

COMMUNICATION

A silver-manganese dual cocatalyst for selective reduction of carbon dioxide into carbon monoxide over a potassium hexatitanate photocatalyst with water†

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A Ag-Mn dual cocatalyst deposited on a $\text{K}_2\text{Ti}_6\text{O}_{13}$ photocatalyst significantly enhances photocatalytic CO_2 reduction into CO by water with extremely high selectivity such as 98% by using H_2O as an electron donor, owing to the properties of Ag and MnO_x species for promoting CO and O_2 formation, respectively.

In recent years, the photocatalytic reduction of CO_2 with water into useful compounds has been widely studied to achieve less CO_2 emission for global environmental issues and utilization of CO_2 as a carbon source. Various heterogeneous photocatalysts have been reported for the reduction of CO_2 with water to produce formate, CO, CH_3OH , and CH_4 .¹ Among these possible reductive products from CO_2 , the most useful product would be CO since it is a valuable chemical intermediate for further chemical syntheses and easily separable from the aqueous reaction media to the gas phase.

In the typical photocatalytic CO_2 reduction system in aqueous solution, two reactions competitively can occur, i.e., photocatalytic reduction of CO_2 to form CO and photocatalytic water splitting into H_2 and O_2 , where the reductive products are CO and H_2 , respectively, and the common oxidative product is O_2 .²

But, the redox potential of H^+/H_2 is more positive than that of CO_2/CO , so the reduction of protons (H^+) to H_2 is thermodynamically easier than that of CO_2 to CO. Thus, it seems especially challenging to reduce only CO_2 molecules selectively in an aqueous solution in principle. Recently, it was discovered that deposited Ag

nanoparticles could function as the active cocatalyst for CO_2 reduction to form CO.² Recently, many kinds of Ag-modified photocatalysts to produce CO, H_2 and O_2 have been reported, such as Ag/BaLa₄Ti₄O₁₅,² Ag/Ga₂O₃,³ Ag/La₂Ti₂O₇,⁴ and so on.⁵ Although some developed photocatalysts exhibited high activity or high selectivity for the CO_2 reduction,⁶ the efficiency has not been high enough to put into practice still now. As for the selectivity toward CO evolution, although it was less than 70% several years ago,² it has become higher such as 94% with Ag/CaTiO₃⁷ and 96% over Ag/SrNb₂O₆⁸ quite recently. It is noted that, in some cases, as was discussed in our previous paper,⁹ the O_2 evolution was not always stoichiometric both in water splitting and CO_2 reduction. Many reported papers had proposed the possible reasons for the nonstoichiometric formation of O_2 , such as high overpotential required for O_2 evolution and some side reactions.^{9,10} And it has also been reported that some metal oxides (such as IrO₂, RuO₂, CoO_x, MnO_x, etc.) can act as the water oxidation cocatalyst for water splitting but rarely for CO_2 reduction so far.¹¹

In these years, some dual cocatalysts with proper structures including core-shell type and two separated metal/oxide particles, such as Ag/Cu,¹² Pt/Cu₂O,¹³ Ag/CrO_x,¹⁴ and Cr/Rh¹⁵ have been proved to enhance the activity of CO_2 conversion or water splitting by taking advantage of the synergistic function of dual active sites for both reductive and oxidative reactions simultaneously, or the modification of the cocatalyst surface suppressing the backward reaction.^{14–16} Recently, a combination of Ag and Mn was examined as a dual cocatalyst deposited on TiO₂ photocatalyst to promote CO formation from a mixture of NaHCO₃ and H₂SO₄ in an aqueous solution although O_2 evolution and selectivity toward CO evolution were not clearly mentioned.¹⁷

In the present study, we examined potassium hexatitanate ($\text{K}_2\text{Ti}_6\text{O}_{13}$, referred to as KTO), which is one of the well-known functional materials with wide applications in many fields such as, electrochemistry,¹⁸ ion exchange,¹⁹ and photocatalyst,²⁰ and has been modified with each typical cocatalyst to be studied as a photocatalyst for steam reforming of methane,^{20a} water splitting,^{20b,c} and dye degradation.^{20d} Here, we found for the first

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time that deposition of a Ag-Mn dual cocatalyst on a KTO photocatalyst can much improve the photocatalytic CO₂ reduction into CO by using H₂O as an electron donor with very high CO selectivity of 98% among the reductive products.

A KTO sample was fabricated by a flux method, as mentioned in ESI†. The crystal structure of K₂Ti₆O₁₃ and its purity was confirmed by XRD (Fig. S2, ESI†). The SEM image revealed that the samples consisted of rod-like crystals (Fig. S3, ESI†), confirming that the molten salt flux can enhance the crystallization and regulate the crystal growth of each facet to form the unique hexagonal rod-like morphology of alkali hexatitanates.^{20b} The bandgap of the bare KTO was estimated to be 3.56 eV by a diffuse reflectance (DR) UV-visible spectrum and the Davis–Mott equation.²¹

A cocatalyst consisting of one or two components was loaded on the KTO sample by a photodeposition (PD) method (See ESI†).¹⁴ The loading amount of cocatalyst was determined by XRF. Even if the desired amount of the source compound was used, the actually loaded amount of cocatalyst was much less than the desired value for some elements such as Cr, Mn, Co, and Ni, which would be very sensitive to the conditions. The samples are referred to as Ag(x)-M(y)/KTO, where x and y mean the actual loading amount of Ag and M (wt %) determined by XRF.

The photocatalytic activity test for CO₂ reduction with water was carried out using a CO₂ bubbling flow reaction system (Fig. S1, ESI†) as mentioned in ESI†. In most cases, CO, H₂ and O₂ were produced under photoirradiation. Since no other reductive products than CO and H₂ were observed, the selectivity toward CO evolution, $S_{CO}(\%) = 100 \times R_{CO} / (R_{CO} + R_{H_2})$, and the ratio of the consumed electron and hole, $R(e^-/h^+) = (R_{CO} + R_{H_2}) / 2R_{O_2}$, were calculated,²² where R_{CO} , R_{H_2} , and R_{O_2} present the production rate of CO, H₂, and O₂, respectively.

The results of photocatalytic reaction tests over eight samples loaded with different cocatalysts were shown in Fig. S4. Among them, only the Ag(1.0)-Mn(0.09)/KTO sample exhibited higher CO formation rate than the Ag(1.0)/KTO sample, with the highest selectivity ($S_{CO}=97.2\%$).

According to the optimization of the Ag and Mn loading amount (Fig. S5 and S6, ESI†), it was found that the optimum loading amounts were in the range of 0.5–2.0 wt% for Ag and 0.10–0.13 wt% for Mn, and the Ag(1.0)-Mn(0.12)/KTO sample exhibited the highest CO production rate (10.6 $\mu\text{mol h}^{-1}$) with very high selectivity ($S_{CO}=98.2\%$). It is noted that the selectivity toward CO evolution was the highest among the published data so far.

Further, the Ag(0.5)-Mn(0.13)/KTO sample realized an efficient O₂ evolution giving an almost ideal redaction/oxidation products ratio with high activity (Fig. S5, ESI†). Fig. 1 shows a time course of the reaction test with the Ag(0.5)-Mn(0.13)/KTO sample. The initial high production rate of CO would originate from the initial state of well-dispersed Ag cocatalyst particles.^{5d} Although the O₂ evolution was insufficient in the induction period, which may be due to photoadsorption of O₂ on the photocatalyst surface or some competitive side reactions.^{9,10} But it gradually increased with irradiation time and the stoichiometric production of CO and O₂ was continuously observed for 24 hours, revealing the equivalent consumption of photoexcited electrons and holes, i.e. $R(e^-/h^+)=1.1$.

The blank tests confirmed that the CO molecules predominantly originated from molecular CO₂ (Table S1, ESI†). Based on these results, it was proved that the dual Ag-Mn cocatalyst could enhance the photocatalytic CO₂ reduction to CO.

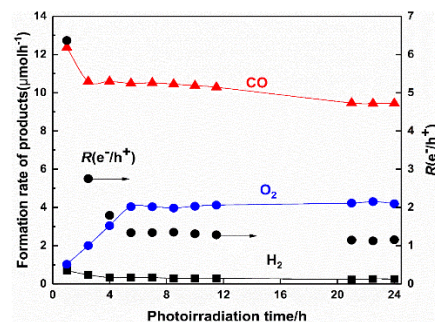


Fig. 1 Time course of the production rates of CO, H₂, and O₂, and $R(e^-/h^+)$ with the Ag(0.5)-Mn(0.13)/KTO sample in the photocatalytic CO₂ reduction test.

To clarify the effects and roles of the Ag-Mn dual cocatalyst, four samples, the bare KTO, Mn/KTO, Ag/KTO, and Ag-Mn/KTO samples, were examined as follows. As for the photocatalytic activity (Fig. 2), the Mn(0.15)/KTO sample exhibited similar or lower activity to produce both CO and H₂ compared with the bare KTO sample, demonstrating that the Mn cocatalyst cannot work solely. On the other hand, the formation rate of CO was strongly enhanced by loading the Ag cocatalyst and further improved with the Ag-Mn dual cocatalyst, confirming the obvious contribution of Ag cocatalyst and the further contribution of the dual cocatalyst for the CO₂ reduction. The CO evolution rate with the Ag(1.0)-Mn(0.12)/KTO sample was 42 times higher than those with both the bare KTO and Mn(0.15)/KTO samples, and almost 2 times higher than that with the Ag(1.0)/KTO sample. The stability and durability of the sample were repeatedly confirmed for two times under the same condition (Fig. 1 and S7, ESI†).

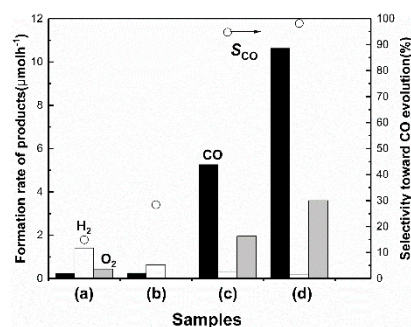


Fig. 2 Formation rate of products in the photocatalytic CO₂ reduction with H₂O over the various samples; (a) KTO, (b) Mn(0.15)/KTO, (c) Ag(1.0)/KTO, and (d) Ag(1.0)-Mn(0.12)/KTO. Photocatalyst: 0.3 g, reaction solution volume: 0.4 L, additive: 0.5 M NaHCO₃, CO₂ flow rate: 30 mL min⁻¹, light source: a 100 W high pressure Hg lamp.

DR UV-visible spectra of these samples are shown in Fig. S8 (ESI†). Both the Ag(1.0)/KTO sample and the Ag(1.0)-Mn(0.09)/KTO sample (Fig. S8c and S8d, ESI†) showed clearly a large broad band assignable to localized surface plasmon resonance (LSPR) of Ag nanoparticles at almost the same position around the 530 nm, suggesting that Ag

nanoparticles were present on the KTO surface, and they would be almost similar state irrespective of the presence of the Mn species.

The state and local structure of the dual cocatalyst were investigated by using X-ray absorption fine structure (XAFS). Fig. 3A shows Ag K-edge X-ray absorption near edge structures (XANES) of the prepared samples and two reference samples. The absorption edges (25519 eV) in the spectra of the photocatalyst samples were consistent with that of Ag foil (25519 eV) but different from that of Ag₂O (25521 eV), and the spectral feature of XANES for the photocatalyst samples is similar to that for Ag foil. The Fourier transforms of EXAFS spectra also showed almost the same feature for the photocatalyst samples and Ag foil (Fig. S9, ESI[†]). These facts indicate that the Ag species loaded on the surface of both the Ag(1.0)/KTO and Ag(1.0)-Mn(0.09)/KTO samples were metallic. Thus, it was revealed that the coexistence of Mn species did not vary the metallic state of Ag cocatalyst.

Fig. 3B shows Mn K-edge XANES of the prepared samples and some reference compounds such as Mn foil, MnO, Mn₂O₃, and MnO₂. The absorption edges for the prepared samples were not strictly consistent with those for the references, meaning that the Mn species deposited on the photocatalyst samples had different local structures from these typical manganese oxides. In detail, the edge position of the spectra for the Ag(1.0)-Mn(0.09)/KTO and Mn(0.15)/KTO samples (Fig. 3Be and 3Bf) were close to that for Mn₂O₃ (Fig. 3Bc). However, the main peak position for the two samples was close to that for MnO (Fig. 3Bb) and the second peak at the post edge for the Mn(0.15)/KTO sample was close to that for the main peak for MnO₂ (Fig. 3Bd). The Fourier transforms of EXAFS spectra of the photocatalyst samples also showed different features from those of the reference oxides (Fig. S10, ESI[†]). Thus, the Mn species deposited on the KTO surface would have the unique local structures, suggesting that they are not aggregated as a single phase of manganese oxide particles but well dispersed on the surface with unique local structure and valences.

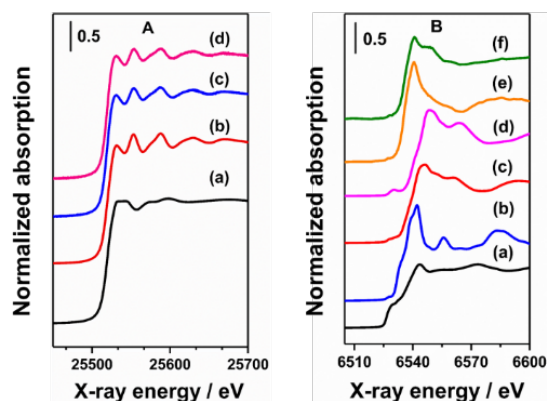


Fig. 3 [A] Ag K-edge XANES of (a) Ag₂O, (b) Ag foil, (c) Ag(1.0)/KTO, and (d) Ag(1.0)-Mn(0.09)/KTO, and [B] Mn K-edge XANES of (a) Mn foil, (b) MnO, (c) Mn₂O₃, (d) MnO₂, (e) Ag(1.0)-Mn(0.09)/KTO, and (f) Mn(0.15)/KTO.

SEM images of the Ag(1.0)/KTO and Ag(1.0)-Mn(0.12)/KTO samples show the presence of additional particles on the KTO

crystals, although it is difficult to distinguish the Ag and Mn species on the latter sample (Fig. S11, ESI[†]). TEM images of the above four samples were shown in Fig. 4. Comparing the Mn(0.15)/KTO sample (Fig. 4b) with the bare KTO sample (Fig. 4a), no nanoparticles were found to deposit on the surface of the KTO sample, and no Mn species were detected by EDS mapping due to the extremely low loading amount. However, as mentioned above, it was believed that the Mn species were well dispersed on the surface. For the Ag(1.0)/KTO sample (Fig. 4c and 4c') and the Ag(1.0)-Mn(0.12)/KTO sample (Fig. 4d and 4d'), Ag nanoparticles with the size less than 20 nm were observed and proved by the EDS mapping (Fig. S12, ESI[†]). The presence of Mn species was not confirmed also on the Ag(1.0)-Mn(0.09)/KTO sample.

Finally, to clarify the role of the MnO_x species, the photocatalytic tests of O₂ evolution from an aqueous solution of Ag(NO₃) were conducted. Compared with the bare KTO and Ag(0.5)/KTO samples, the Mn(0.15)/KTO and Ag(0.5)-Mn(0.13)/KTO samples exhibited larger amount of O₂ evolutions with higher rates, especially the Mn(0.15)/KTO sample did as shown in Fig. 5, even though the loading amount of the Mn species was very low. Here, it was clearly evidenced that the Mn species is beneficial to the O₂ evolution, which is supported by literatures.²³ In the present result, the photocatalyst with a Ag-Mn dual cocatalyst exhibited the highest activity for photocatalytic CO₂ reduction, while it showed lower activity than the photocatalyst with a single Mn cocatalyst for the oxygen evolution test, meaning that the addition of Ag nanoparticles seems to decrease the oxidative activity. A part of Ag species loaded on the oxidative sites may react with holes competitively or change the state of the MnO_x species.

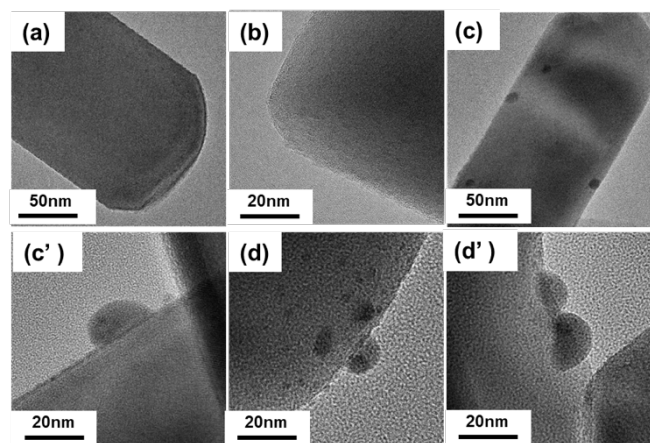


Fig. 4 TEM images of the prepared samples, (a) bare KTO, (b) Mn(0.15)/KTO, (c,c') Ag(1.0)/KTO, and (d,d') Ag(1.0)-Mn(0.09)/KTO.

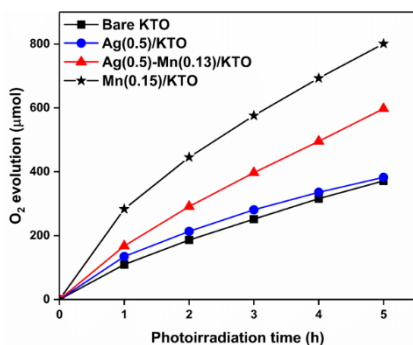
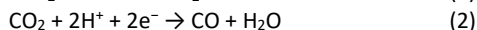
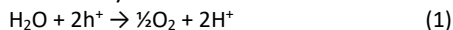


Fig. 5 Time course of O₂ evolution over the prepared photocatalysts. Sacrificial reagents: 0.5 M of AgNO₃ solution. Light source: a 100 W high pressure Hg lamp.

In conclusion, it was found that the KTO sample loaded with both Ag metal and manganese oxide species such as Ag(0.5)-Mn(0.13)/KTO samples exhibited the highest activity (10 μmol h⁻¹) and the highest selectivity (*S*_{CO}=98%) with the stoichiometric production ratio of the oxidative and reductive products, which showed almost 2 times higher CO production rate than that of the Ag(1.0)/KTO sample. The MnO_x cocatalyst can enhance the oxidative reaction, i.e., the O₂ evolution (Eq. 1), which leads to the improvement of CO evolution (Eq. 2) with synergistic effect of Ag cocatalyst. Here, the dual cocatalyst, i.e., the combination of Ag and MnO_x species, simultaneously contribute to the reductive and oxidative reactions, respectively, realized the photocatalytic CO₂ reduction to CO with a higher reaction rate and a higher selectivity such as 98%.



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Conflicts of interest

There are no conflicts to declare.

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