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EDGE ARTICLE

Efficient photocatalytic carbon monoxide production from ammonia and carbon dioxide by the aid of artificial photosynthesis

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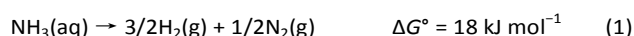
Ammonium bicarbonate (NH₄HCO₃) was generated by the absorption of carbon dioxide (CO₂) into an aqueous solution of ammonia (NH₃). NH₄HCO₃ was successfully used to achieve highly efficient photocatalytic conversion of CO₂ to carbon monoxide (CO). NH₃ and/or ammonium ions (NH₄⁺) derived from NH₄HCO₃ in aqueous solution were decomposed into nitrogen (N₂) and hydrogen (H₂). Stoichiometric amounts of the N₂ oxidation product and the CO and H₂ reduction products were generated when the photocatalytic reaction was carried out in aqueous NH₄HCO₃ solution. NH₃ and/or NH₄⁺ functioned as electron donors in the photocatalytic conversion of CO₂ to CO. A CO formation rate of 0.5 mmol h⁻¹ was obtained using 500 mg of catalyst (approximately 7500 ppm) in ambient conditions (303 K, 101.3 kPa). Our results demonstrated that NH₄HCO₃ is a novel inorganic sacrificial reagent, which can be used to increase the efficiency of photocatalytic CO production to achieve one step CO₂ capture, storage and conversion.

Introduction

The production of chemical feedstocks and hydrocarbon fuels from CO₂ is a promising approach to alleviate the global energy crisis and global warming.¹ Conversion of CO₂ to CO using clean and renewable solar energy is the first step to store energy in chemicals because CO can be further converted into other highly valuable chemicals using the Fischer–Tropsch process.² A variety of heterogeneous and homogeneous photocatalysts have been reported to achieve the conversion of CO₂ to CO.^{3–5} However, the formation rate of CO has been limited to a few tens of μmol h⁻¹ or hundreds of μmol h⁻¹ g⁻¹ because of the high energy barrier to CO₂ reduction and inefficient light utilization.^{6,7} Furthermore, CO₂ is not easily adsorbed onto catalytic surfaces nor activated by photoirradiation because of its high thermodynamic stability. This further reduces the efficiency of the photocatalytic conversion of CO₂.

Water (H₂O) is widely used as an electron donor in the photocatalytic conversion of CO₂ to CO.^{7–12} However, the overall water splitting into H₂ and O₂ is more thermodynamically favorable than the reduction of CO₂ in aqueous solution. Hence, CO₂ reduction competes with overall water splitting. Moreover, the solubility of CO₂ in pure H₂O is only 0.033 mol L⁻¹ (at 298 K and 101.3 kPa),¹³ which further

limits the efficiency of CO₂ conversion by H₂O using heterogeneous photocatalysts. Therefore, it would be meaningful to find a readily available, highly efficient, and abundant in nature and industries electron donor (sacrificial reagent) other than water for the photocatalytic conversion of CO₂. NH₃ and NH₄⁺ in aqueous solution can be readily oxidized to N₂, NO₂⁻, and NO₃⁻ using a photocatalyst.^{14–17} The decomposition of aqueous NH₃ to H₂ and N₂ requires a standard Gibbs free energy change ΔG° of 18 kJ mol⁻¹ (Equation (1)).¹⁸ This is significantly smaller than that required for the decomposition of H₂O to H₂ and O₂ (237 kJ mol⁻¹; Equation (2)).



Because the photocatalytic oxidation of NH₃ and NH₄⁺ is significantly more favorable than the oxidation of H₂O to O₂,¹⁸ it is possible to use NH₃ and NH₄⁺ as electron donors in the photocatalytic conversion of CO₂. Moreover, NH₃ has been considered for use as an efficient post-combustion CO₂ capture and storage (CCS) reagent because of its high absorption efficiency and loading capacity.¹⁹ The absorption and capture of CO₂ by an aqueous solution of NH₃ results in the formation of NH₄HCO₃.²⁰ Other basic species, such as NaHCO₃ and KHCO₃, have been used to increase the solubility of CO₂ in aqueous solutions.^{21,22} Previous reports have suggested that dissolved CO₂, rather than bicarbonate (HCO₃⁻) or carbonate (CO₃²⁻) ions, is the active species in the reduction of CO₂.^{23,24} Correspondingly, the conversion of CO₂ and/or the selectivity toward CO evolution have been significantly enhanced by the presence of bases in both photocatalytic (PC)

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and photoelectrochemical (PEC) cell systems.^{25, 26} In the present study, we designed the use of NH_4HCO_3 for the efficient photocatalytic conversion of CO_2 to CO in H_2O .

Results and discussion

Flux-mediated crystal growth method shows the advantage of the synthetic control over particle sizes, morphologies, and surface features comparing with that of solid-state reaction method (SSR).²⁷ Modification of these features as a function of flux conditions have been reported to show significant enhancements in both water splitting and CO_2 photoreduction.^{11, 27, 28} $\text{Sr}_2\text{KTa}_5\text{O}_{15}$ has been reported to show good conversion of CO_2 and selectivity toward CO evolution when used as a photocatalyst in the conversion of CO_2 by H_2O in our previous work.²⁹ In the present study, $\text{Sr}_2\text{KTa}_5\text{O}_{15}$ was fabricated by a modified flux method, using a mixture of NaCl and KCl as the flux. The resultant catalyst was confirmed to have tetragonal tungsten bronze (TTB) structure (Figure S1A), and its real chemical formula was determined to be $\text{Sr}_{1.6}\text{K}_{0.35}\text{Na}_{1.45}\text{Ta}_5\text{O}_{15}$ using ICP-OES. Its morphology was observed by SEM, and was found to consist of a mixture of nanorods and nanoparticles (Figure S1B).

Figure 1 shows the time courses of the photocatalytic conversion of CO_2 in H_2O and aqueous solutions of NaHCO_3 and NH_4HCO_3 . In pure H_2O , only 16.8 μmol of CO was evolved after 5 h of photoirradiation (Figure 1A), and the main reduction product was H_2 (139.0 μmol). These results were consistent with previous reports.^{25, 29} In this system, overall water splitting proceeded more readily than CO_2 reduction, resulting in the generation of H_2 as the major product, rather than CO . The amount of CO evolved in 0.1 M aqueous NaHCO_3 solution after 5 h of photoirradiation (448.7 μmol) was 26.7 times higher than that evolved in pure H_2O (Figure 1B). However, the formation of H_2 (94.7 μmol) was not significantly affected by NaHCO_3 . Thus, NaHCO_3 greatly enhanced the conversion of CO_2 to CO without affecting the water splitting process.²⁵ In both pure H_2O and 0.1 M aqueous NaHCO_3 , stoichiometric amounts of O_2 were evolved continuously during the reaction, implying that H_2O functioned as an electron donor in the reduction of CO_2 . Moreover, the

evolution of CO increased dramatically in 0.1 M aqueous NH_4HCO_3 solution; 1600 μmol (1.6 mmol) of CO was evolved after 5 h of photoirradiation (Figure 1C). This is 94.2 times greater than the amount evolved in pure H_2O . The selectivity of the reaction toward CO evolution was calculated and the details were shown in supporting information. The selectivity toward CO evolution in 0.1 M aqueous NH_4HCO_3 (86.2%) was similar to that in aqueous NaHCO_3 (82.5%). The production of gaseous products was negligible in blank tests conducted without either a catalyst or photoirradiation (Figure S2A and B). Thus, both are necessary for the photocatalytic conversion of CO_2 to CO to proceed. Without Ag cocatalyst, H_2 was formed as main product (Figure 2C), both of N_2 and O_2 were detected as oxidation products, however, the amount of these gases was far beyond the stoichiometric amount. Tiny amount of CO was formed after 5-hour photoirradiation (14.9 μmol). Ag cocatalysts were important in photocatalytic conversion of CO_2 to CO , which is thought to be the active sites. H_2 , CO , and N_2 were obtained without a continuous CO_2 flow (Figure S2D). However, H_2 was generated as a major product, suggesting a very low selectivity toward CO evolution (less than 30%). This suggested that CO_2 presence significantly increases the selectivity of the photocatalytic conversion of CO_2 toward CO evolution in NH_4HCO_3 solution. NH_4HCO_3 can be formed directly by the absorption of CO_2 in an aqueous solution of NH_3 ; wherein H_2 and CO can be produced from CO_2 and NH_3 via artificial photosynthesis. Thus, our designed system can achieve carbon capture and utilization (CCU) in a single process.

N_2 , rather than O_2 , was generated as the oxidation product during photoirradiation in the presence of NH_4HCO_3 (Figure 1C). This demonstrated that H_2O did not function as an electron donor in this system. Instead, NH_3 and/or NH_4^+ functioned as electron donors, because the ΔG° of NH_3 (aq) oxidation (18 kJ mol^{-1}) is significantly lower than that of water oxidation (237 kJ mol^{-1}). Analysis of the liquid phase showed that neither NO_2^- nor NO_3^- were present during photoirradiation (Figure S3). Other gaseous NO_x products, such as N_2O and NO , were not detected by gas chromatography (GC). These results indicated that NH_3 and/or NH_4^+ were oxidized only to N_2 in this photocatalytic system. Hence, by

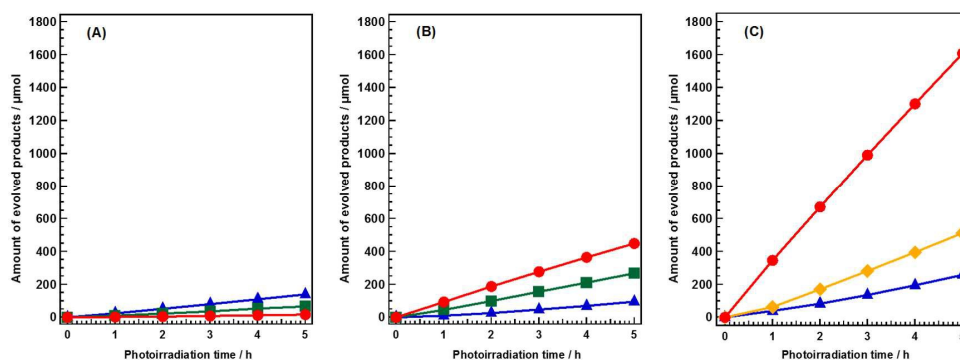


Figure 1 Time courses of CO (circle), O_2 (square), N_2 (lozenge), and H_2 (triangle) evolutions during the photocatalytic conversion of CO_2 over Ag -modified $\text{Sr}_{1.6}\text{K}_{0.35}\text{Na}_{1.45}\text{Ta}_5\text{O}_{15}$. Amount of catalyst: 0.5 g; cocatalyst loading: 1.0 wt.% Ag ; light source: 400 W high-pressure Hg lamp; water volume: 1.0 L; CO_2 flow rate: 30 mL min^{-1} ; additive: (A) none, (B) 0.1 M NaHCO_3 , or (C) 0.1 M NH_4HCO_3 .



Table 1 Photocatalytic conversion of CO₂ over Ag-modified Sr_{1.6}K_{0.35}Na_{1.45}Ta₅O₁₅ with different additive concentrations. Amount of catalyst: 0.5 g; cocatalyst loading: 1.0 wt.% Ag; light source: 400 W high-pressure Hg lamp; water volume: 1.0 L; CO₂ flow rate: 30 mL min⁻¹.

| Entry | NH ₄ HCO ₃ / M ^[a] | Formation rate / μmol h ⁻¹ ^[b] | | | | Selec. (%) ^[c] | e ⁻ /h ⁺ ^[d] |
|------------------|---|--|----------------|----------------|-------|---------------------------|---|
| | | H ₂ | O ₂ | N ₂ | CO | | |
| 1 | 0 | 35.9 | 16.3 | trace | 3.6 | 9.2 | 1.21 |
| 2 | 0.01 | 16.9 | 7.0 | 12.3 | 54.5 | 76.3 | 1.17 |
| 3 | 0.05 | 23.8 | trace | 42.3 | 146.7 | 86.1 | 1.34 |
| 4 | 0.1 | 48.4 | trace | 94.3 | 270.4 | 84.8 | 1.13 |
| 5 | 0.5 | 119.8 | trace | 193.6 | 512.9 | 81.1 | 1.09 |
| 6 | 0.8 | 175.4 | trace | 213.3 | 520.0 | 74.8 | 1.09 |
| 7 | 1.0 | 290.1 | trace | 258.1 | 550.7 | 65.5 | 1.09 |
| 8 ^[e] | - | 235.0 | trace | 244.9 | 547.2 | 70.0 | 1.06 |

^[a]Additive concentration used for CO₂ conversion. ^[b]Formation rate after 5 h of irradiation. ^[c]Selectivity toward CO evolution. ^[d]Ratio of consumed electrons to holes after 5 h of irradiation. ^[e]0.5 M aqueous NH₃ solution was used as the additive, instead of NH₄HCO₃.

using NH₄HCO₃, we succeeded in controlling the oxidation product, in addition to enhancing the conversion of CO₂.

The ratio of electrons to holes consumed in the photocatalytic conversion of CO₂ was calculated to be 2.0 after 1 h of photoirradiation (Figure S4). Given that the total number of electrons generated must be the same as the number of holes, this ratio indicates that significantly more electrons were consumed than holes in the initial stages of photoirradiation. We noted that the state of Ag was changed from metallic to Ag⁺ on the surface of catalyst measured by XPS (Figure S5), however, it might be not the main reason for the excess of electron consumption. We calculated that if all Ag⁰ was changed to Ag⁺ in the first hour, the consumed holes were still only 469 μmol, which was much less than the consumed electrons (770 μmol). NH₄⁺ can be reduced to NH₃ and •H by photogenerated electrons. Hydrazine (N₂H₄) has been determined to be an intermediate species in the photocatalytic decomposition of NH₃ and/or NH₄⁺ to H₂ and N₂ using Pt/TiO₂.¹⁴ Stoichiometric amounts of products, including H₂ and N₂, were not obtained in the initial stages of photoirradiation due to the formation of hydrazine. In our system, it is also possible to form hydrazine at the beginning, however, hydrazine is reported to be reacted with CO₂ to form zwitterionic intermediate and carbamate-type species,³⁰ which made the detection of intermediate oxidation species much more difficult. Nevertheless, stoichiometric amounts of products were obtained after 2 h of photoirradiation (Figure S4), indicating that the total decomposition of NH₃ and/or NH₄⁺ occurred sooner.

The above results demonstrate that the highly efficient photocatalytic conversion of CO₂ to CO was achieved in our system. The stoichiometric amounts of H₂, N₂ and CO generated indicated that NH₃ and/or NH₄⁺ functioned as electron donors in the photocatalytic conversion of CO₂. Significantly greater photocatalytic activity was obtained using NH₃ and/or NH₄⁺, compared to reactions using H₂O as an electron donor under the same conditions. NH₃ and/or NH₄⁺ are suitable for use in practical applications because NH₃ is

industrially produced in large quantities. Furthermore, in our photocatalytic system, NH₃ and/or NH₄⁺ can be completely decomposed to N₂, which is an inert and non-toxic gas.

Table 1 shows the effects of NH₄HCO₃ concentration on the photocatalytic conversion of CO₂. In pure H₂O, overall water splitting proceeded as the dominant reaction. Hence, the evolution of CO was negligible (Entry 1). When the photocatalytic reaction was carried out in 0.01 M aqueous NH₄HCO₃ the production of H₂ resulting from water splitting was dramatically suppressed (Entry 2). Because the oxidation of NH₃ and/or NH₄⁺ to N₂ proceeds more readily than the oxidation of H₂O to O₂, the formation rate of O₂ in 0.01 M aqueous NH₄HCO₃ was less than half that in pure H₂O. Even low concentrations of NH₄HCO₃ (0.01 M) significantly increased the formation rate of CO, indicating that the presence of NH₄HCO₃ is vital to achieving high photocatalytic activity. NH₄HCO₃ can also be used to increase the pH of the reaction solution, to offset the decrease in pH caused by the dissolution of CO₂. With CO₂ flowing, the pH of the reaction solution based on pure H₂O was 3.95, which increased to 5.88 with the addition of 0.01 M NH₄HCO₃. Increasing the pH also increases the amount of CO₂ that can be dissolved in the reaction solution.³¹ Generally, the formation rate of CO increases with increasing pH, because the reaction rate largely depends on the concentration of substrate. Therefore, the addition of NH₄HCO₃ contributed to the efficient conversion of CO₂ and the good selectivity toward CO evolution. Increasing the concentration of NH₄HCO₃ from 0.01 M to 0.05 M completely suppressed the overall water splitting reaction, since only N₂ was generated as an oxidation product (Entry 3). The formation rate of CO increased with the concentration of NH₄HCO₃. Increasing the NH₄HCO₃ concentration from 0.1 M to 1.0 M increased the formation rate of CO to 550.7 μmol h⁻¹ except the selectivity toward CO evolution decreased slightly, from 86.1% to 65.5% (Entry 4 to 7). As previously discussed, NH₄HCO₃ can be synthesized by flowing CO₂ through an aqueous solution of NH₃. To determine whether NH₃ functions as an electron donor under a flow of CO₂, we carried out the



photocatalytic conversion of CO₂ in an aqueous solution of NH₃ (Entry 8). The formation rate of CO was 547.2 μmol h⁻¹ in *ca.* 0.5 M aqueous NH₃, indicating that NH₃ functions efficiently as an electron donor under these conditions. The ratio of photogenerated electrons to holes (e⁻/h⁺) was estimated to be around 1.0 in reactions with high concentrations of aqueous NH₄HCO₃ after 5 h of photoirradiation. This further supports the hypothesis that NH₃ and/or NH₄⁺ function as effective electron donors during the photocatalytic conversion of CO₂.

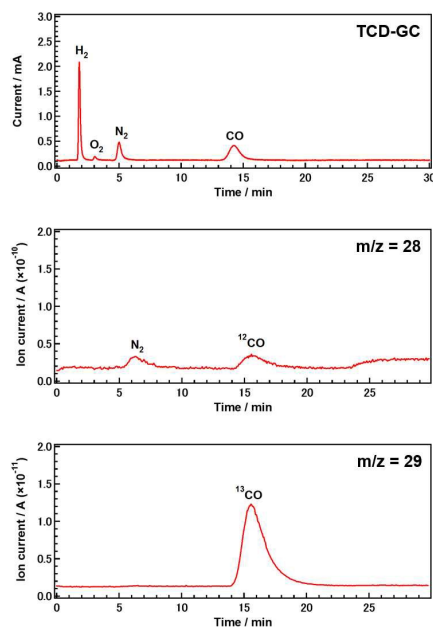


Figure 2 Gas chromatogram and mass spectra ($m/z = 28$ and 29) obtained during the photocatalytic conversion of $^{13}\text{CO}_2$ using Ag-modified $\text{Sr}_{1.6}\text{K}_{0.35}\text{Na}_{1.45}\text{Ta}_5\text{O}_{15}$. Amount of catalyst: 0.5 g; cocatalyst loading: 5.0 wt.% Ag; light source: 400 W high-pressure Hg lamp; water volume: 1.0 L; CO₂ flow rate: 30 mL min⁻¹; additive: 0.5 M NH₄HCO₃.

To confirm that CO evolution originated from CO₂ introduced in the gas phase, rather than from carbon contaminants, we conducted an isotopic labeling experiment. Figure 2 shows mass spectra ($m/z = 28$ and 29) obtained during the photocatalytic conversion of $^{13}\text{CO}_2$ in 0.5 M aqueous NH₄HCO₃ over Ag-modified $\text{Sr}_{1.6}\text{K}_{0.35}\text{Na}_{1.45}\text{Ta}_5\text{O}_{15}$ after 0.5 h of photoirradiation. Gaseous samples were introduced into a

mass spectrometer (MS) after separation by thermal conductivity detector-gas chromatography (TCD-GC). CO was observed in both the gas chromatogram and the mass spectra. The peak positions in the mass spectra were consistent with those in the chromatogram. The major product was ^{13}CO , rather than ^{12}CO . The presence of a small amount of ^{12}CO may be due to the direct decomposition of NH₄HCO₃ since the decomposition of NH₄HCO₃ was observed in samples without a CO₂ flow (Figure S2C). The amount of ^{13}CO estimated by mass spectrometry was approximately equal to the amount of CO determined using a flame ionization detector (FID-GC) (Figure S6). These results demonstrate that CO was predominantly generated from CO₂ introduced in the gas phase, rather than from other carbon resources.

The recycle test was also performed to confirm the stability and durability of our catalyst and system using the $\text{Sr}_{1.6}\text{K}_{0.35}\text{Na}_{1.45}\text{Ta}_5\text{O}_{15}$ photocatalyst repeatedly for three times under the same conditions (Figure S7). In the second cycle, there is a slight loss by *ca.* 10% of CO evolution activity during 5 h photoirradiation as compared to the first run, however, the evolution of H₂ showed no obvious changes. The slight loss of activity should be due to the change of Ag cocatalyst (Figure S5).²⁹ The photocatalytic activity of CO, N₂, and H₂ were stabilized at *ca.* 0.5, 0.19 and 0.07 mmol h⁻¹, respectively, during the second and third runs. The structure of catalyst itself was stable during the three cycles (Figure S8). These results suggested that the photocatalyst and the system exhibit favorable stability to form CO, N₂, and H₂ during the photocatalytic conversion of CO₂.

To confirm the versatility of NH₄HCO₃ as a general electron donor in photocatalytic reactions, we carried out the photocatalytic conversion of CO₂ in aqueous NH₄HCO₃ solution over 4 types of photocatalysts. All these photocatalysts have been already reported to show good activity and high selectivity toward CO evolution in the photocatalytic conversion of CO₂ using H₂O as an electron donor.^{25, 32-34} As shown in Table 2, all the photocatalysts showed good activity for conversion of CO₂ and high selectivity toward CO evolution. The activities of the photocatalysts were significantly increased in aqueous NH₄HCO₃ solution, compared with their reported activities in pure H₂O or aqueous NaHCO₃.³²⁻³⁴ N₂ was detected as the only oxidation product and the e⁻/h⁺ ratio was approximately equal to 1.0. These results indicated that NH₃ and/or NH₄⁺ was easily decomposed to N₂ gas by the

Table 2 Photocatalytic conversion of CO₂ over Ag-modified catalysts in aqueous NH₄HCO₃ solution. Amount of catalyst: 0.5 g; cocatalyst loading: 5.0 wt.% Ag; light source: 400 W high-pressure Hg lamp; water volume: 0.95 L; CO₂ flow rate: 30 mL min⁻¹; additive: 0.5 M NH₄HCO₃.

| Entry | Catalyst | Formation rate / μmol h ⁻¹ [a] | | | Selec. (%) ^[b] | e ⁻ /h ⁺ [c] |
|-------|--|---|----------------|-------|---------------------------|------------------------------------|
| | | H ₂ | N ₂ | CO | | |
| 1 | ZnGa ₂ O ₄ /Ga ₂ O ₃ | 125.2 | 191.4 | 532.0 | 80.9 | 1.14 |
| 2 | ZnGa ₂ O ₄ | 39.4 | 94.2 | 305.4 | 88.6 | 1.22 |
| 3 | La ₂ Ti ₂ O ₇ | 5.9 | 17.4 | 41.6 | 87.6 | 0.91 |
| 4 | SrO/Ta ₂ O ₅ | 2.71 | 11.5 | 42.9 | 94.1 | 1.32 |

^[a]Formation rate after 5 h of irradiation. Trace of O₂ was detected in the samples. ^[b]Selectivity toward CO evolution. ^[c]Ratio of consumed electrons to holes after 5 h of irradiation.



photocatalysts tested.

Conclusions

We designed a highly efficient process for the photocatalytic conversion of CO₂ to CO in aqueous NH₄HCO₃ solution. The stoichiometric formation of CO, H₂, and N₂ indicated that NH₃ and/or NH₄⁺ were consumed as electron donors, instead of H₂O. NH₄HCO₃ was determined to be an effective electron donor for the photocatalytic conversion of CO₂, whereby CO₂ can be captured, stored, and efficiently converted into CO. This novel inorganic additive is suitable for use in carbon capture and utilization process. This new process is a promising way to control the conversion of CO₂ to CO and efficiently produce H₂ and CO.

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NH_4HCO_3 was determined to be an effective electron donor for the photocatalytic conversion of CO_2 , whereby CO_2 can be captured, stored, and efficiently converted into CO .

