Photocatalytic System using Iron-Based Catalysts: Effect of External Ions on CO_2-to-CO Conversion

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Summary: Herein, we report four self-assembly Iron(II/III) complex consisting triethanolamine (TEOA) as ligand and an **$Fe^{III}(TPA)Cl_3$** (TPA= 3-(2-pyridine methyl) amine) as contrast catalyst, for photochemical reduction of CO_2 to CO under visible light. The photocatalytic systems were assembled by $[Ru(bpy)_3]Cl_2$ as photosensitizer, and 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo-[d]-imidazole (BIH) as electron donor. Experiments are conducted to study the relationship between CO production and the external ions. Different external counterions are provided to assist the discussion of the influence of these external ions on catalysis. Density functional theory calculations confirmed that the external ions have an effect on the CO yield. Moreover, a mechanism involving proton-coupled electron transfer is proposed.

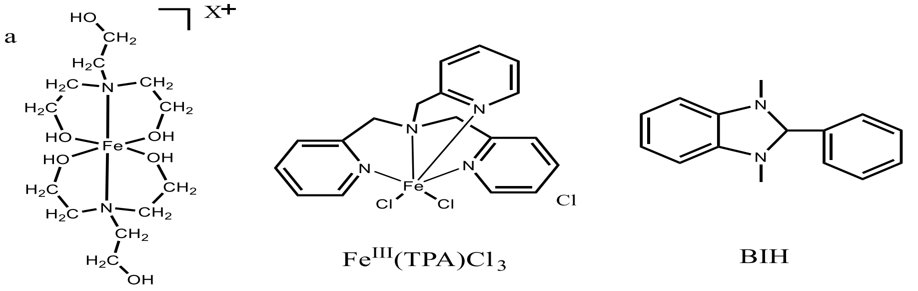
Key words: Photocatalytic, CO_2-to-CO conversion, External ions, Iron-Based Catalysts, Density functional theory.

Introduction

Visible-light-driven reduction of CO_2 to CO has been of considerable interest in the area of photochemistry for many years. Since Lehn et al. pioneering work in 1986, in which the photocatalytic reduction of CO_2 using Co polypyridine complexes in a homogeneous system [1], the development of low-cost, highly efficient and stable photocatalysts remains a constant challenge. Recent studies have mainly focused on the development of efficient and inexpensive photocatalytic systems. Molecular catalytic systems containing Fe complexes as catalysts have exhibited its potential for the photocatalytic reduction of CO_2. However, examination of the influence of external ions toward CO production using non-noble metal catalysts, such as Fe-based catalyst [2-6], is scarce and worthy further exploration. P. Neta *et al.* [7] and our group [8] reported $[Fe(TEOA)_2]Cl_2$ as catalysts and only a low efficiency of CO_2-CO conversion or hydrogen evolution was obtained. Herein, we utilized **[Ru]** ($[Ru(bpy)_3]Cl_2$) as PSs and BIH (1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo-[d]-im idazole) as sacrificial reductant for photocatalytic reduction CO_2 to CO. In this study, instead of focusing on the preparation of new photocatalysts, we concentrated on studying the simple Fe-based catalysts for the production of CO by tuning the external ions and valence state of Fe.

Experimental and discussion

The examined photocatalytic reactions employed Fe complexes with two kinds valence states, Fe(III) and Fe(II), and three anions Cl^-, Br^- and SO_4^{2-}, $Fe^{III}(TPA)Cl_3$. (TPA= 3-(2-pyridine methyl) amine) was prepared as a contrast catalyst. The following complexes were prepared and utilized as catalysts: $Fe^{III}(TEOA)_2Cl_3$; $Fe^{II}(TEOA)_2Cl_2$; $Fe^{III}(TEOA)_2Br_3$; $Fe^{II}(TEOA)_2SO_4$; $Fe^{III}(TPA)Cl$



$Fe^{III}(TPA)Cl_3$

BIH

Fig. 1: Structures of five catalysts and BIH: a. TEOA as the ligand, X=2 or 3, the anions are Cl^-, Br^- or SO_4^{2-}, respectively.

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Comparative experiments were studied using a variety of iron salts ($FeCl_3$, $FeCl_2\cdot 2H_2O$, $FeBr_3$ and $FeSO_4\cdot 7H_2O$). All experiments were performed in homogeneous solutions. DMF (N, N-Dimethylformamide) was used as solvent and mixed with TEOA in ratio of 1/5 (v/v, Fig. S1). In each of these experiments, 0.2 mM [Ru] was used as the photosensitizer. Since TEOA is a weak base (pK_a=7.8, in water), Fe ions are easily formed to polymeric hydroxides upon exposure to air. Accordingly, the reaction solutions were deoxygenated with argon before the addition of catalysts. The solution's pH (from 7.8 to 4.1) was adjusted via addition of CH_3COOH, as a consequence, the concentration of Fe polymeric hydroxides decreased, however, a decrease in catalytic efficiency occurred (Fig. S2). TEOA played multiple roles in the reaction process, acting as an electron donor [9] and CO_2 adsorbent [10], as well as a ligand [11-13]. TEOA coordinates with Fe^{3+} and Fe^{2+} in solutions and generates the TEOA complexes ($Fe^{III}(TEOA)_2Cl_3$, $Fe^{II}(TEOA)_2Cl_2$, $Fe^{III}(TEOA)_2Br_3$, and $Fe^{II}(TEOA)_2SO_4$), respectively. The solutions to be irradiated were firstly purged with CO_2 until saturated. The temperature of all solutions was controlled at room temperature using circulatory alcohol as the cooling liquid.

Fig 2 shows the photocatalytic production of CO with different Fe complexes as catalysts under visible light ($410 \leq \lambda \leq 750$ nm) irradiation. In the case of $Fe^{II}(TEOA)_2Cl_2$, its turnover number (TON) of 32 (109 μmol) for CO production was greater than the other studied complexes ($Fe^{III}(TEOA)_2Cl_3$ 28, $Fe^{III}(TEOA)_2Br_3$ 15.5 and $Fe^{II}(TEOA)_2SO_4$ 12.5) and $Fe^{III}(TPA)Cl_3$ (TPA = 3(2-pyridine methyl) amine, TON_{CO} = 18.5). Interestingly, when BIH (1,3-dimethyl-2-phenylbenzimidazoline) was added to the photocatalytic system using $Fe^{II}(TEOA)_2Cl_2$ as catalyst, TON of CO production increased 3-fold to 89 (303 μmol). The reason for this phenomenon is due to the BIH being a stronger electron-donor than TEOA [14]. Furthermore, a large excess of TEOA restrained the dissociation of TEOA ligand from the metal center, promoting the stability of the complex catalysts.

After 10 h of irradiation and reached the point where CO_2 no longer produces CO, for photocatalytic systems with $Fe^{II}(TEOA)_2Cl_2$ and $Fe^{III}(TEOA)_2Cl_3$ as catalysts, respectively, the same amount of photosensitizer [Ru] were reloaded, and in the comparative experiments, no [Ru] was added to the photocatalytic systems, only the $Fe^{III}(TEOA)_2Br_3$ and $Fe^{II}(TEOA)_2SO_4$ as catalysts are reloaded, respectively. Under CO_2 atmosphere, the catalysts $Fe^{II}(TEOA)_2Cl_2$ and $Fe^{III}(TEOA)_2Cl_3$ were added again into the same photocatalytic system with another 10 h of irradiation (Table S1), TON_{CO} (turnover of number) were 31 and 27.1 once again, respectively. Furthermore, when the other photocatalysts where subjected to the same experiment, CO production were not detected. This result indicates that catalysts $Fe^{II}(TEOA)_2Cl_2$ and $Fe^{III}(TEOA)_2Cl_3$ are durable during the photocatalytic process, and that the decomposition of [Ru], rather than catalysts, may be the major constraint limiting durability of the system. Hence, we can Fig out that the $Fe^{II}(TEOA)_2Cl_2$ and $Fe^{III}(TEOA)_2Cl_3$ could acted as photocatalysts for reduction of CO_2 with [Ru], and $Fe^{II}(TEOA)_2Cl_2$ was the most efficient one among these five complexes studied.

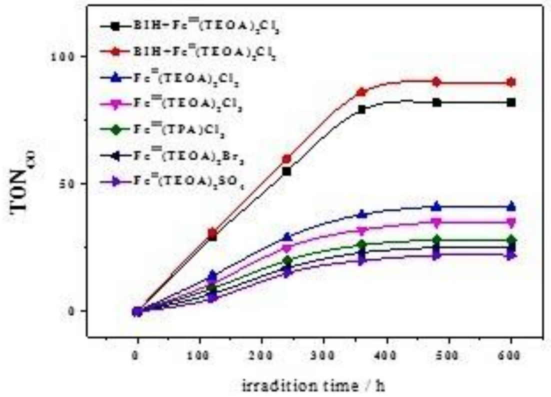


Fig. 2: Photocatalytic formation of CO formed from CO_2 as a function irradiation time: solution [TEOA/DMF =1/5(v/v)] that contained [Ru](0.2 mM) and one of Fe complexes (preprepared or self-assembled, 1.9 mM) or BIH (29 mM) and all of them saturated by CO_2. Solution were irradiated using a Xe lamp through filters and giving light within the scope of $410\leq \lambda \leq 750$ nm.

Isotopic labeling experiment using $^{13}CO_2$ as the substrate confirmed that the CO product originates from the photocatalytic conversion of CO_2 (Fig. S3).

The number of incident photons, measured using a classical iron ferrioxalate ($K_3Fe(C_2O_4)_3$) chemical actinometer, was 2.01×10^{24} photons per hour. According to quantum yield calculations [15] and using known parameters [16], the quantum yield of CO formation is Φ_{co} = 0.00072 %.

Fig 3 shows the electronic absorption spectra of [Ru] during photolysis in TEOA and DMF mixed solution, which was performed by UV-Vis spectrophotometry. The spectra shows the metal-to-ligand $d\pi \rightarrow \pi^*$ charge transition about 455 nm [17]. With the growth of the photolysis time, [Ru] decomposes rapidly in the absence of $FeCl_3$ (Fig A in Fig 3). However, $FeCl_3$ added to the system, the decomposition of [Ru] was sluggish (Fig B in Fig 3). As shown in the Fig 3, [Ru] is excited and reductively quenched by TEOA, whose concentration is at least 200 times higher than [Ru](0.2 mM [Ru] vs 50 mM TEOA at minimum).Since there is no CO generated when the system is absent of TEOA. We assume that BIH is only a more superior electron donor than TEOA, while TEOA is both a ligand and electron donor in the system. Also from the Fig 2, we could prove that Fe^{II} complex catalyst is superior to Fe^{III} complex since the approach for Fe^{II} to be reduced to Fe^{I} is easier. However, $FeCl_3$ is more stable and easier to save compare to $FeCl_2$, thus $FeCl_3$ seems to be more superior as catalyst scoure in this system. When $FeBr_3$ and $FeSO_4$ as catalyst source for photocatalytic performance, 12.4 and 10.3 TON are obtained respectively, these indicate that counter ions were shown to play an important role in governing the degree of Photocatalytic CO_2 to CO. Such dependence of Photocatalytic CO_2 to CO on the nature of the anions may be explored in the development of other Photocatalytic system.

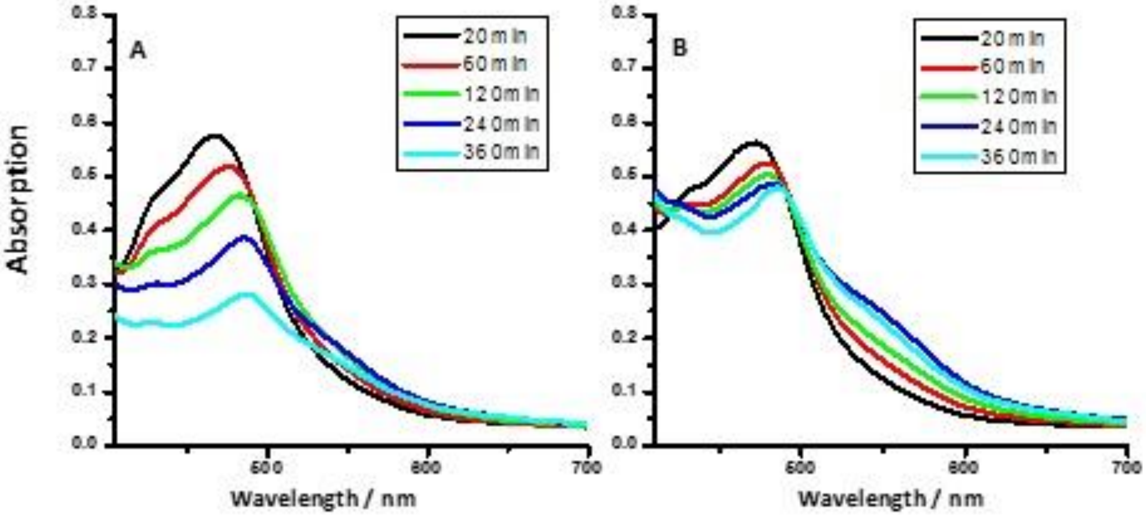


Fig. 3: The electronic absorption spectra at different irradiation times: [Ru](4×10^{-5} M) and solution is TEOA/DMF =1/5(v/v), A without and B with $FeCl_3$(1×10^{-5} M). Xe lamp through filters giving light within the scope of $410 \leq \lambda \leq 750$ nm.

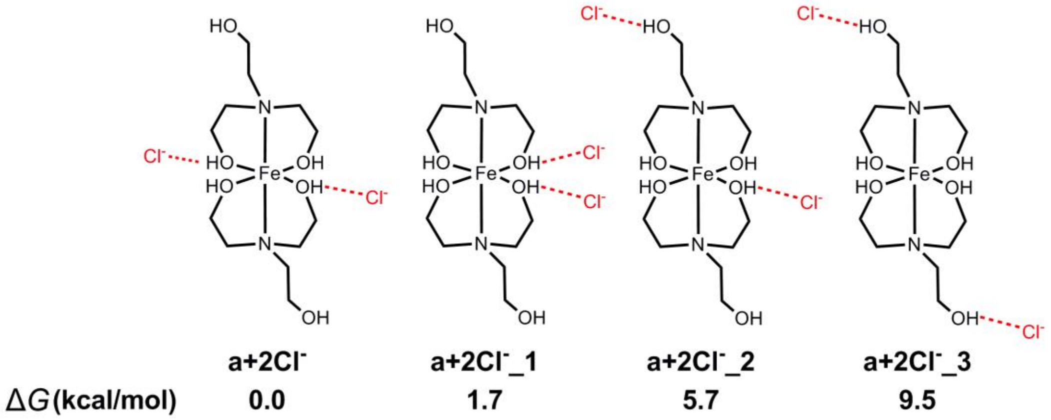


Fig 4: The relative stability of four kinds of structure for Chlorine ion couple with complexes in different positions in DMF.

As shown in Fig 5, when CO_2 was bonded to the complex's central metal, the energy band gap was 4.99 eV in the reaction if the Cl^- was involved. However, when the energy band gap was 5.09 eV, if the Cl^- was not involved. The difference between the values was 0.1 eV, which also proved that the reaction was more favorable when external ions were involved. Therefore, external ions were crucial in the photocatalytic reduction of CO_2, and could influence the overall outcome of the reaction.

Additionally, Cl^- in the complexes played an important role in CO_2 reduction. As shown in Fig 6, bond length stretched by 0.008~0.016 Å when different counter anions were coupled with the central metal in DMF. These results were consistent with the experimental results, where the catalytic effect of central Fe(II) metal with halogen ions, especially Cl^-, was superior. The results showed that when SO_4^{2-} coordinated with the complexes, the bond length reached a maximum of 2.056 Å, and therefore, bond cleavage occurred allowing CO_2 to attack the central ion and undergo reduction. However, $[Fe^{II}(TEOA)_2]SO_4$ catalyst was not optimal for CO_2 catalytic reduction, because the volume of SO_4^{2-} in its spatial structure was much larger than that of other external ions in the experiment. This created vast steric hindrance, making it very difficult for CO_2 to attack.

On the basis of the present work and previous results [18], and according to previous literature reports [19], the process of Fe(III) to Fe(II) is a rapid process during the photocatalytic system, and the key catalytic step is the combination of Fe(I) with carbon dioxide, hence, we propose the following mechanism (Scheme 1). In the lower Fe oxidation state, one CO_2 are attached to Fe, then by a three proton and four electron (PCET) process, H_2 and CO are generated, meanwhile, the Fe catalyst are regenerated. Among these five Fe catalysts, the catalysts with chloridion as the external ions, $Fe^{III}(TEOA)_2Cl_3$ and $Fe^{II}(TEOA)_2Cl_2$ have better catalytic effect.

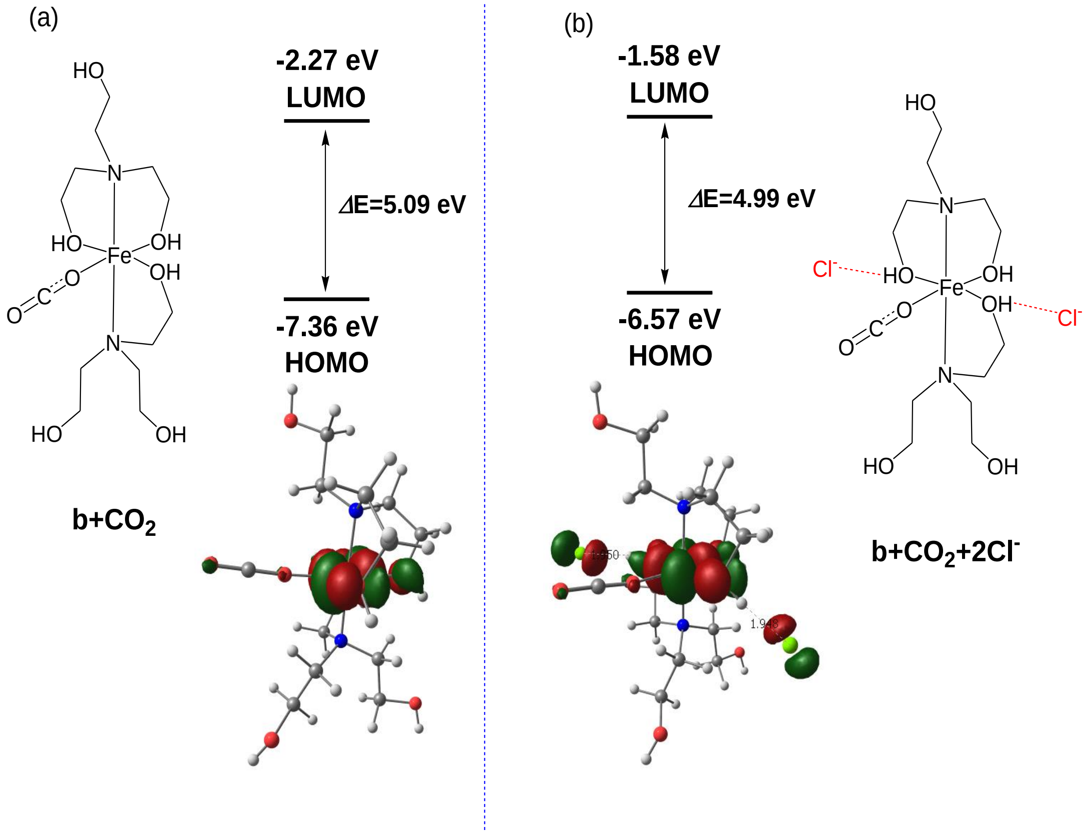
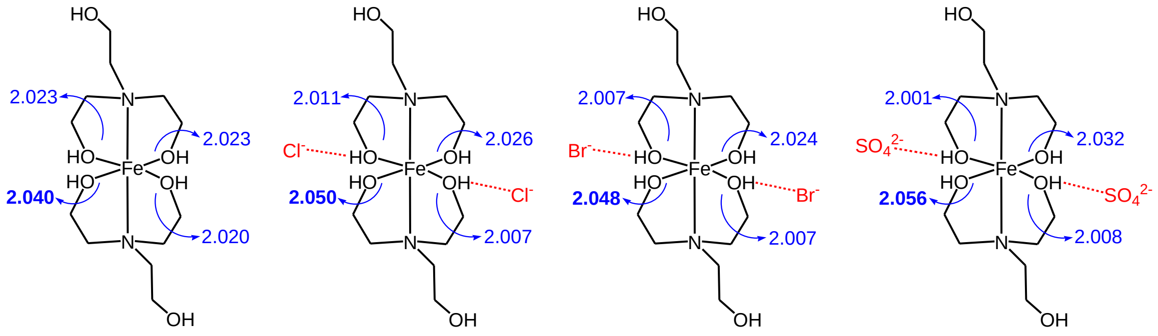
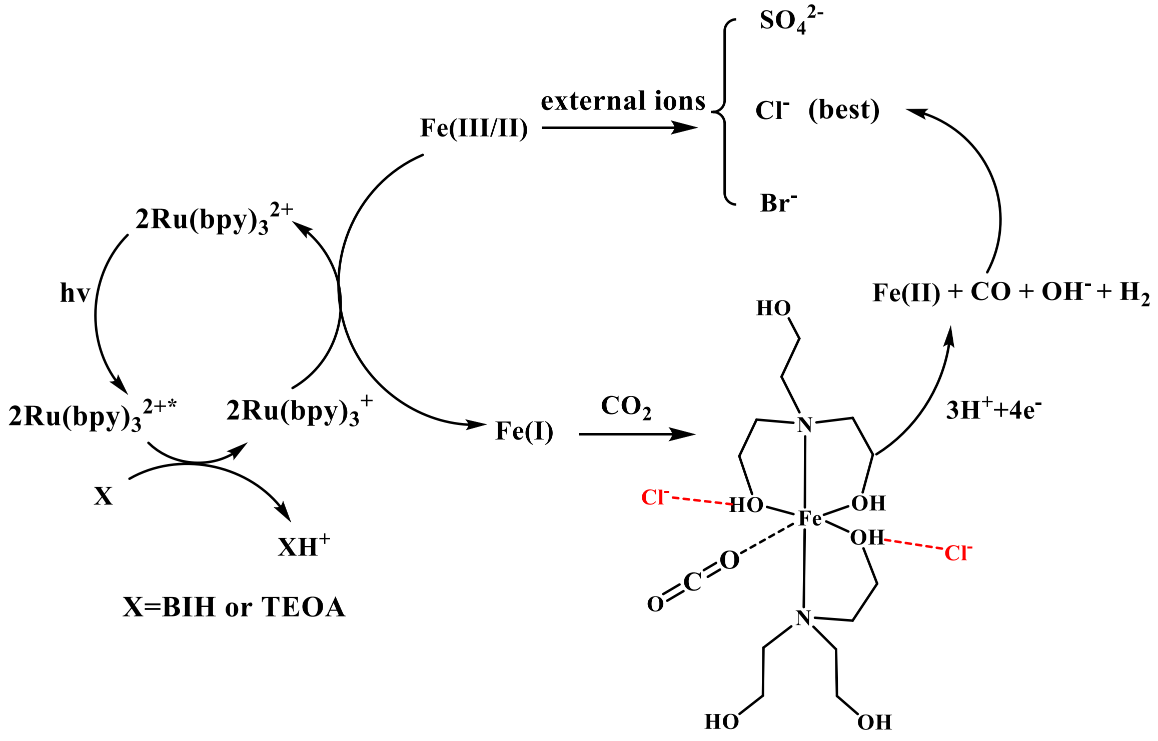


Fig. 5: Iso-grams and HOMO and LUMO orbital energies of $Fe(TEOA)_2$ bonded to CO_2 without external Cl^- involvement (a) and with external Cl^- involvement (b).



a **a+2Cl⁻** **a+2Br⁻** **a+2SO₄²⁻**

Fig. 6: The change of bond length when different counter anions couple with the central metal in DMF.



Scheme-1: Proposed mechanism for the photosensitized Catalytic reduction of CO_2 to CO.

Conclusions

In conclusion, we investigated the effect of external ions on the photocatalytic reduction of CO_2 to CO using several Fe-based homogeneous catalysts. The photocatalytic systems are irradiated under visible light ($410 \leq \lambda \leq 750$ nm). All catalysts are easily prepared or self-assembled. During photocatalytic CO_2 reduction, the catalysts maintains activity probably due to the superfluous TEOA in the system that restrains its dissociation.

The presented photocatalytic systems are simple, where CO production over 10 h occurs with a TONs of ca. 89 for CO is obtained (negligible amount of H_2 is formed). Based on experiments and calculations, Different external counterions were proved to have different effects in governing the degree of photocatalytic CO_2 to CO. These results are significant for the preparation of photocatalysts, provided reference for the selection of external ions.

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