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Stoichiometric evolutions of CO, H₂, and O₂ were achieved for the photocatalytic conversion of CO₂ by H₂O as an electron donor using Ag-loaded Zn-modified Ga₂O₃. The selectivity toward the evolution of CO over H₂ can be controlled by varying the addition of Zn species in the Ag-loaded Zn-modified Ga₂O₃ photocatalyst. The production of H₂ gradually decreased with increasing amounts of Zn species from 0.1 to 10.0 mol%, whereas the evolution of CO was almost unchanged. The XRD, XAFS, and XPS measurements revealed that a ZnGa₂O₄ layer was generated on the surface of Ga₂O₃ by modification with the Zn species. The formation of the ZnGa₂O₄ layer eliminated the proton reduction sites on Ga₂O₃, although the crystallinity, surface area, morphology of Ga₂O₃, the particle size, and chemical state of Ag did not change. In conclusion, we designed a highly selective photocatalyst for the conversion of CO₂ by H₂O as an electron donor using Ag (cocatalyst for the CO evolution), ZnGa₂O₄ (inhibitor of the H₂ production), and Ga₂O₃ (photocatalyst).

Introduction

Conversion of CO₂ into useful carbon sources such as CO, HCOOH, HCHO, CH₃OH, and CH₄ is currently attracting considerable interest because of the demand for methods to recycle CO₂ as a natural resource.¹⁻³ In order to achieve the reduction of CO₂, H₂ or CH₄ is usually fed as a reducing agent.^{1,4} However, H₂O is the preferred reductant, because it is a rich source of hydrogen, harmless, and abundant. The photocatalytic conversion of CO₂ by H₂O over heterogeneous photocatalysts, regarded as artificial photosynthesis, is a promising route for sustainable energy development.⁵⁻⁷ If H_2O does function as the electron donor then it is important to obtain a stoichiometric ratio between the amount of O₂ evolved and CO₂ reduced. Moreover, the reduction of H⁺, released from H₂O molecules, usually competes with CO₂ reduction when several heterogeneous materials are used as photocatalysts for the reduction of CO₂ by H₂O. Generally, the production of H₂ via the reduction of H^{\star} is the dominant pathway.^{5,8} Therefore, to achieve high selectivity in the photocatalytic conversion of CO₂ by H₂O, the electrons generated through the oxidation of H₂O must be controlled to selectively reduce CO₂.

Although various photocatalysts such as TiO₂,^{9,10} BiVO₄,¹¹ $ZnGa_2O_4, ^{12}$ and $Zn_2GeO_4^{\ 13}$ have been reported for the reduction of CO_2 with H_2O under photoirradiation, the evolution of O_2 was not observed in these reactions. Therefore, the function of H₂O as an electron donor in this reaction is a controversial subject. Moreover, the synthesis gas (syngas for short, H₂ and CO), a raw feed material in the Fischer-Tropsch synthesis and other syngas-to-syncrude technologies, can be directly produced through the photocatalytic conversion of CO₂ using H₂O as an electron donor. The adjustment of synthesis gas composition (H₂:CO ratio) is essential for the Fischer–Tropsch technology.¹⁴ Thus, the selectivity between CO and H_2 in the photocatalytic conversion of CO₂ by H₂O needs to be finely tuned. Sayama et al. found that Cu-modified ZrO_2 could produce CO and H_2 with the evolution of O_2 in an aqueous solution of NaHCO₃.¹⁵ However, the selectivity of the generated electrons for reducing CO_2 was quite low, indicating that the main reaction was still the reduction of H^+ into H_2 . Recently, Kudo et al. reported that the modification of $ALa_4Ti_4O_{15}$ (A = Ca, Sr, and Ba) with Ag nanoparticles was effective for enhancing the formation of CO from the photocatalytic reduction of CO₂ with H₂O, thus improving the selectivity toward CO evolution over H_2 production. 16 In addition, KCaSrTa_5O_{15} was reported to be active for the photocatalytic conversion of CO₂ to CO utilizing H₂O as an electron donor.^{17,18} However, controlling the

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selectivity of the generated electrons for the reduction of CO₂ was difficult with Ag-loaded KCaSrTa₅O₁₅. Previously, we found that the selectivity toward CO evolution surpasses 90% for the photocatalytic conversion of CO₂ by H₂O over Ag-loaded Znmodified Ga_2O_3 , although the production of H_2 proceeded preferentially over Ag-loaded Ga2O3.19 Addition of the Zn species into the Ag-loaded Ga2O3 promoted the selectivity toward CO evolution because of the suppression of H₂ production. Therefore, understanding the role of the Zn species in the highly selective photocatalytic conversion of CO₂ by H₂O is necessary for further photocatalyst development. In this study, we achieved to control the H₂ production without affecting the evolution of CO from the photocatalytic conversion of CO₂ by H₂O over Ag-loaded, Zn-modified Ga₂O₃ by simply changing the addition of Zn species. The formation of a ZnGa₂O₄ structure on the surface of Ga₂O₃ was demonstrated in terms of XRD, XAFS, and XPS measurements, and the function of $ZnGa_2O_4$ structure on tuning the H₂ production was also discussed.

Experimental Section

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Ga₂O₃ was fabricated by the precipitation method as reported previously.¹⁹ Ga(NO₃)₃•xH₂O (12 g, Kojundo, 99.999%) was first dissolved in distilled water (200 mL). Then an aqueous ammonia solution (28 wt%) was added dropwise to the aqueous solution of Ga(NO₃)₃•xH₂O until a pH value of approximately 8.9 was reached. A white precipitate was centrifuged, washed extensively with distilled water (500 mL), and dried at 353 K in air to obtain the gallium hydroxide precursor. Ga₂O₃ was obtained by calcining the precursor at 1273 K for 6 h. Zn-modified Ga₂O₃ was synthesized by an impregnation method. The as-prepared Ga₂O₃ was dispersed in an aqueous solution containing various amounts of $Zn(NO_3)_2$ by ultrasonication. After drying under vacuum at room temperature, the solid mixture of Ga_2O_3 and $Zn(NO_3)_2$ was calcined at 1223 K for 6 h. The amount of Zn species varied from 0 to 10.0 mol% of the total amount of metal species (Ga atom and Zn atom).

The photocatalytic reaction including the photodeposition of Ag cocatalyst was carried out in a flow system using an inner-irradiation-type reaction vessel at room temperature and ambient pressure. The Zn-modified Ga_2O_3 or Ga_2O_3 photocatalyst (1.0 g) was dispersed in ultra-pure water (1.0 L) containing AgNO₃ (9.36×10^{-5} M), and CO₂ (99.999%) was bubbled into the solution at a flow rate of 30.0 mL min⁻¹ to purge the air in the reaction system. The Ag cocatalyst (1.0 wt%) was deposited on photocatalyst under UV light irradiation of a 400 W high-pressure mercury lamp for 4 h. Then NaHCO₃ (0.1 mol L^{-1}) was added to the same solution, and the suspension was irradiated under the same mercury lamp with a quartz filter connected to a cooling water system. Gaseous products such as H₂, O₂, and CO were analyzed by thermal conductivity detector-gas chromatography (TCD-GC) using a GC-8A chromatograph (Shimadzu Corp.) equipped with a Molecular Sieve 5A column (carrier gas: Ar), and by flame

ionization detector-gas chromatography (FID-GC) using a methanizer and a Shincarbon ST column (carrier gas: N_2).

The UV-Vis diffuse reflectance spectra (UV-Vis DRS) were measured by a JASCO V-670 spectrometer equipped with an integrating sphere. Spectralon®, which was supplied by Labsphere Inc., was used as a standard reflection sample such as BaSO₄. The structure and crystallinity of Zn-modified Ga₂O₃ samples were characterized by X-ray diffraction (XRD) using a Rigaku Multi Flex powder X-ray diffractometer. The Zn K-edge (9659 eV) and Ga K-edge (10367 eV) X-ray absorption fine structure (XAFS) measurements were made in the transmission mode at the BL01B1 beamline of the SPring-8 synchrotron radiation facility (Hyogo, Japan). The spectra were reduced with the Rigaku REX2000 program Ver. 2.5.9 (Rigaku Corp.). The XPS measurement was acquired using an X-ray photoelectron spectrometer (ESCA 3400, Shimadzu Corp.). The Brunauer-Emmett-Teller (BET) surface area was measured by N₂ adsorption at 77 K using a volumetric gas adsorption apparatus (BELmini, Bel Japan, Inc.). SEM images were obtained from a Field Emission Scanning Electron Microscope (FE-SEM, SU-8220, Hitachi High-Technologies) equipped with an energy-dispersive X-ray spectroscope (EDS) at an acceleration voltage of 3.0 kV.

Results and Discussion



Fig. 1 Rates of CO (black), O₂ (white), and H₂ (gray) evolution and selectivity toward CO evolution in the photocatalytic conversion of CO₂ by H₂O over Agloaded Zn-modified Ga₂O₃ with various amounts of Zn species. Reaction conditions: Amount of catalyst, 1.0 g; cocatalyst: 1.0 wt%; volume of water, 1.0 L; flow rate of CO₂, 30 mL min⁻¹; concentration of NaHCO₃, 0.1 mol L⁻¹; light source, high-pressure mercury lamp (400 W).

Figure 1 shows the formation rates of CO, H_2 , and O_2 and selectivity toward CO evolution for the photocatalytic conversion of CO₂ by H_2O over Ag-loaded Zn-modified Ga₂O₃ with various amounts of Zn species. All photocatalysts tested could stoichiometrically produce CO, H_2 , and O_2 under photoirradiation. Other reduction products, such as CH₄ in the gas phase or HCOOH, HCHO, and CH₃OH in the solution, were not detected by FID-GC and HPLC. These results indicate that H_2O acted as an electron donor and the number of photogenerated electrons used in the reduction of CO₂ and H^+ was similar to that of photogenerated holes consumed by the oxidation of H_2O . However, the selectivity of the generated

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electrons toward the reduction of CO₂ was guite different, and depended on the amount of Zn species. The formation rate of H₂ over the Ag-loaded Ga₂O₃ without the Zn species was much higher than that of CO, hence the selectivity of the generated electrons toward the reduction of CO₂ was only 28.5%. When Ga_2O_3 was modified with 0.1 mol% of Zn species, the production of H₂ was suppressed. The formation rate of H₂ decreased proportionally with the increase in the amount of Zn species, and was negligible for Zn species concentrations higher than 3.0 mol%. In contrast, the formation rate of CO was not influenced by the amount of Zn species added. Eventually, the selectivity for CO evolution over Ag-loaded Znmodified Ga₂O₃ gradually increased with elevated amounts of Zn species. When the Zn content was more than 3.0 mol%, the selectivity for CO evolution approached 100%, implying that only the reduction of CO₂ and oxidation of H₂O proceeded on the Ag-loaded Zn-modified Ga₂O₃. On the other hand, the rate of O₂ evolution declined with the increased Zn content, which accompanied with the decrease of H₂ production.



Fig. 2 UV-Vis DRS of Zn-modified Ga₂O₃ with various Zn loading amount.



Fig. 3 (A) XRD patterns of bare Ga_2O_3 (a) and Zn-modified Ga_2O_3 with 0.1 mol% (b), 0.5 mol% (c), 1.0 mol% (d), 3.0 mol% (e), 5.0 mol% (f), and 10.0 mol% (g) of Zn species; (B) The enlarged XRD patterns of all samples at 2ϑ ranged from 36.0° to 40.0°. (C) The change of crystallite size in Zn-modified Ga_2O_3 with various amounts of Zn species.

The UV-Vis diffuse reflectance spectra of bare Ga₂O₃ and Zn-modified Ga₂O₃ with various amounts of Zn species are shown in Figure 2. The bare Ga₂O₃ exhibited an absorption edge at 265 nm and the bandgap energy of Ga₂O₃ was estimated as 4.6 eV according to the Davis–Mott's equation $([F(R)*hv]^2)$.²⁰ Modification of Ga₂O₃ with different amounts of Zn species did not change the absorption edge of the spectra, thus the addition of Zn species did not contribute to the band structure of Ga₂O₃ to alter selectivity toward CO evolution in the photocatalytic conversion of CO₂

Zn-modified Ga₂O₃ was treated at high temperature after the impregnation of Ga_2O_3 with $Zn(NO_3)_2$, which means that the Zn ions should either form a new compound at the surface of Ga_2O_3 or be incorporated into the bulk structure of Ga_2O_3 . Figure 3(A) shows the XRD patterns of bare Ga₂O₃ and Znmodified Ga₂O₃ with various amounts of Zn species. Ga₂O₃ was calcined at 1273 K before the introduction of Zn species, thus all the samples exhibited the same monoclinic structure, β -Ga2O3, which is a thermally stable phase of the five polymorphic phases of Ga₂O₃. For the addition of Zn species from 0.1 mol% to 1.0 mol%, the XRD patterns of Zn-modified Ga₂O₃ were similar to that of bare Ga₂O₃. However, a diffraction peak representing the (311) facet of the ZnGa₂O₄ structure was observed in the XRD pattern of 3.0 mol% Znmodified Ga₂O₃. This indicates that the Zn species react with Ga₂O₃ to generate ZnGa₂O₄, and the crystallinity of the ZnGa₂O₄ structure in Zn-modified Ga₂O₃ is promoted by adding higher amounts of Zn species. Furthermore, the diffraction peak of ZnGa₂O₄ became sharper and higher as the amount of Zn species was increased. When the amount of Zn species reached 10.0 mol%, the peaks for the (311), (400), (422), and (440) facets of ZnGa₂O₄ were clearly observed. Therefore, based on the XRD results, the formation of highly crystalline ZnGa2O4 may be responsible for the highly selective photocatalytic conversion of CO_2 by H_2O , because the 3.0 mol%, 5.0 mol%, and 10.0 mol% Zn-modified Ga₂O₃ exhibited much higher selectivity toward CO evolution than the other samples.

When a foreign metal ion is inserted into a crystal structure, the substitution of the original lattice ion or the residual stress from a new mixed compound usually results in the peak shift of the XRD pattern associated with the change in the interplanar distance.²¹⁻²³ Figure 3(B) shows the magnified XRD patterns of all samples in the 2ϑ range from 36.0° to 40.0°. The diffraction peaks of Zn-modified Ga₂O₃ with various amounts of Zn ions did not shift significantly in comparison to those of bare Ga₂O₃. The ionic radius of Zn²⁺ (0.074 nm) is larger than that of Ga³⁺ (0.062 nm);^{21,22} however, the unaltered peak position in the XRD pattern implies that the Zn ion does not act as a dopant in the bulk Ga₂O₃ lattice. Furthermore, this result indicates that the formation of ZnGa₂O₄ in the Zn-modified Ga₂O₃ with larger amounts of Zn ions did not generate enough residual stress to distort the

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 Ga_2O_3 structure.²³ The crystallite sizes of bare Ga_2O_3 and Znmodified Ga_2O_3 derived from Scherrer's equation using the FWHM (Full Width of Half Maximum) of the XRD peaks are displayed in Figure 3(C). The crystallite size of bulk Ga_2O_3 remained in spite of the added amount of Zn ions, thus the crystallinity of Ga_2O_3 was stable during the process of modification with Zn species. Based on these results, we concluded that the Zn species are located on the surface of Ga_2O_3 , and $ZnGa_2O_4$ is generated when a large amount of Zn species is added.



Fig. 4 The Zn K-edge XANES spectra of Zn foil (a), ZnO (b), $ZnGa_2O_4$ (c) and Zn-modified Ga_2O_3 with different amount of Zn species: 0.1 mol% (d), 0.5 mol% (e), 1.0 mol% (f), 3.0 mol% (g), 5.0 mol% (h), and 10.0 mol% (i).



Fig. 5 The Zn K-edge EXAFS (A) and Fourier transforms of EXAFS (B) spectra of Zn foil (a), ZnO (b), ZnGa₂O₄ (c) and Zn-modified Ga₂O₃ with different amount of Zn species: 0.1 mol% (d), 0.5 mol% (e), 1.0 mol% (f), 3.0 mol% (g), 5.0 mol% (h), and 10.0 mol% (i).

To examine the relationship between the selectivity toward CO evolution and the Zn modification, especially for the addition of a small amount of Zn species, the chemical state and local structure of the Zn species were analyzed by XAFS measurements. Figure 4 and 5 show the Zn K-edge XANES, EXAFS, and Fourier transforms (FT) of k^3 -weighted EXAFS spectra of Zn-modified Ga₂O₃ with various amounts of Zn species. Zinc foil, ZnO, and ZnGa₂O₄ were used as references. The ZnGa₂O₄ reference was fabricated by calcining a mixture of ZnO and Ga₂O₃ at 1473 K for 20 h, and it showed the typical XRD pattern of spinel type ZnGa₂O₄. The absorption edge of Zn-modified Ga₂O₃ samples in the Zn-K edge XANES spectra (Figure 4) are similar to those of the ZnO and ZnGa₂O₄. references, thus the chemical state of the Zn species is divalent. However, the spectrum of Zn-modified Ga₂O₃ samples with 0.1 mol% Zn species was quite different from those of ZnO and ZnGa₂O₄. Therefore, we speculate that the introduction of a tiny amount of Zn species by the impregnation method resulted in the isolated dispersion of Zn ions in the surface layer of Ga₂O₃ and a different local structure for the Zn species compared to that of ZnGa₂O₄. Moreover, as the amount of Zn increased, the XANES spectra became increasingly similar to that of ZnGa₂O₄, indicating that further addition of Zn ions could cause a gradual change in the local structure of the Zn species. For samples with more than 3.0 mol% of Zn species, the spectra were identical to that of ZnGa₂O₄. This result is in agreement with the XRD measurements. In the corresponding FT of the EXAFS spectra shown in Figure 5(B), the first coordination peaks are attributed to the Zn-O shell for both the ZnO and ZnGa₂O₄ references (*ca.* 1.98 Å). The position of the second coordination peak is assigned to the Zn-Ga shell for the ZnGa₂O₄ reference (*ca.* 3.46 Å), and is longer than that of the Zn-Zn shell peak for the ZnO reference (ca. 3.22 Å). All samples of Zn-modified Ga₂O₃ exhibited a Zn-O shell peak at the same characteristic position as the ZnO and ZnGa2O4 samples, and the intensity of the Zn-O shell peak increased with increasing Zn addition. A weak shell peak was observed in the spectrum of 0.1 mol% Zn-modified Ga₂O₃ at the same position as the Zn-Zn shell peak of the ZnO reference, implying that the highly dispersed Zn species mainly exist as ZnO on the surface of Ga₂O₃. However, the second shell peak of the 0.5 mol% sample appeared at the characteristic distance of the Zn-Ga shell, which indicates that the local structure of ZnGa₂O₄ was formed in Zn-modified ${\sf Ga}_2{\sf O}_3$ with 0.5 mol% Zn addition. The peak corresponding to the Zn-Ga shell became higher and sharper with the addition of Zn up to 3.0 mol%, and then remained unchanged with further increases in the amount of Zn. The Zn-K edge XAFS results confirm that the introduction of a tiny amount of Zn species (>0.1 mol%) into Ga₂O₃ could result in the formation of the $ZnGa_2O_4$ structure, which was not detected by XRD measurements.

On the other hand, Figure 6 and 7 exhibit the Ga K-edge XANES, EXAFS, and FT of the EXAFS spectra of Zn-modified Ga₂O₃ samples with Ga₂O₃ and ZnGa₂O₄ as the references. The XANES spectra of Zn-modified Ga₂O₃ with various amounts of Zn species were identical to that of bulk Ga₂O₃. For the FT of the EXAFS spectra, the spectral shape of Zn-modified Ga₂O₃ was also consistent with that of bulk Ga₂O₃ and the intensity of the two coordination peaks were similar for each sample. These results suggest that the local structure of Ga ions in the Zn-modified Ga₂O₃ was not disturbed by the addition of Zn species.

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Fig. 6 The Ga K-edge XANES spectra of Ga_2O_3 (a), $ZnGa_2O_4$ (b) and Zn-modified Ga_2O_3 with different amount of Zn species: 0.1 mol% (c), 0.5 mol% (d), 1.0 mol% (e), 3.0 mol% (f), 5.0 mol% (g), and 10.0 mol% (h).



Fig. 7 The Ga K-edge EXAFS (A) and Fourier transforms of EXAFS (B) spectra of Ga_2O_3 (a), $ZnGa_2O_4$ (b) and Zn-modified Ga_2O_3 with different amount of Zn species: 0.1 mol% (c), 0.5 mol% (d), 1.0 mol% (e), 3.0 mol% (f), 5.0 mol% (g), and 10.0 mol% (h).



Fig. 8 The surface ratios of Zn ions to total metal ions (Zn and Ga) and the specific surface area of Zn-modified Ga_2O_3 with various Zn contents.

Since the introduced Zn species could react with Ga_2O_3 to generate the $ZnGa_2O_4$ crystal structure with the bulk phase of Ga_2O_3 remaining unchanged, the surface of Ga_2O_3 is expected to be covered with a layer of $ZnGa_2O_4$. XPS measurement is a surface-sensitive technique because the probing depth of XPS usually varies between 1.5 and 6 nm depending on the kinetic energy of the photoelectrons.²⁴ Figure 8 displays the dependence of the surface ratio of Zn atoms to total metal atoms (Zn and Ga), estimated by XPS measurement (Figure S1), View Article Online DOI: 10.1039/C5CY01280E ARTICLE

on the ratio of the mixture in the starting material for Znmodified Ga₂O₃. When the amount of Zn species added increased from 0.1 mol% to 1.0 mol%, the surface ratio of Zn atoms to total metal atoms sharply increased from 2.4 mol% to 4.8 mol%. Further increase in the amount of Zn species resulted in a continuous rise in the surface ratio of Zn atoms to total metal atoms. Therefore, the high-temperature treatment of the Zn(NO₃)₂-impregnated Ga₂O₃ starting material promotes the surface reaction between $Zn(NO_3)_2$ and Ga_2O_3 to form the $ZnGa_2O_4$ layer at the surface of Ga_2O_3 when the Zn content is higher than 0.1 mol%. The coverage and thickness of the $ZnGa_2O_4$ layer on the surface of Ga_2O_3 would increase with greater loadings of Zn(NO₃)₂. In addition, the specific surface area of Zn-modified Ga₂O₃ measured by the BET method is also shown in Figure 8. The surface area of the modified Ga₂O₃ did not vary proportionally with the generation of the ZnGa₂O₄ layer on the surface of Ga₂O₃; thus, the thin ZnGa₂O₄ layer must grow evenly on the surface of Ga_2O_3 .

Figure 9 shows the SEM images of Ag-loaded Ga₂O₃ with and without modification by Zn species. As shown, formation of ZnGa₂O₄ layer on the surface of Ga₂O₃ with various amounts of Zn species caused insignificant changes in the particle size compared to bare Ga₂O₃. Moreover, the morphology of each Zn-modified Ga_2O_3 with different amounts of Zn species was similar to that of bare Ga₂O₃. These results are consistent with XRD and BET measurement. In addition, the Ag particles by the photodeposition method were aggregated on the Ga2O3 and Zn-modified Ga₂O₃ photocatalysts observed in the SEM images (Figure 9 and S2), and the size and the dispersion of Ag particles were similar for each sample. The weak surface plasmon absorptions at the visible region in the UV-Vis DRS of Ag-loaded Ga₂O₃ and Ag-loaded Zn-modified Ga₂O₃ (Figure S3) were attributed to the aggregation and poor dispersion of Ag particles. The chemical state of Ag particles prepared by the photodeposition method was proved to be metallic Ag shown in Figure S4 and S5. The atomic ratio of Ag was nearly constant in the Ag-loaded Zn-modified Ga2O3 samples with different Zn content (Table S1). It is clear that the physical and chemical properties of Ag particles deposited on the Ga₂O₃ and Zn-modified Ga₂O₃ photocatalysts were not dominated by the variation of Zn addition. Therefore, the improvement of the selectivity towards CO evolution over Ag-loaded Zn-modified Ga_2O_3 is related to the formation of the $ZnGa_2O_4$ layer on the surface of Ga₂O₃.

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Fig. 9 SEM images of Ag-loaded bare Ga_2O_3 (a) and Ag-loaded Zn-modified Ga_2O_3 with 0.1 mol% (b), 0.5 mol% (c), 1.0 mol% (d), 3.0 mol% (e), 5.0 mol% (f), and 10.0 mol% (g) of Zn species.

Table 1. The formation rate of gas products and selectivity toward CO evolution in the photocatalytic conversion of CO₂ by H₂O over various photocatalysts^[a]

Photocatalysts ^[b]	Formation rate (μ mol h ⁻¹)			Selectivity toward
	H ₂	0 ₂	со	CO evolution (%)
Bare $Ga_2O_3^{[c]}$	268	139	5.4	2.0
Ag/Ga ₂ O ₃	280	181	111	28.4
$Ag/ZnGa_2O_4/Ga_2O_3^{[d]}$	8.9	60.6	108	92.4
Ag/ZnGa ₂ O ₄ ^[e]	2.1	28.9	50.8	96.0
$Ag/(Ga_2O_3+ZnGa_2O_4)^{[f]}$	233	165	109	31.9

[a] Reaction conditions: Amount of catalyst, 1.0 g; volume of water, 1.0 L; flow rate of CO₂, 30 mL min⁻¹; concentration of NaHCO₃, 0.1 mol L⁻¹; light source, high-pressure mercury lamp (400 W). [b] Ag cocatalyst was loaded by the photodeposition method and the loading amount was 1.0 wt%. [c] Ga₂O₃ without Ag cocatalyst and Zn species modification. [d] The modification amount of Zn species was 3.0 mol%. [e] ZnGa₂O₄ was synthesized by the solid state reaction with calcination at 1223 K. [f] The physical mixture with the same composition as the ZnGa₂O₄/Ga₂O₃ photocatalyst.

The function of the ZnGa₂O₄ layer on the surface of Ga₂O₃ was further confirmed by the reaction using bare Ga₂O₃, pure phase ZnGa₂O₄, and the physical mixture of Ga₂O₃ and $ZnGa_2O_4$ as shown in Table 1. The extremely high formation rate of H₂ and low rate of CO evolution over bare Ga₂O₃ without Ag loading and Zn modification clarifies that a large number of active sites exist for the reduction of H^+ on the surface of bare Ga₂O₃. In comparison, the loading of metallic Ag particles on bare Ga_2O_3 did not decrease the H_2 production but enhanced the evolution of CO, indicating that the deposition of Ag particles created the preferable active sites for the conversion of CO2 without affecting the reduction reaction of H^{+} . The obvious suppression of H_2 production by the introduction of Zn species into Ag-loaded Ga₂O₃ catalyst proves that the generation of the ZnGa₂O₄ layer on the surface of Ga₂O₃ could erase the active sites for the reduction reaction of H^{+} . Furthermore, the evolution of CO, H_2 , and O_2 in a stoichiometric ratio was obtained over the Ag-loaded ZnGa₂O₄ photocatalyst, and the selectivity for CO evolution over H₂ was similar to that over Ag-loaded Zn-modified Ga₂O₃ (Table 1). This result means the Ag-loaded ZnGa2O4 catalyst itself possesses suitable active sites for the conversion of CO₂ and oxidation of H_2O except for the reduction of H^+ . When $ZnGa_2O_4$ was physically mixed with Ga₂O₃, the evolution of H₂ still dominated because the proton reduction sites on the surface of Ga_2O_3 are not covered by $ZnGa_2O_4$. Therefore, the $ZnGa_2O_4$ layer modified on the surface of Ga₂O₃ has a characteristic role to inhibit the production of H₂.



Fig. 10 A proposed mechanism for the photocatalytic conversion of CO₂ in and by H_2O over Ag-loaded Ga_2O_3 (A), Ag-loaded Zn-modified Ga_2O_3 with low Zn content (B), and Ag-loaded Zn-modified Ga_2O_3 with high Zn content (C).

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Based on the above described results, it can be proposed a functioning mechanism of the modification of Ag-loaded Ga₂O₃ with ZnGa₂O₄ layer in the photocatalytic conversion of CO₂ by H₂O in Figure 10. Undoubtedly, the photocatalytic reaction on Zn-modified Ga₂O₃ is triggered by the absorption of photons, leading to the generation of electrons and holes in the bulk of photocatalyst. The photoexcited electrons subsequently migrate to the surface active sites to participate in the reduction of CO_2 and H^+ , while the holes oxidize H_2O into O_2 . The metallic Ag particle deposited on Ga₂O₃ and Zn-modified Ga2O3 photocatalysts with the similar particle size and dispersion functions as a cocatalyst to capture the photoexcited electrons for the reduction of CO_2 . Thus, similar activity for the evolution of CO over the Ag-loaded Zn-modified Ga_2O_3 with different Zn contents (0 mol% to 10 mol%) is attributable to the same extraction efficiency of electrons from Ga_2O_3 and Zn-modified Ga_2O_3 by the Ag particles. Moreover, the crystallinity and surface area of Ga₂O₃ are almost unaltered after modification with the ZnGa₂O₄ layer, which maintains the formation rate of CO in the photocatalytic conversion of CO_2 by H_2O .

Due to the existence of a large number of active sites for the reduction of H^+ on the surface of Ga_2O_3 , the evolution of H_2 is the main reaction over Ag-loaded Ga_2O_3 (Figure 10(A)). The selectivity toward CO evolution against the H₂ production over Ag-loaded Zn(0.1 mol%)-modified Ga₂O₃ is still lower than 50%, indicating that tiny amount of Zn species with ZnO structure is insufficient to block the active sites for the reduction of H^{+} . The modification of Ga_2O_3 with Zn species higher than 0.5 mol% causes the surface reaction between Zn^{2+} and Ga_2O_3 to generate $ZnGa_2O_4$ structure, thus the active sites for the H_2 production on the surface of Ga_2O_3 are eliminated (Figure 10(B)). The growth of the ZnGa₂O₄ layer on the surface of Ga₂O₃ with the increase in Zn species addition results in the further decrease of the number of active sites for H_2 production (Figure 10(C)). Moreover, the band gap of Ga_2O_3 (4.6 eV) is larger than that of $ZnGa_2O_4$ (4.2 eV, estimated by $[F(R)^*hv]^{1/2})^{25}$ and the valence band potential of Ga₂O₃ is 0.8 eV more positive than that of ZnGa₂O₄ (Figure S6). For this reason, the conduction band of ZnGa₂O₄ is located at more negative potential than that of Ga₂O₃. The combination of ZnGa₂O₄ and Ga₂O₃ heterostructure could facilitate the photogenerated electrons transfer from $ZnGa_2O_4$ to Ga_2O_3 ,²² which diminishes the electron density in the ZnGa₂O₄ structure for the reduction of H^{+} . Therefore, the evolution of H_2 is suppressed with the increase of Zn content in Ag-loaded Znmodified Ga_2O_3 . In addition, stoichiometric amount of O_2 evolved over Ag-loaded Zn-modified Ga2O3 photocatalysts reveals that the formation of ${\rm ZnGa_2O_4}$ layer on the surface of Ga₂O₃ keeps the H₂O oxidation sites remaining, because higher valence band of ZnGa2O4 structure leads to the migration of holes from Ga_2O_3 to $ZnGa_2O_4$. The decrease of O_2 evolution with the introduction of Zn species is owing to the suppression of H₂ production which consumes the photoexcited electrons donated from the oxidation of H₂O.

The mixture of CO and $\rm H_2,$ which is well known as synthesis gas, is one of the most crucial raw materials in the chemical

industry. Especially, since it is very difficult to adjust the ratio of H₂ by CO (so-called, H₂/CO ratio) depending on products of the Fischer–Tropsch technology. In this study, the synthesis gas was produced *via* the photocatalytic conversion of CO₂ with H₂O as an electron donor over Ag-loaded Zn-modified Ga₂O₃ photocatalysts and the ratio of H₂ to CO was finely controlled by the straightforward alteration of Zn addition.

Conclusions

Stoichiometric amounts of CO, H₂, and O₂ were evolved in the photocatalytic conversion of CO₂ by H₂O as an electron donor using an Ag-loaded Zn-modified ${\sf Ga}_2{\sf O}_3$ photocatalyst. The production of H₂ gradually decreased with increasing amounts of Zn species from 0.1 to 10.0 mol%, whereas the evolution of CO was almost unchanged. Consequently, the selectivity toward CO evolution increased to almost 100%. Characterization using UV-Vis DRS, XRD, XAFS, XPS, BET and SEM measurements confirmed that a ZnGa₂O₄ layer was generated on the surface of Ga_2O_3 by the addition of Zn species, and the band structure, crystallinity, surface area, morphology of Ga₂O₃, the particle size, dispersion, and chemical state of Ag cocatalyst were not affected. The ZnGa₂O₄ layer has a special function to suppress the reduction of H^{\dagger} in the photocatalytic conversion of CO₂ by H₂O over Ag-loaded Zn-modified Ga₂O₃ photocatalyst. Since the generation ratio of H₂ to CO can be finely tuned by using the Ag-loaded Znmodified Ga₂O₃ photocatalyst, it is a promising way to produce synthesis gas through the photocatalytic conversion of CO_2 by H₂O.

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Notes and references

- 1 E. V. Kondratenko, G. Mul, J. Baltrusaitis, G. O. Larrazábal, and J. Pérez-Ramírez, Energy *Environ. Sci.*, 2013, *6*, 3112.
- 2 G. Centi, E. A. Quadrelli and S. Perathoner, *Energy Environ. Sci.*, 2013, **6**, 1711.
- 3 N. Wang, S. Yan and Z. Zou, *Curr. Org. Chem.*, 2013, **17**, 2454.
- 4 M. Fan, A. Abdullah and S. Bhatia, ChemCatChem, 2009, 1, 192.
- 5 A. Kubacka, M. Fernández-García and G. Colón, *Chem. Rev.*, 2012, **112**, 1555.
- 6 W. Tu, Y. Zhou and Z. Zou, Adv. Mater., 2014, 26, 4607.
- 7 W. Fan, Q. Zhang and Y. Wang, Phys. Chem. Chem. Phys., 2013, 15, 2632.

- 8 K. Li, A. Handoko, M. Khraisheh and J. Tang, *Nanoscale*, 2014, 6, 9767.
- 9 T. Inoue, A. Fujishima, S. Konishi and K. Honda, *Nature*, 1979, 277, 637.
- 10 I. H. Tseng, J. C. S. Wu and H. Y. Chou, *J. Catal.*, 2004, **221**, 432.
- 11 Y. Liu, B. Huang, Y. Dai, X. Zhang, X. Qin, M. Jiang and M. H. Whangbo, *Catal. Commun.*, 2009, **11**, 210.
- 12 S. C.Yan, S. X. Ouyang, J. Gao, M. Yang, J. Y. Feng, X. X. Fan, L. J. Wan, Z. S. Li, J. Ye, Y. Zhou and Z. Zou, *Angew. Chem., Int. Ed.*, 2010, **49**, 6400.
- 13 Q. Liu, Y. Zhou, J. Kou, X. Chen, Z. Tian, J. Gao, S. Yan and Z. Zou, J. Am. Chem. Soc., 2010, 132, 14385.
- 14 A. D. Klerk and E. Furimsky, in *Catalysis in the Refining of Fischer-Tropsch Syncrude*, Royal Society of Chemistry, London, **2010**, pp. 7.
- 15 K. Sayama and H. Arakawa, J. Phys. Chem., 1993, 97, 531.
- 16 K. lizuka, T. Wato, Y. Miseki, K. Saito and A. Kudo, J. Am. Chem. Soc., 2011, **133**, 20863.
- 17 T. Takayama, K. Tanabe, K. Saito, A. Iwase and A. Kudo, *Phys. Chem. Chem. Phys.*, 2014, **16**, 24417.
- 18 T. Takayama, A. Iwase and A. Kudo, *Bull. Chem. Soc. Jpn.*, 2015, **88**, 538.
- 19 K. Teramura, Z. Wang, S. Hosokawa, Y. Sakata and T. Tanaka, *Chem. Eur. J.*, 2014, **20**, 9906.
- 20 X. Wang, Q. Xu, M. Li, S. Shen, X. Wang, Y. Wang, Z. Feng, J. Shi, H. Han and C. Li, Angew. Chem. Int. Ed., 2012, 51, 13089.
- 21 Y. Sakata, Y. Matsuda, T. Yanagida, K. Hirata, H. Imamura and K. Teramura, *Catal. Lett.*, 2008, **125**, 22.
- 22 X. Wang, S. Shen, S. Jin, J. Yang, M. Li, X. Wang, H. Han and C. Li, *Phys. Chem. Chem. Phys.*, 2013, **15**, 19380.
- 23 W. Water and S. Chu, Mater. Lett., 2002, 55, 67.
- 24 H. Zhang, X. Li and G. Chen, J. Mater. Chem., 2009, 19, 8223.
- 25 M. Zhong, Y. Li, T. Tokizono, M. Zheng, I. Yamada and J. Delaunay, J. Nanopart. Res., 2012, 14, 804.

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Tuning the selectivity toward CO evolution in the photocatalytic conversion of CO₂ by H₂O through the modification of Ag-loaded Ga₂O₃ with a ZnGa₂O₄ layer

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The formation and growth of $ZnGa_2O_4$ layer on the Ag-loaded Zn-modified Ga_2O_3 photocatalyst effectively controlled the generation ratio of CO to H_2 in the photocatalytic conversion of CO₂ by H_2O .

