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### **EDGE ARTICLE**

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

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Ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>) was generated by the absorption of carbon dioxide (CO<sub>2</sub>) into an aqueous solution of ammonia (NH<sub>3</sub>). NH<sub>4</sub>HCO<sub>3</sub> was successfully used to achieve highly efficient photocatalytic conversion of CO<sub>2</sub> to carbon monoxide (CO). NH<sub>3</sub> and/or ammonium ions (NH<sub>4</sub><sup>+</sup>) derived from NH<sub>4</sub>HCO<sub>3</sub> in aqueous solution were decomposed into nitrogen (N<sub>2</sub>) and hydrogen (H<sub>2</sub>). Stoichiometric amounts of the N<sub>2</sub> oxidation product and the CO and H<sub>2</sub> reduction products were generated when the photocatalytic reaction was carried out in aqueous NH<sub>4</sub>HCO<sub>3</sub> solution. NH<sub>3</sub> and/or NH<sub>4</sub><sup>+</sup> functioned as electron donors in the photocatalytic conversion of CO<sub>2</sub> to CO. A CO formation rate of 0.5 mmol h<sup>-1</sup> was obtained using 500 mg of catalyst (approximately 7500 ppm) in ambient conditions (303 K, 101.3 kPa). Our results demonstrated that NH<sub>4</sub>HCO<sub>3</sub> is a novel inorganic sacrificial reagent, which can be used to increase the efficiency of photocatalytic CO production to achieve one step CO<sub>2</sub> capture, storage and conversion.

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#### Introduction

The production of chemical feedstocks and hydrocarbon fuels from  $CO_2$  is a promising approach to alleviate the global energy crisis and global warming.¹ Conversion of  $CO_2$  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  $CO_2$  to  $CO.^{3-5}$  However, the formation rate of CO has been limited to a few tens of  $\mu$ mol  $h^{-1}$  or hundreds of  $\mu$ mol  $h^{-1}$  g<sup>-1</sup> because of the high energy barrier to  $CO_2$  reduction and inefficient light utilization. $^{6,7}$  Furthermore,  $CO_2$  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  $CO_2$ .

Water  $(H_2O)$  is widely used as an electron donor in the photocatalytic conversion of  $CO_2$  to  $CO.^{7-12}$  However, the overall water splitting into  $H_2$  and  $O_2$  is more thermodynamically favorable than the reduction of  $CO_2$  in aqueous solution. Hence,

CO<sub>2</sub> reduction competes with overall water splitting. Moreover, the solubility of CO<sub>2</sub> in pure  $\rm H_2O$  is only 0.033 mol  $\rm L^{-1}$  (at 298 K and 101.3 kPa),<sup>13</sup> which further limits the efficiency of CO<sub>2</sub> conversion by  $\rm H_2O$  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 CO<sub>2</sub>. NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> in aqueous solution can be readily oxidized to N<sub>2</sub>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup> using a photocatalyst. <sup>14-17</sup> The decomposition of aqueous NH<sub>3</sub> to H<sub>2</sub> and N<sub>2</sub> requires a standard Gibbs free energy change  $\Delta G^{\circ}$  of 18 kJ mol<sup>-1</sup> (eqn (1)). <sup>18</sup> This is significantly smaller than that required for the decomposition of H<sub>2</sub>O to H<sub>2</sub> and O<sub>2</sub> (237 kJ mol<sup>-1</sup>; eqn (2)).

$$NH_3(aq) \rightarrow \frac{3}{2}H_2(g) + \frac{1}{2}N_2(g) \Delta G^\circ = 18 \text{ kJ mol}^{-1}$$
 (1)

$${\rm H_2O(l)} \to {\rm H_2(g)} + {\scriptstyle \frac{1}{2}{\rm O_2(g)}} \ \Delta G^{\circ} = 237 \ {\rm kJ \ mol^{-1}}$$
 (2)

Because the photocatalytic oxidation of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> is significantly more favorable than the oxidation of H<sub>2</sub>O to O<sub>2</sub>, <sup>18</sup> it is possible to use NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> as electron donors in the photocatalytic conversion of CO<sub>2</sub>. Moreover, NH<sub>3</sub> has been considered for use as an efficient post-combustion CO<sub>2</sub> capture and storage (CCS) reagent because of its high absorption efficiency and loading capacity. <sup>19</sup> The absorption and capture of CO<sub>2</sub> by an aqueous solution of NH<sub>3</sub> results in the formation of NH<sub>4</sub>HCO<sub>3</sub>. <sup>20</sup> Other basic species, such as NaHCO<sub>3</sub> and KHCO<sub>3</sub>, have been used to increase the solubility of CO<sub>2</sub> in aqueous

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solutions.21,22 Previous reports have suggested that dissolved CO<sub>2</sub>, rather than bicarbonate (HCO<sub>3</sub><sup>-</sup>) or carbonate (CO<sub>3</sub><sup>2-</sup>) 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) and photoelectrochemical (PEC) cell systems. 25,26 In the present study, we designed the use of NH<sub>4</sub>HCO<sub>3</sub> for the efficient photocatalytic conversion of CO<sub>2</sub> to CO in H<sub>2</sub>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).27 Modification of these features as a function of flux conditions have been reported to show significant enhancements in both water splitting and CO2 photoreduction. 11,27,28 Sr<sub>2</sub>KTa<sub>5</sub>O<sub>15</sub> has been reported to show good activity and selectivity toward CO evolution when used as a photocatalyst in the conversion of CO<sub>2</sub> by H<sub>2</sub>O in our previous work.<sup>29</sup> In the present study, Sr<sub>2</sub>KTa<sub>5</sub>O<sub>15</sub> 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. S1A†), and its real chemical formula was determined to be Sr<sub>1.6</sub>K<sub>0.35</sub>Na<sub>1.45</sub>Ta<sub>5</sub>O<sub>15</sub> 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 CO2 in H2O and aqueous solutions of NaHCO3 and NH<sub>4</sub>HCO<sub>3</sub>. In pure H<sub>2</sub>O, only 16.8 μmol of CO was evolved after 5 h of photoirradiation (Fig. 1A), and the main reduction product was H<sub>2</sub> (139.0 µmol). These results were consistent with previous reports.<sup>25,29</sup> In this system, overall water splitting proceeded more readily than CO2 reduction, resulting in the generation of H<sub>2</sub> 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 H<sub>2</sub>O (Fig. 1B). However, the formation of H<sub>2</sub> (94.7 µmol) was not significantly affected by NaHCO3. Thus,

NaHCO<sub>3</sub> greatly enhanced the conversion of CO<sub>2</sub> to CO without affecting the water splitting process.25 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 CO<sub>2</sub>. Moreover, the evolution of CO increased dramatically in 0.1 M aqueous NH<sub>4</sub>HCO<sub>3</sub> 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 NH<sub>4</sub>HCO<sub>3</sub> (86.2%) was similar to that in aqueous NaHCO<sub>3</sub> (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 CO<sub>2</sub> to CO to proceed. Without Ag cocatalyst, H<sub>2</sub> was formed as main product (Fig. S2C†), both of N<sub>2</sub> and O<sub>2</sub> 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 conversation of CO<sub>2</sub> to CO, which is thought to be the active sites. H2, CO, and N2 were obtained without a continuous CO<sub>2</sub> flow (Fig. S2D†). However, H<sub>2</sub> was generated as a major product, suggesting a very low selectivity toward CO evolution (less than 30%). This suggested that CO<sub>2</sub> 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 NH<sub>3</sub>; wherein H<sub>2</sub> and CO can be produced from CO<sub>2</sub> and NH<sub>3</sub> via artificial photosynthesis. Thus, our designed system can achieve carbon capture and utilization (CCU) in a single process.

N<sub>2</sub>, rather than O<sub>2</sub>, was generated as the oxidation product during photoirradiation in the presence of NH<sub>4</sub>HCO<sub>3</sub> (Fig. 1C). This demonstrated that H2O did not function as an electron donor in this system. Instead, NH<sub>3</sub> and/or NH<sub>4</sub> functioned as electron donors, because the  $\Delta G^{\circ}$  of NH<sub>3</sub>(aq) oxidation (18 kJ mol<sup>-1</sup>) is significantly lower than that of water oxidation (237 kJ mol<sup>-1</sup>). Analysis of the liquid phase showed that neither NO<sub>2</sub>

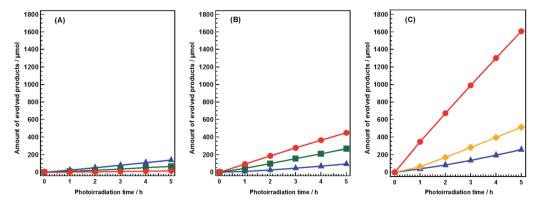


Fig. 1 Time courses of CO (circle), O2 (square), N2 (lozenge), and H2 (triangle) evolutions during the photocatalytic conversion of CO2 over Agmodified Sr<sub>1.6</sub>K<sub>0.35</sub>Na<sub>1.45</sub>Ta<sub>5</sub>O<sub>15</sub>. Amount of catalyst: 0.5 g; cocatalyst loading: 1.0 wt% Ag; light source: 400 W high-pressure Hg lamp; water volume: 1.0 L; CO<sub>2</sub> flow rate: 30 mL min<sup>-1</sup>; additive: (A) none, (B) 0.1 M NaHCO<sub>3</sub>, or (C) 0.1 M NH<sub>4</sub>HCO<sub>3</sub>.

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nor  $\mathrm{NO_3}^-$  were present during photoirradiation (Fig. S3†). Other gaseous  $\mathrm{NO_x}$  products, such as  $\mathrm{N_2O}$  and  $\mathrm{NO}$ , were not detected by gas chromatography (GC). These results indicated that  $\mathrm{NH_3}$  and/or  $\mathrm{NH_4}^+$  were oxidized only to  $\mathrm{N_2}$  in this photocatalytic system. Hence, by using  $\mathrm{NH_4HCO_3}$ , we succeeded in controlling the oxidation product, in addition to enhancing the conversion of  $\mathrm{CO_2}$ .

The ratio of electrons to holes consumed in the photocatalytic conversion of CO2 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<sup>+</sup> 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<sup>0</sup> was changed to Ag<sup>+</sup> in the first hour, the consumed holes were still only 469 µmol, which was much less than the consumed electrons (770 µmol). NH<sub>4</sub><sup>+</sup> can be reduced to NH<sub>3</sub> and 'H by photogenerated electrons. Hydrazine (N2H4) has been determined to be an intermediate species in the photocatalytic decomposition of NH<sub>3</sub> and/or NH<sub>4</sub><sup>+</sup> to H<sub>2</sub> and N<sub>2</sub> using Pt/TiO<sub>2</sub>. 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 CO<sub>2</sub> 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 (Fig. S4†), indicating that the total decomposition of NH<sub>3</sub> and/ or NH<sub>4</sub><sup>+</sup> 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  $H_2O$  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  $NH_4HCO_3$  concentration on the photocatalytic conversion of  $CO_2$ . In pure  $H_2O$ , 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  $NH_4HCO_3$  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  $H_2O$  to  $O_2$ , the formation rate of  $O_2$  in 0.01 M aqueous  $NH_4HCO_3$  was less than half that in pure  $H_2O$ . Even low concentrations of  $NH_4HCO_3$  (0.01 M) significantly increased the formation rate of  $CO_3$  indicating that the presence of  $NH_4HCO_3$ 

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 H<sub>2</sub>O was 3.95, which increased to 5.88 with the addition of 0.01 M NH<sub>4</sub>HCO<sub>3</sub>. Increasing the pH also increases the amount of CO<sub>2</sub> 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 NH<sub>4</sub>HCO<sub>3</sub> contributed to the efficient conversion of CO<sub>2</sub> 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 NH<sub>4</sub>HCO<sub>3</sub>. Increasing the NH<sub>4</sub>HCO<sub>3</sub> concentration from 0.1 M to 1.0 M increased the formation rate of CO to 550.7  $\mu$ mol h<sup>-1</sup> except the selectivity toward CO evolution decreased slightly, from 86.1% to 65.5% (entry 4 to 7). As previously discussed, NH<sub>4</sub>HCO<sub>3</sub> can be synthesized by flowing CO<sub>2</sub> 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  $\mu$ mol h<sup>-1</sup> 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<sup>-</sup>/h<sup>+</sup>) was estimated to be around 1.0 in reactions with high concentrations of aqueous NH<sub>4</sub>HCO<sub>3</sub> after 5 h of photoirradiation. This further supports the hypothesis that NH<sub>3</sub> and/or NH<sub>4</sub><sup>+</sup> function as effective electron donors during the photocatalytic conversion of CO<sub>2</sub>.

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  $NH_4HCO_3$  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 $^{-1}$ 

		Forma	tion rate	0.1. (			
Entry	NH <sub>4</sub> HCO <sub>3</sub> <sup>a</sup> /M	$H_2$	$O_2$	$N_2$	СО	Selec. <sup>c</sup> (%)	$e^-/h^{+d}$
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

<sup>&</sup>lt;sup>a</sup> Additive concentration used for CO<sub>2</sub> conversion. <sup>b</sup> Formation rate after 5 h of irradiation. <sup>c</sup> Selectivity toward CO evolution. <sup>d</sup> Ratio of consumed electrons to holes after 5 h of irradiation. <sup>e</sup> 0.5 M aqueous NH<sub>3</sub> solution was used as the additive, instead of NH<sub>4</sub>HCO<sub>3</sub>.

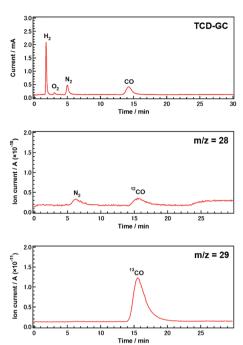


Fig. 2 Gas chromatogram and mass spectra (m/z=28 and 29) obtained during the photocatalytic conversion of  $^{13}\text{CO}_2$  using Agmodified  $\text{Sr}_{1.6}\text{K}_{0.35}\text{Na}_{1.45}\text{Ta}_5\text{O}_{15}$ . Amount of catalyst: 0.5 g; cocatalyst loading: 5.0 wt% Ag; light source: 400 W high-pressure Hg lamp; water volume: 1.0 L;  $\text{CO}_2$  flow rate: 30 mL min $^{-1}$ ; additive: 0.5 M NH<sub>4</sub>HCO<sub>3</sub>.

modified  $Sr_{1.6}K_{0.35}Na_{1.45}Ta_5O_{15}$  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 NH<sub>4</sub>HCO<sub>3</sub> since the decomposition of NH<sub>4</sub>HCO<sub>3</sub> was observed in samples without a CO<sub>2</sub> 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<sub>2</sub> 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  $Sr_{1.6}K_{0.35}$ - $Na_{1.45}Ta_5O_{15}$  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†).<sup>29</sup> 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<sub>2</sub>.

Table 2 Photocatalytic conversion of  $CO_2$  over Ag-modified catalysts in aqueous  $NH_4HCO_3$  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;  $CO_2$  flow rate: 30 mL min<sup>-1</sup>; additive: 0.5 M  $NH_4HCO_3$ 

		Formati h <sup>-1</sup>	ion rate <sup>a</sup>			
Entry	Catalyst	$H_2$	$N_2$	CO	Selec. <sup>b</sup> (%)	e <sup>-</sup> /h <sup>+c</sup>
1	ZnGa <sub>2</sub> O <sub>4</sub> /Ga <sub>2</sub> O <sub>3</sub>	125.2	191.4	532.0	80.9	1.14
2	$ZnGa_2O_4$	39.4	94.2	305.4	88.6	1.22
3	$La_2Ti_2O_7$	5.9	17.4	41.6	87.6	0.91
4	SrO/Ta <sub>2</sub> O <sub>5</sub>	2.71	11.5	42.9	94.1	1.32

<sup>&</sup>lt;sup>a</sup> Formation rate after 5 h of irradiation. O<sub>2</sub> was not detected in any of the samples. <sup>b</sup> Selectivity toward CO evolution. <sup>c</sup> Ratio of consumed electrons to holes after 5 h of irradiation.

To confirm the versatility of NH<sub>4</sub>HCO<sub>3</sub> as a general electron donor in photocatalytic reactions, we carried out the photocatalytic conversion of CO<sub>2</sub> in aqueous NH<sub>4</sub>HCO<sub>3</sub> 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<sub>2</sub> using H<sub>2</sub>O as an electron donor.<sup>25,32-34</sup> As shown in Table 2, all the photocatalysts showed good activity for conversion of CO<sub>2</sub> and high selectivity toward CO evolution. The activities of the photocatalysts were significantly increased in aqueous NH<sub>4</sub>HCO<sub>3</sub> solution, compared with their reported activities in pure H<sub>2</sub>O or aqueous NaHCO<sub>3</sub>.<sup>32-34</sup> N<sub>2</sub> was detected as the only oxidation product and the e<sup>-</sup>/h<sup>+</sup> ratio was approximately equal to 1.0. These results indicated that NH<sub>3</sub> and/or NH<sub>4</sub><sup>+</sup> was easily decomposed to N<sub>2</sub> gas by the photocatalysts tested.

#### Conclusions

We designed a highly efficient process for the photocatalytic conversion of  $CO_2$  to CO in aqueous  $NH_4HCO_3$  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  $H_2O$ .  $NH_4HCO_3$  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. 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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**Edge Article** 

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