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 (eqn (1)).¹⁸ This is significantly smaller than that required for the decomposition of H₂O to H₂ and O₂ (237 kJ mol⁻¹; eqn (2)).

\[
\text{NH}_3(aq) \rightarrow \frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{N}_2(g) \Delta G° = 18 \text{ kJ mol}^{-1} \quad (1)
\]

\[
\text{H}_2\text{O}(l) \rightarrow \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \Delta G° = 237 \text{ kJ mol}^{-1} \quad (2)
\]

Because the photocatalytic oxidation of NH₃ and NH₄⁺ is significantly more favorable than the oxidation of H₂O to O₂,¹⁹ 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

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† Electronic supplementary information (ESI) available: Experimental details, calculations and characterizations. See DOI: 10.1039/c7sc01851g
solutions. Previous reports have suggested that dissolved CO2, rather than bicarbonate (HCO3-) or carbonate (CO32-) ions, is the active species in the reduction of CO2. 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) and photoelectrochemical (PEC) cell systems. In the present study, we designed the use of NH4HCO3 for the efficient photocatalytic conversion of CO2 to CO in H2O.

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). Modification of these features as a function of flux conditions have been reported to show significant enhancements in both water splitting and CO2 photoreduction. Sr2KTa5O15 has been reported to show good activity and selectivity toward CO evolution when used as a photocatalyst in the conversion of CO2 by H2O in our previous work. In this system, overall water splitting proceeds with 5 h of photoirradiation (Fig. 1A), and the main reduction product was H2 (139.0 mol). These results were consistent with previous reports. In this system, overall water splitting proceeded more readily than CO2 reduction, resulting in the generation of H2 as the major product, rather than CO. The amount of CO evolved in 0.1 M aqueous NaHCO3 solution after 5 h of photoirradiation (448.7 μmol) was 26.7 times higher than that evolved in pure H2O (Fig. 1B). However, the formation of H2 (94.7 μmol) was not significantly affected by NaHCO3. Thus, NaHCO3 greatly enhanced the conversion of CO2 to CO without affecting the water splitting process. In both pure H2O and 0.1 M aqueous NaHCO3, stoichiometric amounts of O2 were evolved continuously during the reaction, implying that H2O functioned as an electron donor in the reduction of CO2. Moreover, the evolution of CO increased dramatically in 0.1 M aqueous NH4HCO3 solution; 1600 μmol (1.6 mmol) of CO was evolved after 5 h of photoirradiation (Fig. 1C). This is 94.2 times greater than the amount evolved in pure H2O. The selectivity of the reaction toward CO evolution was calculated and the details were shown in ESI. The selectivity toward CO evolution in 0.1 M aqueous NH4HCO3 (86.2%) was similar to that in aqueous NaHCO3 (82.5%). The production of gaseous products was negligible in blank tests conducted without either a catalyst or photoirradiation. Thus, both are necessary for the photocatalytic conversion of CO2 to CO to proceed. Without Ag cocatalyst, H2 was formed as main product (Fig. S2F), both of N2 and O2 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 CO2 to CO, which is thought to be the active sites. H2, CO, and N2 were obtained without a continuous CO2 flow (Fig. S2D). However, H2 was generated as a major product, suggesting a very low selectivity toward CO evolution (less than 30%). This suggested that CO2 presence significantly increases the selectivity of the photocatalytic conversion of CO2 toward CO evolution in NH4HCO3 solution. NH4HCO3 can be formed directly by the absorption of CO2 in an aqueous solution of NH3, wherein H2 and CO can be produced from CO2 and NH3 via artificial photosynthesis. Thus, our designed system can achieve carbon capture and utilization (CCU) in a single process.

N2, rather than O2, was generated as the oxidation product during photoirradiation in the presence of NH4HCO3 (Fig. 1C). This demonstrated that H2O did not function as an electron donor in this system. Instead, NH3 and/or NH4+ functioned as electron donors, because the ΔG° of NH3(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 NO2- nor NO3- was detected as oxidation products.
nor NO$_3^-$ were present during photoirradiation (Fig. S3†). Other gaseous NO$_x$ products, such as N$_2$O 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 using NH$_4$HCO$_3$, we succeeded in controlling the oxidation product, in addition to enhancing the conversion of CO$_2$.

The ratio of electrons to holes consumed in the photocatalytic conversion of CO$_2$ was calculated to be 2.0 after 1 h of photoirradiation (Fig. S4†). Given that the total number of electrons generated must be the same as the number of holes, this ratio indicates that 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 (Fig. S5†), however, it might be not the main reason for the excess of electron consumption. We calculated that if all Ag$^0$ was changed to Ag$^+$, the ratio of electrons to holes consumed in the photo-catalytic conversion of CO$_2$ was less than half that in pure H$_2$O. Even low concentrations of NH$_4$HCO$_3$ (0.01 M) significantly increased the formation rate of CO, indicating that the presence of NH$_4$HCO$_3$ is vital to achieving high photocatalytic activity. NH$_4$HCO$_3$ can also be used to increase the pH of the reaction solution, to offset the decrease in pH caused by the dissolution of CO$_2$. With CO$_2$ flowing, the pH of the reaction solution based on pure H$_2$O was 3.95, which increased to 5.88 with the addition of 0.01 M NH$_4$HCO$_3$. Increasing the pH also increases the amount of CO$_2$ that can be dissolved in the reaction solution.$^{23}$ 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 NH$_4$HCO$_3$ contributed to the efficient conversion of CO$_2$ and the good selectivity toward CO evolution. Increasing the concentration of NH$_4$HCO$_3$ from 0.01 M to 0.05 M completely suppressed the overall water splitting reaction, since only N$_2$ was generated as an oxidation product (entry 3). The formation rate of CO increased with the concentration of NH$_4$HCO$_3$. Increasing the NH$_4$HCO$_3$ concentration from 0.1 M to 1.0 M increased the formation rate of CO to 550.7 $\mu$mol h$^{-1}$ except the selectivity toward CO evolution decreased slightly, from 86.1% to 65.5% (entry 4 to 7). As previously discussed, NH$_4$HCO$_3$ can be synthesized by flowing CO$_2$ through an aqueous solution of NH$_3$. To determine whether NH$_3$ functions as an electron donor under a flow of CO$_2$, we carried out the photocatalytic conversion of CO$_2$ in an aqueous solution of NH$_3$ (entry 8). The formation rate of CO was 547.2 $\mu$mol h$^{-1}$ in ca. 0.5 M aqueous NH$_3$, indicating that NH$_3$ 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 NH$_4$HCO$_3$ after 5 h of photoirradiation. This further supports the hypothesis that NH$_3$ and/or NH$_4^+$ function as effective electron donors during the photocatalytic conversion of CO$_2$.

To confirm that CO evolution originated from CO$_2$ introduced in the gas phase, rather than from carbon contaminants, we conducted an isotopic labeling experiment. Fig. 2 shows mass spectra (m/z = 28 and 29) obtained during the photocatalytic conversion of $^{13}$CO$_2$ in 0.5 M aqueous NH$_4$HCO$_3$ over Ag-

Table 1 Photocatalytic conversion of CO$_2$ over Ag-modified Sr$_{1.6}$-K$_{0.35}$Na$_{1.45}$Ta$_5$O$_{15}$ 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; CO$_2$ flow rate: 30 mL min$^{-1}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>NH$_4$HCO$_3$/M</th>
<th>H$_2$</th>
<th>O$_2$</th>
<th>N$_2$</th>
<th>CO</th>
<th>Selectivity (%)</th>
<th>e$^-$/h$^+$</th>
</tr>
</thead>
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<td>16.3</td>
<td>Trace</td>
<td>3.6</td>
<td>9.2</td>
<td>1.21</td>
</tr>
<tr>
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<td>0.01</td>
<td>16.9</td>
<td>7.0</td>
<td>12.3</td>
<td>54.5</td>
<td>76.3</td>
<td>1.17</td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>23.8</td>
<td>Trace</td>
<td>42.3</td>
<td>146.7</td>
<td>86.1</td>
<td>1.34</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>48.4</td>
<td>Trace</td>
<td>94.3</td>
<td>270.4</td>
<td>84.8</td>
<td>1.13</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>119.8</td>
<td>Trace</td>
<td>193.6</td>
<td>512.9</td>
<td>81.1</td>
<td>1.09</td>
</tr>
<tr>
<td>6</td>
<td>0.8</td>
<td>175.4</td>
<td>Trace</td>
<td>213.3</td>
<td>520.0</td>
<td>74.8</td>
<td>1.09</td>
</tr>
<tr>
<td>7</td>
<td>1.0</td>
<td>290.1</td>
<td>Trace</td>
<td>258.1</td>
<td>550.7</td>
<td>65.5</td>
<td>1.09</td>
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<td>8</td>
<td>—</td>
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<td>Trace</td>
<td>244.9</td>
<td>547.2</td>
<td>70.0</td>
<td>1.06</td>
</tr>
</tbody>
</table>

$^a$ Additive concentration used for CO$_2$ 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 NH$_3$ solution was used as the additive, instead of NH$_4$HCO$_3$. 

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modified Sr$_{1.6}$K$_{0.35}$Na$_{1.45}$Ta$_5$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 $^{13}$CO may be due to the direct decomposition of NH$_4$HCO$_3$ since the decomposition of NH$_3$HCO$_3$ was observed in samples without a CO$_2$ flow (Fig. S2D†). 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) (Fig. S6†). These results demonstrate that CO was predominantly generated from CO$_2$ 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 Sr$_{1.6}$K$_{0.35}$Na$_{1.45}$Ta$_5$O$_{15}$ photocatalyst repeatedly for three times under the same conditions (Fig. 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 H$_2$ showed no obvious changes. The slight loss of activity should be due to the change of Ag cocatalyst (Fig. S5†). The photocatalytic activity of CO, N$_2$, and H$_2$ 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 (Fig. S8†). These results suggested that the photocatalyst and the system exhibit favorable stability to form CO, N$_2$, and H$_2$ during the photocatalytic conversion of CO$_2$.

To confirm the versatility of NH$_4$HCO$_3$ as a general electron donor in photocatalytic reactions, we carried out the photocatalytic conversion of CO$_2$ in aqueous NH$_4$HCO$_3$ 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 CO$_2$ using H$_2$O as an electron donor.$^{25,32–34}$ As shown in Table 2, all the photocatalysts showed good activity for conversion of CO$_2$ and high selectivity toward CO evolution. The activities of the photocatalysts were significantly increased in aqueous NH$_4$HCO$_3$ solution, compared with their reported activities in pure H$_2$O or aqueous NaHCO$_3$. N$_2$ was detected as the only oxidation product and the e$^-$/h$^+$ ratio was approximately equal to 1.0. These results indicated that NH$_3$ and/or NH$_4^+$ was easily decomposed to N$_2$ gas by the photocatalysts tested.

**Table 2** Photocatalytic conversion of CO$_2$ over Ag-modified catalysts in aqueous NH$_4$HCO$_3$ solution. 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; CO$_2$ flow rate: 30 mL min$^{-1}$; additive: 0.5 M NH$_4$HCO$_3$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>H$_2$</th>
<th>N$_2$</th>
<th>CO</th>
<th>Selectivity (%)</th>
<th>e$^-$/h$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZnGa$_2$O$_4$/Ga$_2$O$_3$</td>
<td>125.2</td>
<td>191.4</td>
<td>532.0</td>
<td>80.9</td>
<td>1.14</td>
</tr>
<tr>
<td>2</td>
<td>ZnGa$_2$O$_4$</td>
<td>39.4</td>
<td>94.2</td>
<td>305.4</td>
<td>88.6</td>
<td>1.22</td>
</tr>
<tr>
<td>3</td>
<td>La$_5$Ti$_2$O$_7$</td>
<td>5.9</td>
<td>17.4</td>
<td>41.6</td>
<td>87.6</td>
<td>0.91</td>
</tr>
<tr>
<td>4</td>
<td>Sr/Ta$_2$O$_3$</td>
<td>2.71</td>
<td>11.5</td>
<td>42.9</td>
<td>94.1</td>
<td>1.32</td>
</tr>
</tbody>
</table>

$^a$ Form rate after 5 h of irradiation. O$_2$ was not detected in any of the samples. $^b$ Selectivity toward CO evolution. $^c$ Ratio of consumed electrons to holes after 5 h of irradiation.

**Conclusions**

We designed a highly efficient process for the photocatalytic conversion of CO$_2$ to CO in aqueous NH$_4$HCO$_3$ solution. The stoichiometric formation of CO, H$_2$, and N$_2$ indicated that NH$_3$ and/or NH$_4^+$ were consumed as electron donors, instead of H$_2$O. NH$_4$HCO$_3$ 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. 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 CO$_2$ to CO and efficiently produce H$_2$ and CO.

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Notes and references

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