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. 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. A variety of heterogeneous and homogeneous photocatalysts have been reported to achieve the conversion of CO2 to CO. 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. 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. 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), 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. The decomposition of aqueous NH3 to H2 and N2 requires a standard Gibbs free energy change ΔG° of 18 kJ mol⁻¹ (eqn (1)) which is significantly smaller than that required for the decomposition of H2O to H2 and O2 (237 kJ mol⁻¹; eqn (2)).

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

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

Because the photocatalytic oxidation of NH3 and NH4+ is significantly more favorable than the oxidation of H2O to O2, 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. The absorption and capture of CO2 by an aqueous solution of NH3 results in the formation of NH4HCO3. Other basic species, such as NaHCO3 and KHCO3, have been used to increase the solubility of CO2 in aqueous...
solutions. Previous reports have suggested that dissolved $\text{CO}_2$, rather than bicarbonate ($\text{HCO}_3^-$) or carbonate ($\text{CO}_3^{2-}$) ions, is the active species in the reduction of $\text{CO}_2$. Correspondingly, the conversion of $\text{CO}_2$ and/or the selectivity toward $\text{CO}$ 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 $\text{NH}_3\text{HCO}_3$ for the efficient photocatalytic conversion of $\text{CO}_2$ to $\text{CO}$ in $\text{H}_2\text{O}$.

### 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 $\text{CO}_2$ photoreduction. $\text{Sr}_2\text{K}_3\text{Ta}_5\text{O}_{15}$ has been reported to show good activity and selectivity toward $\text{CO}$ evolution when used as a photocatalyst in the conversion of $\text{CO}_2$ by $\text{H}_2\text{O}$ in our previous work. In the present study, $\text{Sr}_2\text{K}_3\text{Ta}_5\text{O}_{15}$ 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 (Fig. S1‡), 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 (Fig. S1B†).

Fig. 1 shows the time courses of the photocatalytic conversion of $\text{CO}_2$ in $\text{H}_2\text{O}$ and aqueous solutions of $\text{NaHCO}_3$ and $\text{NH}_4\text{HCO}_3$. In pure $\text{H}_2\text{O}$, only 16.8 mmol of CO was evolved after 5 h of photoirradiation (Fig. 1A), and the main reduction product was $\text{H}_2$ (139.0 μmol). These results were consistent with previous reports. In this system, overall water splitting proceeded more readily than $\text{CO}_2$ reduction, resulting in the generation of $\text{H}_2$ as the major product, rather than $\text{CO}$. The amount of $\text{CO}$ evolved in 0.1 M aqueous $\text{NaHCO}_3$ solution after 5 h of photoirradiation (448.7 μmol) was 26.7 times higher than that evolved in pure $\text{H}_2\text{O}$ (Fig. 1B). However, the formation of $\text{H}_2$ (94.7 μmol) was not significantly affected by $\text{NaHCO}_3$. Thus, $\text{NaHCO}_3$ greatly enhanced the conversion of $\text{CO}_2$ to $\text{CO}$ without affecting the water splitting process. In both pure $\text{H}_2\text{O}$ and 0.1 M aqueous $\text{NaHCO}_3$, stoichiometric amounts of $\text{O}_2$ were evolved continuously during the reaction, implying that $\text{H}_2\text{O}$ functioned as an electron donor in the reduction of $\text{CO}_2$. Moreover, the evolution of $\text{CO}$ increased dramatically in 0.1 M aqueous $\text{NH}_4\text{HCO}_3$ solution; 1600 μmol (1.6 mmol) of $\text{CO}$ was evolved after 5 h of photoirradiation (Fig. 1C). This is 94.2 times greater than the amount evolved in pure $\text{H}_2\text{O}$. The selectivity of the reaction toward $\text{CO}$ evolution was calculated and the details were shown in ESI.† The selectivity toward $\text{CO}$ evolution in 0.1 M aqueous $\text{NH}_4\text{HCO}_3$ (86.2%) was similar to that in aqueous $\text{NaHCO}_3$ (82.5%). The production of gaseous products was negligible in blank tests conducted without either a catalyst or photoirradiation (Fig. S2A and B†). Thus, both are necessary for the photocatalytic conversion of $\text{CO}_2$ to $\text{CO}$ to proceed. Without Ag cocatalyst, $\text{H}_2$ was formed as main product (Fig. S2C†), both of $\text{N}_2$ and $\text{O}_2$ were detected as oxidation products, however, the amount of these gases was far beyond the stoichiometric amount. Tiny amount of $\text{CO}$ was formed after 5 hour photoirradiation (14.9 μmol). Ag cocatalysts were important in photocatalytic conversion of $\text{CO}_2$ to $\text{CO}$, which is thought to be the active sites. $\text{H}_2$, $\text{CO}$, and $\text{N}_2$ were obtained without a continuous $\text{CO}$ flow (Fig. S2D†). However, $\text{H}_2$ was generated as a major product, suggesting a very low selectivity toward $\text{CO}$ evolution (less than 30%). This suggested that $\text{CO}_2$ presence significantly increases the selectivity of the photocatalytic conversion of $\text{CO}_2$ toward $\text{CO}$ evolution in $\text{NH}_4\text{HCO}_3$ solution. $\text{NH}_4\text{HCO}_3$ can be formed directly by the absorption of $\text{CO}_2$ in an aqueous solution of $\text{NH}_3$; wherein $\text{H}_2$ and $\text{CO}$ can be produced from $\text{CO}_2$ and $\text{NH}_3$ via artificial photosynthesis. Thus, our designed system can achieve carbon capture and utilization (CCU) in a single process.

$\text{N}_2$, rather than $\text{O}_2$, was generated as the oxidation product during photoirradiation in the presence of $\text{NH}_4\text{HCO}_3$ (Fig. 1C). This demonstrated that $\text{H}_2\text{O}$ did not function as an electron donor in this system. Instead, $\text{NH}_3$ and/or $\text{NH}_4^+$ functioned as electron donors, because the $\Delta G$ of $\text{NH}_4^+(aq)$ 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 $\text{NO}_2$...
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 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 (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$^+$ in the first hour, the consumed holes were still only 469 μmol, which was much less than the consumed electrons (770 μmol). NH$_4^+$ can be reduced to NH$_3$ and ‘H’ by photogenerated electrons. Hydrazine (N$_2$H$_2$) has been determined to have been an intermediate species in the photocatalytic decomposition of NH$_3$ and/or NH$_4^+$ to H$_2$ and N$_2$ using Pt/TiO$_2$. Stoichiometric amounts of products, including H$_2$ and N$_2$, 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 reactivated with CO$_2$ to form zwitterionic intermediate and carbamate-type species, which made the detection of intermediate oxidation species much more difficult. Nevertheless, stoichiometric amounts of products were obtained after 2 h of photoirradiation (Fig. S4†), indicating that the total decomposition of NH$_3$ and/or NH$_4^+$ occurred sooner.

The above results demonstrate that the highly efficient photocatalytic conversion of CO$_2$ to CO was achieved in our system. The stoichiometric amounts of H$_2$, N$_2$ and CO generated indicated that NH$_3$ and/or NH$_4^+$ functioned as electron donors in the photocatalytic conversion of CO$_2$. Significantly greater photocatalytic activity was obtained using NH$_3$ and/or NH$_4^+$, compared to reactions using H$_2$O as an electron donor under the same conditions. NH$_3$ and/or NH$_4^+$ are suitable for use in practical applications because NH$_3$ is industrially produced in large quantities. Furthermore, in our photocatalytic system, NH$_3$ and/or NH$_4^+$ can be completely decomposed to N$_2$, which is an inert and non-toxic gas.

Table 1 shows the effects of NH$_4$HCO$_3$ concentration on the photocatalytic conversion of CO$_2$. In pure H$_2$O, 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 NH$_4$HCO$_3$ the production of H$_2$ resulting from water splitting was dramatically suppressed (entry 2). Because the oxidation of NH$_3$ and/or NH$_4^+$ to N$_2$ proceeds more readily than the oxidation of H$_2$O to O$_2$, the formation rate of O$_2$ in 0.01 M aqueous NH$_4$HCO$_3$ 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. 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 μmol 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 μmol 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-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>Selec.$^c$ (%)</th>
<th>e$^-$/h$^+$$^d$</th>
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<tr>
<td>1</td>
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<td>Trace</td>
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<td>146.7</td>
<td>86.1</td>
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<td>84.8</td>
<td>1.13</td>
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<td>0.5</td>
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<td>74.8</td>
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<td>1.0</td>
<td>290.1</td>
<td>Trace</td>
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<td>550.7</td>
<td>65.5</td>
<td>1.09</td>
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<td>—</td>
<td>235.0</td>
<td>Trace</td>
<td>244.9</td>
<td>547.2</td>
<td>70.0</td>
<td>1.06</td>
</tr>
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</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 Sr1.6K0.35Na1.45Ta5O15 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 13CO, rather than 12CO. The presence of a small amount of 12CO may be due to the direct decomposition of NH4HCO3 since the decomposition of NH4HCO3 was observed in samples without a CO2 flow (Fig. S2D†). The amount of 13CO 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 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 Sr1.6K0.35Na1.45Ta5O15 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 H2 showed no obvious changes. The slight loss of activity should be due to the change of Ag cocatalyst (Fig. 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 (Fig. 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.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>H2</th>
<th>N2</th>
<th>CO</th>
<th>Selectivity (%)</th>
<th>e−/h+</th>
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<tr>
<td>1</td>
<td>ZnGa2O4/Ga2O3</td>
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<td>191.4</td>
<td>532.0</td>
<td>80.9</td>
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<td>39.4</td>
<td>94.2</td>
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<td>La2Ti2O7</td>
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<td>17.4</td>
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<tr>
<td>4</td>
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<td>11.5</td>
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<td>94.1</td>
<td>1.32</td>
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</table>

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.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 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 NH4+ was 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.

Acknowledgements

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Notes and references

27 J. Boltersdorf, N. King and P. A. Maggard, CrystEngComm, 2015, 17, 2225–2241.