 1 The structures of Co$_2$L, CoL^1, PEI-Co and the proposed catalysis process of PEI-Co for CO_2-to-CO conversion.

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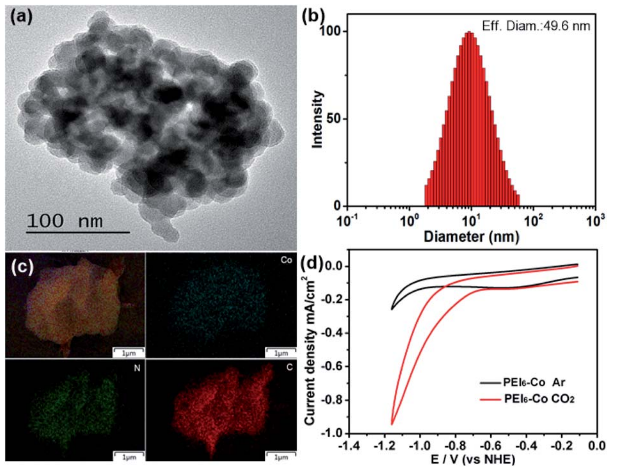

Fig. 1 (a) TEM image of PEI_6-Co. (b) DLS data of PEI_6-Co. (c) Mapping images of PEI_6-Co. (d) CV curves of PEI_6-Co in CH_3CN/H_2O (4 : 1) solution under an Ar (black) and CO_2 atmosphere (red) at 25 °C.

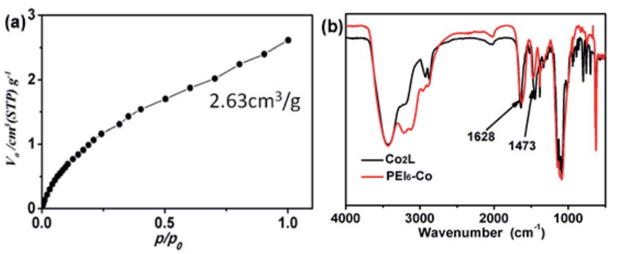

Fig. 2 (a) The adsorption curve for carbon dioxide of PEI_6-Co. (b) IR spectra of PEI_6-CO (red) and $\mathbf{Co_2L}$ (black) after adsorption of CO_2.

Table 1 Comparison of photocatalytic carbon dioxide reduction of PEI*x*-Co[a]

Entry	Catalyst	n_{H_2} (μmol)	n_{CO} (μmol)	Selectivity of CO	Activity (mmol g^{-1})
1	PEI_4-Co	0.35	4.35	93%	870
2	PEI_5-Co	0.36	4.71	93%	942
3	PEI_6-Co	0.34	5.84	95%	1170
4	PEI_7-Co	0.30	5.09	96%	1020
5	PEI_8-Co	0.26	4.90	95%	981

[a] Reaction conditions: PEI*x*-Co (5 μg), $[Ru(phen)_3]$ $(PF_6)_2$ (0.4 mM), TEOA (0.3 M), 5 mL CH_3CN/H_2O (v/v = 4 : 1) solution, 25 °C, 12 h. 450 nm LED lamp (100 mW cm^{-2}, irradiation area 0.8 cm^2).

is similar to that of $\mathbf{Co_2L}$, so that they may function synergistically in the photocatalytic reactions. Besides, PEI has been commonly used as a CO_2 absorbent in the past research of electrocatalytic reduction of CO_2.[35] As a result, when PEI_6-Co is used as a heterogeneous catalyst for the reduction of CO_2 in water containing system, the selectivity for CO reaches up to 95%, and the yield for CO_2-to-CO conversion reaches 1170 mmol g^{-1}, which is almost 2.8 times of molecular catalyst mononuclear cobalt $\mathbf{CoL^1}$ and comparable with that of dinuclear cobalt catalyst $\mathbf{Co_2L}$.

$\mathbf{Co_2L}$ and $\mathbf{CoL^1}$ were prepared according to the literature.[25] PEI*x*-Co (*x* represents the N/Co ratio) was synthesized through the coordination between the amine groups of PEI and cobalt ions and the exact contents of cobalt in the catalyst are listed in Table S1 (see ESI†). At the beginning, the formation of PEI_6-Co was characterized by TEM, DLS, element mapping, XPS and cyclic voltammetry measurements. As shown in Fig. 1a, PEI_6-Co was formed as a nanoparticle which resulted from the coordination crosslinking between the amino groups of PEI and Co ions. DLS measurement in Fig. 1b shows that the average diameter of this nanocomposite is about 50 nm. The elemental mapping images confirm that the Co, N and C elements uniformly distributed over the nanostructures of PEI_6-Co (Fig. 1c). The XPS measurement shows that there are only Co, N, C, O and Cl element in PEI_6-Co (Fig. S1†). These results indicate that amine groups in the PEI chain can coordinates with the cobalt ions, causing the long chain of the PEI to be twisted and crosslinked to form nanoparticles and giving the chance for cobalt centers to get closer. Besides, the redox property of PEI_6-Co was investigated using cyclic voltammogram (CV). The results in Fig. 1d show that compared with the CV curve under argon condition, the current has an obvious enhancement under CO_2 atmosphere and the onset potential ($E_{onset} = -0.62$ V *vs.* NHE) is more negative than that of $\mathbf{Co_2L}$ ($E_{onset} = -0.68$ V *vs.* NHE, Fig. S2†) and $\mathbf{CoL^1}$ ($E_{onset} = -0.76$ V *vs.* NHE, Fig. S3†), indicating that PEI_6-Co can reduce CO_2 more easily than $\mathbf{Co_2L}$ and CoL.[1] Besides, the redox potential of photosensitizer $[Ru(phen)_3]^{3+/2+*}$ was reported as −0.84 V *vs.* NHE,[26] which is more negative than the onset potential of PEI_6-Co to CO_2 reduction, thus, it is feasible for $[Ru(phen)_3](PF_6)_2$ to donate electrons to PEI_6-Co under light irradiation, which is one of the foundations for driving the reduction of CO_2.

In addition, to examine the gathering ability of PEI_6-Co to CO_2, CO_2 adsorption experiment was carried out. As shown in Fig. 2a, PEI_6-Co has an adsorption capacity of 2.63 cm^3 g^{-1} towards CO_2. The IR spectra in Fig. 2b shows that after the treatment of CO_2 atmosphere, both PEI_6-Co and $\mathbf{Co_2L}$ have two peaks at 1628 cm^{-1} and 1473 cm^{-1}, which belong to the stretching vibrations of the carbonate group. All these results indicate that PEI_6-Co, just like the molecular catalyst binuclear cobalt $\mathbf{Co_2L}$, has the ability of adsorbing CO_2, which is favorable for the reduction of CO_2 in the heterogeneous catalysis process.

Encouraged by the positive results above, we optimized the atom ratio of N and Co in the catalysts for the reduction of CO_2. In the photoreaction system, the reaction solutions were prepared by adding photocatalyst PEI*x*-Co and photosensitizer $[Ru(phen)_3](PF_6)_2$ to CH_3CN/H_2O (v/v = 4 : 1) solutions with triethanolamine (TEOA) as a reducing agent. The quartz reaction bottle was sealed by the rubber tube and filled with CO_2 for 30 min, then, followed by the irradiation of a 450 nm LED light. With the increase of N/Co ratio in the catalyst, the yield of CO product shows a volcano-type trend (Table 1). The highest yield of 1170 mmol g^{-1} for CO is achieved when the ratio between N and Co reaches 6 : 1. This result indicates that the appropriate coordination structure is feasible for the reduction of CO_2. When the ratio of N/Co is low (entries 1 and 2), the uncoordinated N atoms is insufficient to adsorb CO_2. While too

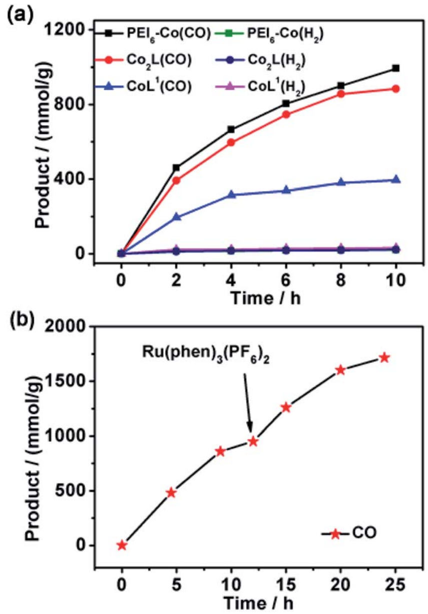

Fig. 3 (a) Comparison of photocatalytic carbon dioxide reduction yield of PEI_6-Co **Co_2L** and **CoL^1**. (b) Stability test of PEI_6-CO.

Table 2 Photocatalytic carbon dioxide reduction control experiment of PEI_6-CO

Entry	n_{H_2} (μmol)	n_{CO} (μmol)	Selectivity of CO (%)	Activity (mmol g^{-1})
1[a]	0	0.17	100%	34
2[b]	0	0	—	0
3[c]	0	0	—	0
4[d]	0	0	—	0
5[e]	0	0	—	0
6	0.34	5.84	95%	1170

[a] No PEI_6-Co. [b] No TEOA. [c] No photosensitizer. [d] No light. [e] 100% Ar.

much N atoms would saturate the cobalt center and prevent it from acting as an active center to catalyze CO_2 reduction (entries 4 and 5). Besides, in the liquid phase, only trace amount of formate (~0.4 μmol) was detected by ion chromatograph (Fig. S4†). In addition, photoreactions with different catalyst dosage show that the production of CO is a first order dependence on the concentration of PEI_6-Co (Fig. S5†).

To investigate the synergistic catalysis effect of PEI_6-Co, the reported dinuclear cobalt cryptate **Co_2L** and mononuclear cobalt **CoL^1** complex were chosen as the counterpoints and the photoreactions were carried out under similar conditions (the amount of Co ion was kept same in these catalysts). As shown in Fig. 3a, for PEI_6-Co, the CO product increased nonlinearly under the visible light irradiation, giving an activity of 1170 mmol g^{-1} for CO_2-to-CO conversion (Fig. 3a, black line). This value is almost 2.8 times of mononuclear cobalt catalyst **CoL^1** (416 mmol g^{-1}, Fig. 3a, blue line) and comparable with dinuclear cobalt catalyst **Co_2L** (884 mmol g^{-1}, Fig. 3a, red line), indicating that the easy-to-synthesized coordination polymer can also achieve the efficient reduction of CO_2 as elaborate molecular catalyst. It is worth noting that when the reaction time reaches 6 h, the evolution rate of CO slows down and even stop. We speculate that the instability of photosensitizer may be a cause of the reaction stopping. Thus we investigate the stability of $[Ru(phen)_3](PF_6)_2$ before and after the photoreaction using mass spectrometry. The results in Fig. S6 and S7† show that one phenanthroline ligand is substituted by two H_2O molecule after 10 h light irradiation and form $[Ru(phen)_2(H_2O)_2](PF_6)_2$, which has no effect for CO_2 reduction as photosensitizer. In addition, the tracking of UV-visible absorption spectrum of $[Ru(phen)_3](PF_6)_2$ shows that the absorbance of $[Ru(phen)_3](PF_6)_2$ decreases with the light irradiation (Fig. S8†). These results suggest that $[Ru(phen)_3](PF_6)_2$ decomposed with the light irradiation. In addition, we performed a cyclic stability test on the reaction system by re-adding the photosensitizer $[Ru(phen)_3](PF_6)_2$ to the stopped photoreactor. The results in Fig. 3b show that with the addition of extra $[Ru(phen)_3](PF_6)_2$, the photoreaction could restart and the evolution rate of CO is almost maintained, which suggests that the decomposition of $[Ru(phen)_3](PF_6)_2$ is the main fact for the reduced rate of CO evolution while PEI_6-Co is relatively stable as a photocatalyst for CO_2 conversion in water containing system.

To illustrate the role of each component in the photoreaction, a sequence of control experiments were carried out (Table 2). In the absence of PEI_6-Co, a little amount of CO generated (Table 2, entry 1), indicating that PEI_6-Co was significant to drive the reduction of CO_2 and $[Ru(phen)_3](PF_6)_2$ could catalyze the conversion of CO_2-to-CO weakly. Further control experiments suggested that the existence of $[Ru(phen)_3](PF_6)_2$, TEOA, and light was indispensable for the generation of CO (Table 2, entries 2–4). Additionally, when Ar was used as the substitution of CO_2 (Table 2, entries 5), no CO was detected in the photocatalytic system, indicating that the producing of CO was originated from the reduction of CO_2 instead of other organic components.

Conclusions

In summary, based on the synergic catalytic strategy of dinuclear cobalt, we designed and synthesized a transition metal coordination polymer PEI_6-Co and investigated its catalytic activity towards CO_2 reduction. The results show that because of the effective adsorption of CO_2 by PEI and the synergic catalytic effect of the adjacent cobalt active sites in PEI_6-Co, the conversion of CO_2-to-CO with high yield of 1170 mmol g^{-1} and selectivity of 95% were achieved in water containing medium. Such performance is almost 2.8 times of mononuclear cobalt catalyst **CoL^1** and comparable with dinuclear cobalt catalyst **Co_2L**. This work provides a prospective strategy for the transformation of molecular catalyst to heterogeneous catalyst in a convenient and cost-effective way.

Conflicts of interest

There are no conflicts to declare.

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