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Dual Photocatalytic Roles of Light: Charge Separation at the Band Gap and Heat via Localized Surface Plasmon Resonance to Convert CO₂ into CO over Silver–Zirconium Oxide

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ABSTRACT: Confirmation of ¹³CO₂ photoconversion into a ¹³C-product is crucial to produce solar fuel. However, the total reactant and charge flow during the reaction is complex; therefore, the role of light during this reaction needs clarification. Here, we chose Ag–ZrO₂ photocatalysts because beginning from adventitious C, negligible products are formed using them. The reactants, products, and intermediates at the surface were monitored via gas chromatography-mass spectrometry and FTIR, whereas the temperature of Ag was monitored via Debye–Waller factor obtained by in situ extended X-ray absorption fine structure. Exposure to ¹³CO₂, H₂, and UV–visible light, ¹³CO selectively formed while 8.6% of the ¹²CO mixed in the product due to the formation of ¹²C-bicarbonate species from air that exchanged with the ¹³CO₂ gas-phase during a 2 h reaction. By choosing the light activation wavelength, the CO₂ photoconversion contribution ratio was charge separated at the ZrO₂ band gap ($\lambda < 248$ nm): 70%, localized at the Ag surface plasmon resonance (LSPR) (330 < $\lambda <$ 580 nm): 28%, and characterized by a thermal energy of 295 K: 2%. LSPR at the Ag surface was converted to heat at temperatures of up to 392 K, which provided an efficient supply of activated H species to the bicarbonate species, combined with separated electrons and holes above the ZrO₂, which generated CO at a rate of 0.66 µmol h⁻¹ g_{cat}⁻¹ with approximately zero order kinetics. Photoconversion of ¹³CO₂ using moisture was also possible. Water photo-oxidation step above ZrO₂ was rate-limited and the side reactions that formed H₂ above the Ag were successfully suppressed instead to produce CO via the Mg²⁺ addition to trap CO₂ at the surface.

1. INTRODUCTION

Numerous studies have investigated photocatalytic CO₂ fuel conversion to initiate a carbon-neutral cycle, which includes the use of solar fuel in contrast to the irreversible consumption of fossil fuels.^{1,2} However, pitfalls exist in these previous investigations that mistake methane and/or C-containing products converted from catalyst impurities as products converted from CO₂.^{1,3-6} Therefore, finding an effective photocatalyst to convert CO₂ (standard formation enthalpy = -393.5 kJ mol⁻¹) using only sustainable energy while confirming labeled ¹³CO₂ conversion, not adventitious C, is essential.^{1,3,6,7-12}

Previous studies have rarely used time course monitoring for isotope labeled-¹³CO₂ to confirm CO₂ conversion. This study monitors the ¹³CO₂ photoreduction time course and investigates the ¹³C and ¹²C product origins. Based on this mechanistic investigation, we observe and clarify the dual roles that UV–visible light has for the first time using ZrO₂-based photocatalysts^{13–15}: (i) charge separation at the band gap (BG) and (ii) heat transformed via localized surface plasmon resonance (LSPR) via extended X-ray absorption fine structure (EXAFS). Temperature monitoring of the Ag via Debye–Waller factor, which was obtained with in situ EXAFS, was direct in comparison with surface-enhanced Raman techniques that use adsorbed probe molecules.

First, this study evaluates the rates of step 2 that follows water photo-oxidation in step 1 below. $^{16-18}$

 $2H_2O \rightarrow O_2 + 2H_2 (or 4H^+ + 4e^-), \Delta_r H^{\circ} = 483.64 \text{ kJ mol}^{-1} (1)$

 $CO_{2} + H_{2} (or 2H^{+} + 2e^{-}) \rightarrow CO + H_{2}O, \Delta_{r}H^{\circ} = 41.16 \text{ kJ mol}^{-1} (2)$ $CO_{2} + H_{2}O \rightarrow CO + O_{2} + H_{2}, \Delta_{r}H^{\circ} = 524.80 \text{ kJ mol}^{-1} (3)$

We analyzed the photocatalytic mechanism in step 2, and we also attempted the photoconversion of $^{13}CO_2$ using moisture (step 3).

2. EXPERIMENTAL METHODS

An aqueous Ag nitrate (>99.8%, Wako Pure Chemical, Japan) solution was reduced in a liquid phase using NaBH₄ (>95%, Wako Pure Chemical) in the presence of ZrO₂ (JRC-ZRO-3, Catalysis Society of Japan; tetragonal phase, specific surface area = 94.4 m² g⁻¹).¹⁷ We varied the sample Ag content between 0.50 and 10 weights (wt.) %. The sample is denoted as Ag–ZrO₂. Mg nitrate (>99.5%, Wako Pure Chemical) was impregnated into the Ag–ZrO₂ aqueous suspension. The molar ratio of Mg:Ag was 1:1. The water was distilled at 358 K, and the powder product was dried at 373 K for 40 h.

The photocatalyst (0.100 g) was placed in a quartz photoreactor and evacuated at 295 K for 2 h while connected to a Pyrex glass circulation system (206.1 mL) and both rotary and diffusion pumps (10^{-6} Pa).¹⁶ We then introduced 2.3 kPa of ¹³CO₂ (¹³C 99.0%, ¹⁷O 0.1%, ¹⁸O 0.7%, chemical purity >99.9%, Cambridge Isotope Laboratories, Inc., Tewksbury, MA, USA) and 21.7 kPa of H₂ (>99.99%). For comparisons, the pressure of ¹³CO₂ and H₂ was varied in the ranges 1.1–6.7 kPa and 21.7–66.7 kPa, respectively. The reactor catalyst was irradiated with UV–visible light from a 500 W xenon arc lamp (Model OPM2-502, Ushio, Japan). The distance between the UV–visible light exit and the photocatalyst was 20 mm. The light intensity was 90.2 mW cm⁻² at the center of the photocatalyst. The intensity distribution of the Xe arc lamp was measured using a spectroradiometer (Model USR45DA, Ushio, Japan) at a position 20 mm apart from the UV–visible light exit (Figure S1, *Supporting Information*). A small portion of distribution lower than $\lambda = 248$ nm exists enabling the BG excitation of ZrO₂. In-profile kinetic data were collected as a function of the light's excitation wavelength by inserting a sharp-cut filter (2.5 mm thick) at the lighthouse exit. We used the UV32 and O58 (Hoya, Japan) types to pass light with $\lambda > 320$ nm and $\lambda > 580$ nm, respectively.^{19,20} Control tests with exposure to ¹³CO₂, H₂, and no light were performed by completely wrapping the reactor with Al foil. We also performed control tests with exposure ¹³CO₂ gas only and UV–visible light. The exchange reaction with 0.67 kPa of ¹³CO₂ was also performed using a similar procedure.

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A packed column of 13X-S molecular sieves (3 m length, 3 mm internal diameter; GL Sciences, Inc., Japan) was employed for online gas chromatography-mass spectrometry analyses (GCMS; Model JMS-Q1050GC, JEOL, Japan).²¹⁻²³ Helium (purity > 99.9999%) was used as the carrier gas at 0.40 MPa. The sampling loop comprised a Pyrex glass system kept under vacuum using rotary and diffusion pumps (10⁻⁶ Pa) connected to the GCMS 1.5 m deactivated fused silica tubes (No. 160-2845-10, Agilent, Santa Clara, CA, USA; internal diameter 250 µm), which were maintained at 393 K during analysis to avoid gas adsorption.

The surface species were monitored with a single-beam Fourier transform infrared (FTIR) instrument (JASCO, Japan; Model FT/IR-4200) equipped with a mercury-cadmium-tellurium-M detector at a constant temperature of 77.4 K.²⁴ A 20 mm- Φ self-supporting disk of ZrO₂ or Ag (5.0 wt. %)–ZrO₂ disk (50 mg) was placed in a quartz photoreaction cell equipped with NaCl windows on both sides. The photoreaction cell was connected to the Pyrex glass circulation system as well as the GCMS to enable simultaneous surface species monitoring via FTIR and isotope distribution in the gas with the GCMS. The photocatalyst disk was evacuated (10⁻⁶ Pa) at 295 K for 2 h prior to FTIR and GCMS measurements.¹⁶

In situ FTIR measurements were performed at 295 K in a range from 4000 to 650 cm⁻¹. The sample disk was irradiated with UV– visible light from a 500 W Xe arc lamp using quartz fiber light guide (San-ei Electric Co., Japan; Model 5 Φ -2B-1000L). The distance between the fiber light exit and sample disk was 50 mm. The light intensity at the center of sample was 88 mW cm⁻². The spectrometer's energy resolution was 1 cm⁻¹. A 10%-cut filter was inserted in front of the photoreaction cell. Data accumulation was between 128 and 256 scans (approximately 2 s per scan).

UV-visible spectra were recorded on a double-beam model V-650 spectrophotometer using D_2 and halogen lamps below and above 340 nm equipped with a photomultiplier tube and an integrated ISV-469 sphere (JASCO) to diffuse reflectance detection within the range from 200 to 800 nm.^{16,23} Data was transformed using the Kubelka–Munk function. A formed polytetrafluoroethylene plate was used as a reference. Absorption–fluorescence spectra were recorded on model FP-8600 (JASCO; Chiba Iodine Resource Innovation Center, Chiba University) using 150-W Xe arc lamp equipped with a photomultiplier tube within the excitation range from 200 and 300 nm and fluorescence range from 300 to 800 nm.

Silver K-edge EXAFS spectra were measured at 290 K in transmission mode at the Photon Factory Advanced Ring, High Energy Accelerator Research Organization (KEK, Tsukuba, Japan) on the NW10A beamline.²⁵ A Si(3 1 1) double-crystal monochromator and a Pt-coated focusing cylindrical mirror were inserted into the path of the X-ray beam. A Piezo transducer was used to detune the X-ray to two thirds of the maximum intensity to suppress higher harmonics. The Ag K-edge absorption energy was calibrated at 25516.5 eV using the X-ray spectrum of a Ag metal foil (40 µm thick).²⁶ A disk (Φ = 10 mm) of a Ag (3.0–5.0 wt. %)–ZrO₂ photocatalyst (125 mg) was set in a Pyrex glass reactor equipped with a Kapton film (Dupont, Wilmington, DE, USA; 50 µm thick) for Xray transmission and a polyethylene terephthalate (PET) film (Teijin, Japan, G2; 50 µm thick) for both UV-visible light and X-ray transmission filled with 2.3 kPa of CO2 and 21.7 kPa of H2. The sample was irradiated with UV-visible light from a Xe arc lamp through the PET film at the beamline.^{18,24,27,28}

The obtained Ag K-edge EXAFS data were analyzed using the XDAP software package.²⁹ The pre-edge background was approximated with a modified Victoreen function, i.e., $C_2/E^2 + C_1/E + C_0$, where *E* is the photon energy. The background for post-edge oscillation, μx , was approximated with a smoothing spline function and was calculated for a particular number of data points:

$$\sum_{i=1}^{\text{Data Points}} \frac{(\mu x_i - \text{background}_i)^2}{\exp(-0.075k_i^2)} \le \text{smoothing factor}$$
(4)

Where k is the angular photoelectron wave number.

Multiple-shell curve fit analyses were performed on the Fourierfiltered k^3 -weighted EXAFS data in k- and R-space (R: interatomic distance) using the empirical amplitude extracted from the EXAFS data for the Ag metal foil (40 µm thick). The R and coordination number (N) values for the Ag–Ag interatomic pair were set to 0.288 9 nm and 12.³⁰ We assumed that the many-body reduction factor, S_0^2 , is identical for both the sample and reference.

The high-resolution transmission electron microscopy (HR-TEM) investigations were performed using a JEM-2100F (JEOL) equipped with a field emission gun at an acceleration voltage of 200 kV.²⁷ The samples were mounted on a Cu mesh (250 mesh per inch) coated with a copolymer film of poly(vinyl alcohol) and formaldehyde (Formvar, Monsanto, St. Louis, MO, USA) and coated with carbon. Chemical compositions and elemental distributions were analyzed using energy dispersive spectra equipped with a Si(Li) detector in the TEM.

3. RESULTS AND DISCUSSION

We first compared the reactions exposed to CO₂ and H₂ using several ZrO₂-based photocatalysts doped with varying amounts of Ag under UV–visible light irradiation (Table 1A-a–e and Figure S2). The major product using these catalysts was always CO. The formation rate using 5.0 wt. % Ag–ZrO₂ (0.57 µmol h⁻¹ g_{cat}⁻¹) was higher by a factor of 3.9 than when using ZrO₂ (0.15 µmol h⁻¹ g_{cat}⁻¹); Table 1A-a, d). When the photocatalyst Ag content varied between 0.50 and 10 wt. %, we were able to maximize the total CO formation rate by using Ag (5.0 wt. %)–ZrO₂ (Table 1A-a–e and Figure S3). We confirmed the predominant photocatalytic formation of ¹³CO, which was derived from ¹³CO₂. However, minor ¹²CO also formed continuously (Figures 1A and S2). Caution should be exercised for formation rates of CO that are of the order of µmol h⁻¹ g_{cat}⁻¹; the rates of tens of mmol h⁻¹ g_{cat}⁻¹ have been reported for

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methane formation.^{2,31} The differences of reaction conditions, products, and their associated free energy change must be carefully

considered; however, this study isotopically clarifies the mechanism from CO_2 to CO activated by light in the course of time.

2	1 ,
3 ⊿	TABLE 1. Sup $(A)^{13}CO(2)$
5	$(A) = CO_2 (2.1)$
6	
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9 10	
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17	$(B)^{13}CO_2(2.)$
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26	(C) Pressure
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29 30	
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34 35	
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38	
39 40	The ¹³ CO a
41	were $0.52 \mu m$
42	ratio in forme
43	inconsistency,
44 45	with Ag $(5.0 v)$
46	adsorbed from
47	The exchange
48 40	that this reaction k
49 50	with adsorbed
51	respectively.
52	$dP_{_{13}CO_2}$
53	$\frac{dt}{dt} = -$
54 55	$P_{13}_{CO_2} + P_{12}_{CO_2}$
56	
57	$\therefore P_{^{12}\mathrm{CO}_2} =$
58 50	
60	

TABLE 1. Summary of kin (A) ¹³ CO ₂ (2.3 kPa) and H	1etic data on photoconv I2 (21.7 kPa)	version of CO2 usin	g the ZrO2-based pho	tocatalyst under UV–visib	le light

E. t.	Catalant	I:-1+:	Formation rate $(\mu mol h^{-1} g_{cat}^{-1})$		
Entry Catalyst	Light irradiated	¹³ CO	¹² CO		
а	ZrO_2	Full light	0.10	0.045	
a'		$\lambda > 320 \text{ nm}$	0.018	0.0084	
b	Ag (0.50 wt. %)-ZrO ₂		0.20	0.11	
с	Ag (3.0 wt. %)–ZrO ₂	Full light	0.38	0.079	
d			0.52	0.049	
ď	Ag (5.0 wt. %)–ZrO ₂	$\lambda > 320 \text{ nm}$	0.15	0.017	
d"		$\lambda > 580 \text{ nm}$	0.0093	0.0034	
e	Ag (10 wt. %)–ZrO ₂	Full light	0.46	0.065	

(B) ¹³CO₂ (2.3 kPa) and H₂O (2.7 kPa)

Entry Catalyst	Catalwat	Formation rate $(\mu mol h^{-1} g_{cat}^{-1})$			
	¹³ CO	¹² CO	H_2		
a	ZrO_2	0.018	0.16	0.074	
b	Ag (5.0 wt. %)–ZrO ₂	0.0031	0.0049	0.15	
с	Mg^{2+} -Ag (5.0 wt. %)-ZrO ₂	0.0010	0.092	< 0.002	

(C) Pressure dependence of CO formation rate using ¹³CO₂, H₂, and Ag (5.0 wt. %)–ZrO₂

Formation rate of ¹³ CO (μ mol h ⁻¹ g _{cat} ⁻¹) Formation rate of ¹² CO (μ mol h ⁻¹ g _{cat} ⁻¹)	H2 pressure (kPa)			
¹³ CO ₂ pressure (kPa)	0	21.7	43.8	66.7
1.1		0.39		
		0.045		
2.2	< 0.0009	0.52	0.59	0.52
2.3	< 0.001	0.049	0.049	0.033
4.8			0.61	
			0.034	
6.7		0.50		0.62
		0.035		0.036

The ¹³CO and ¹²CO formation rates using Ag (5.0 wt. %)–ZrO₂ were 0.52 µmol h⁻¹ g_{cat}⁻¹ and 0.049 µmol h⁻¹ g_{cat}⁻¹, respectively (Figure 1A). The ¹²C ratio in reactant CO₂ was 1.0%, whereas the ¹²C ratio in formed CO was 8.6% (Table 1A-d). To understand this inconsistency, we performed a ¹³CO₂ (0.67 kPa) exchange reaction with Ag (5.0 wt. %)–ZrO₂ under UV–visible light irradiation (Figure 2B). The exchange reaction proceeded with ¹²CO₂, which was adsorbed from air and remained after pretreatment under vacuum. The exchange reaction reached equilibrium after 2 h. We assumed that this reaction followed the first-order kinetics and that the rate constants, k_r and k_r , are the exchange between gas-phase ¹³CO₂ with adsorbed ¹³CO₂, respectively.

$$\frac{\mathrm{d}P_{^{13}\mathrm{CO}_2}}{\mathrm{d}t} = -k_{\mathrm{r}}P_{^{13}\mathrm{CO}_2} + k_{\mathrm{r}}'P_{^{12}\mathrm{CO}_2}$$
(5)

$$P_{{}_{13}\rm{CO}_2} + P_{{}_{12}\rm{CO}_2} = P_{{}_{13}\rm{CO}_2(initial)}$$
(6)

$$\therefore P_{{}^{12}\text{CO}_2} = P_{{}^{12}\text{CO}_2(\text{eqilibrium})} \left\{ 1 - e^{-(k_r + k_r)t} \right\}$$
(7)

Based on the fit (Figure 2B), the sum of the rate constants (k_r + k_r) required to attain an exchange equilibrium was 2.0 h⁻¹. A quicker reaction of 13.5 µmol ¹³CO₂ along the free sites of the Ag (5.0 wt. %)–ZrO₂ surface had a rate constant of 9.0 h⁻¹ in comparison to the ¹³CO₂/¹²CO₂ exchange (3.5 µmol). The converged ¹²CO₂ partial pressure in total CO₂ was 9.3%, which is in good agreement with the ¹²C ratio that formed in the CO (8.6%). We also performed the exchange test when exposed to dark conditions (Figure S4B). The total ¹³CO₂/¹²CO₂ was greater by a factor of 1.46 when exposed to light (Figures S4B and 2B), which suggests that the CO₂-derived species is light activated. ¹³CO began to form after an induction period of 0.5 h due to an exchange delay with the ¹²C surface species (Figure S2, Left), as well as the Ag activation via heating by light (see below).

Using ZrO₂ (Figure 2A), the converged partial pressure of ${}^{12}CO_2$ in the total CO₂ was 7.3%, whereas the ${}^{12}C$ ratio in the total CO was as high as 27% (Table 1A-a and Figure S2A), which suggests the existence of an irreversible CO₂-derived species leading to CO

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formation associated with O vacancy in ZrO_2 (2.3 µmol, Figure 2A and Scheme 1c).^{32,33} The uptake of O atoms at the O vacancy site in ZrO_2 correlated well with the intensity ratio between the Zr 3d and O 1s peaks in the X-ray photoelectron spectra.^{34,35} The O vacancy was more reactive in Ag–ZrO₂ when exposed to UV–visible light due to H activation by Ag (3.5 µmol, Figure 2B), whereas we observed no Ag effects when exposed to dark conditions (Figure S4A, B). The number of total CO₂-derived sites on the ZrO₂ (0.100 g) surface was 1.3 CO₂ molecules per nm², which decreased to 1.1 CO₂ molecules per nm² of Ag–ZrO₂ (Figure 2). This demonstrates that CO₂-derived species were above the ZrO₂ surface and not above Ag.



Figure 1. Time course formation of photocatalytic ¹³CO and ¹²CO during exposure to ¹²CO₂ (2.3 kPa) and H₂ (21.7 kPa) using Ag (5.0 wt. %)–ZrO₂ (0.100 g) irradiated by (A) full UV–visible light and (B) filtered light at $\lambda > 320$ nm.



Figure 2. Time course exchange reaction of $^{13}CO_2$ (0.67 kPa) irradiated by UV-visible light using (A) ZrO₂ and (B) Ag (5.0 wt. %)–ZrO₂. Photocatalyst used was 0.100 g.

The rate dependence on reactant pressure approaching atmospheric pressure was also studied using Ag (5.0 wt. %)–ZrO₂ catalysts (Table 1C). Extremely weak dependence on both the pressure of CO₂ and H₂ was found with a maximum CO formation rate of 0.66 μ mol h⁻¹ g_{cat}⁻¹ at 6.7 kPa CO₂ and 66.7 kPa H₂, demonstrating approximately zero order kinetics due to the strong adsorption of CO₂ and H.

FTIR spectra were measured for the ZrO_2 pretreated under vacuum at 295 K for 2 h. With the adsorption of CO₂ at 295 K for 2 h, peaks appeared at 1,624; 1,421; and 1,220 cm⁻¹, which were assigned to bicarbonate species (monodentate or bridging; Figure 3A1, Left).³⁶ Simultaneously, the ZrO_2 hydroxy peak at 3,700 cm⁻¹ decreased due to a reaction with CO₂ while the bicarbonate hydroxy peak increased at 3615 cm⁻¹ (Figure 3A1, Right). Much weaker shoulder peaks, due to carbonate species, also appeared at 1,553 and 1,334 cm^{-1,37} When exposed to vacuum for 30 s and 7 min, the peaks, due to the bicarbonate species, decrease by 1/2– 2/3 (Figure 3A2, 3, Left). Since carbonate species were present in the pretreated sample under vacuum (data not shown), the changes under both CO₂ and vacuum were minimal and we, therefore, regard carbonate as inert.

We then monitored FTIR changes associated with UV-visible light irradiation (Figure 3B). At 2.3 kPa of ¹³CO₂ and 21.7 kPa of H₂ irradiated by UV-visible light for 2 h, the background level, e.g., the level in the wavenumber region of 3650–3500 cm⁻¹, increased as a result of the IR excitation of UV-visible-excited electrons trapped beneath the conduction band of ZrO₂ (Figure 3B2, 3)^{27,38} while the vibrational peaks of surface species showed negligible change before and after irradiation by UV-visible light. A similar trapping state in CdSe during IR excitation and further hot electron injections from LSPR Au nanoparticles were reported.³⁹ The antisymmetric and symmetric stretching vibration peaks at 1,624 and 1,421 cm⁻¹ for bicarbonate and at 1,553 and 1,334 cm⁻¹ for carbonate in natural CO₂ (Figure 3A, Left) shifted to 1,588 and 1,389 cm^{-1} and 1,518 and 1,304 cm^{-1} in ${}^{13}CO_2$ and H_2 (Figure 3B, Left), respectively, based on the following equation for harmonic oscillation²⁴:

$$\tilde{v} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$
(8)
$$\frac{\tilde{v}_{13_{co}}}{\tilde{v}_{12_{co}}} = \frac{\sqrt{\frac{1}{13} + \frac{1}{16}}}{\sqrt{\frac{1}{12} + \frac{1}{16}}} = 0.97778$$
(9)

where \tilde{v} is the wave number, *c* is the speed of light, *k* is the force constant, and μ is the reduced mass. We chose a peak at 1389 cm⁻¹ to evaluate the amount of change in the bicarbonate species. Under vacuum for 90 s, the bicarbonate peaks decreased to one third of their intensity under ¹³CO₂ and H₂ (Figure 3B1, 2), which corresponds to the amount of exchange between ¹³CO₂ and ¹²CO₂ (2.3 µmol per 0.100 g_{cat}; Figure 2A). The chemisorbed bicarbonate species, which were exchangeable in gaseous CO₂, became bridged while the bicarbonate species desorbed under vacuum since CO₂ monodentately coordinates to the Zr site (Scheme 1b, c).³⁶ Similarly, isotope labeled bicarbonate exchanged with CO₂, which was monitored using attenuated total reflectance IR. Previous studies have suggested these as an intermediate to CO formation above Au.⁴⁰

We also confirmed that the amount of exchange of CO_2 and rate constants (simple adsorption, exchange) negligibly varied between the powder (Figure 2) and disk samples (Figure 3). When exposed to vacuum and UV-visible light for 24 h, the bicarbonate peaks further decreased to 85% of their intensity under vacuum for 90 s (Figure 3B2, 3). The decreased amount was:

2.3
$$\mu$$
mol × $\frac{0.050}{0.100}$ × 0.15 = 0.17 μ mol⁻¹³CO₃H (10)

Scheme 1. Proposed intermediate species starting from CO_2 and H_2 to CO during CO_2 exchange and photocatalytic CO_2 reduction.



Figure 3. FTIR spectra of ZrO_2 (50 mg; A, B) and Ag (5.0 wt. %)– ZrO₂ (50 mg; C, D). (A, C) Under CO₂ for 2 h (1) and under vacuum for 30 s (2) and 7 min (3). (B, D) Under UV-visible light, ¹³CO₂ (2.3 kPa), and H₂ (21.7 kPa) for 2 h (1) and under vacuum for 90 s (2) and 24 h (3).

Wave number (cm⁻¹)

-0.2

-0.4 3800

¹³CO₂, H₂, and UV-visible

2 (D)

1600 1400

(3) Vacuum

(1) ¹³CO₂ + H₂ Light 2 h

(3) Light 24 h under Vacuum

Vacuum 90 s

versus ¹³CO detected by GCMS (0.001 9 µmol). Only 1.1% of the ¹³C-bicarbonate species along the ZrO₂ surface photoconverted to ¹³CO because of the simultaneous occurrence of a reverse reaction to ¹³CO₂. Due to the limitations of the 13X-S molecular sieve column, desorbed ¹³CO₂ could not be quantitatively evaluated using GCMS and the total mass balance starting from bicarbonate was not confirmed. The amount of reduction of ¹³CO₂ to ¹³CO should be related to that of surface O vacancies in ZrO₂. The effects of apparatus-based IR light on photocatalysis should be negligible because no reduction in CO₂ was observed, even in the presence of H₂ (see the following wavelength dependence section, Table 1A-d") nor was significant amount of heat induced in comparison to LSPR-induced heat as a result of UV–visible irradiation (see the following EXAFS section, Table S2-e).

We also monitored the behavior between CO_2 and the Ag (5.0 wt. %)–ZrO₂ photocatalyst using FTIR. The peak position and change in intensity during CO_2 adsorption at 295 K and subsequent evacuation (Figure 3C) were similar to the changes observed when using ZrO_2 (Figure 3A), which demonstrates that both the bicarbonate and carbonate species were above the ZrO_2 surface, not the Ag surface. A relatively greater portion of bicarbonate species remained (3/5–1/3) under vacuum for 30 s and 7 min (Figure 3C) in comparison with the ratio using the ZrO_2 (Figure 3A) based on the amounts of exchanged (chemisorbed) CO_2 , i.e., 2.3 and 3.5 µmol using ZrO_2 and Ag (5.0 wt. %)– ZrO_2 , respectively (Figure 2).

At 2.3 kPa of 13 CO₂ and 21.7 kPa of H₂ was irradiated using UV– visible light for 2 h (Figure 3D), we observed a perfect isotope shift similar to the shift observed using ZrO₂ (Figure 3B and equation 9). However, the intensity of the bicarbonate peak decreased by approximately 50% when exposed to 13 CO₂ and H₂ in comparison with CO₂, which suggests the presence of H₂ activation on Ag and spillover onto the ZrO₂ surface (Scheme 1d). When exposed to vacuum and UV–visible light for 24 h, the bicarbonate peaks further decreased to 89% of their intensity observed under vacuum for 90 s (Figure 3D2, 3). The decreased amount was:

$$3.5 \,\mu\text{mol} \times \frac{0.050}{0.100} \times 0.11 = 0.19 \,\mu\text{mol}^{-13}\text{CO}_3\text{H}$$
 (11)

versus ¹³CO detected by GCMS (0.029 μ mol). Fifteen percent of the ¹³CO₂ at the Ag–ZrO₂ surface photoconverted to ¹³CO. Clearly, Ag promoted intermediate species reduction to CO associated with H supplied from Ag and O vacancy sites in comparison with the ratio (1.1%) using ZrO₂ associated with only O vacancy sites.



Figure 4. Diffuse reflectance UV–visible spectra for the Ag– ZrO_2 samples. The Ag contents were 0, 0.50, 3.0, 5.0, and 10 wt. %.

In the UV-visible spectra for the Ag– ZrO_2 samples, a peak centered at 428 nm was dominant between an Ag composition of 0.5 and 3.0 wt. %, whereas shoulder features centered at 368 and/or 470 nm increased at elevated Ag contents, i.e., 5.0–10 wt. % (Figure 4). These peaks are due to LSPR induced by UV-visible light where the Ag particle size distribution became wider with increased Ag content. The absorption edge was always at 248 nm (Figures 4 and S1), which indicates that the ZrO_2 BG is 5.0 eV.

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As the response to UV light absorption, ZrO_2 samples showed broad and sharp fluorescence peaks at 370 and 396 nm, respectively, with excitation at 200 nm (Figure S5A-a), whereas the peaks were almost extinguished with excitation at 240 nm (Figure S5A-b). The excitation spectra for the two peaks (Figure S5B) and the wavelength dependence of the Xe arc lamp (Figure S1) suggested contribution of light at 200 < λ < 248 nm to charge separation in ZrO₂ (Scheme 1). A fluorescence peak was reported for mean 4 nm-ZrO₂ with excitation at 300 nm and an extension of the excitation wavelength was ascribed to the transition involving extrinsic states.⁴¹ Such an effect involving O vacancy states is also plausible under the conditions using H₂ and UV–visible light shown in this study (Scheme 1c).

Formation rates of CO using ZrO₂ and Ag (5.0 wt. %)–ZrO₂ irradiated under full light (0.15 and 0.57 μ mol h⁻¹ g_{cat}⁻¹; Table 1A-a, d) decreased to 0.027 and 0.17 $\mu mol~h^{\scriptscriptstyle -1}~g_{cat}^{\scriptscriptstyle -1}$, respectively, under light at $\lambda > 320$ nm (Table 1A-a', d'). The rate using Ag (5.0 wt. %)–ZrO₂ irradiated by light at λ > 580 nm further decreased to 0.013 μ mol h⁻¹ g_{cat}⁻¹ (Table 1A-d"). Therefore, for ZrO₂, the CO formation rate decreased by 82% with the filtration of the excitation light at $\lambda > 320$ nm in comparison to a photocatalytic test irradiated under full UV–visible light (Table 1A-a, a'), i.e., UV light at $\lambda < 248$ nm to separate the charges at the ZrO₂ BG (Figure 4) played a significant photocatalytic role in the reduction of CO_2 (82%). For the Ag (5.0 wt. %)–ZrO₂, the CO formation rate decreased by 70% and 98% with the filtration of the excitation light at a λ > 320 nm and $\lambda > 580$ nm, respectively, in comparison with tests under full UV–visible light (Table 1A-d, d', d"). UV light at λ < 248 nm separated the charges at the ZrO₂BG and UV–visible light at 330 < λ < 580 nm induced Ag LSPR (Figures 4 and S1), which also played a significant role in the photocatalytic reduction of CO₂ (i.e., 70% and 28%, respectively).

Total CO formation rates in the blank tests when exposed to ${}^{13}\text{CO}_2$, H₂, and no light were 0.0062 and 0.013 µmol h⁻¹ g_{cat}⁻¹ using ZrO₂ and Ag (5.0 wt. %)–ZrO₂, respectively (Table S1A-a, b). These rates proceeded thermally (295 K, $\frac{1}{2}RT$ = 1.2 kJ mol⁻¹) but were only 4.2% and 2.2% respectively of the corresponding rates under

only 4.2% and 2.2%, respectively, of the corresponding rates under UV-visible light (Table 1A-a, d). The other blank test under ¹³CO₂ and UV-visible light using Ag (5.0 wt. %)–ZrO₂ formed no products above GCMS detection limits (Table S1B-a).

Ag K-edge EXAFS spectra were monitored for Ag (3.0 or 5.0 wt. %)–ZrO₂ under CO₂ (2.3 kPa) and H₂ (21.7 kPa) irradiated using UV–visible light at beamline. In the Fourier transform (FT; Figure 5C), a peak due to a Ag–Ag interatomic scattering of photoelectrons dominated at 0.28 nm (phase shift uncorrected), which demonstrates that the Ag nanoparticles were exclusively metallic.²⁵ In fact, in the HR-TEM images, we observed the metallic Ag(1 1 0) lattice fringes (i.e., the interval 0.287 nm versus the theoretical 0.289 nm³⁰) to be in contact with the tetragonal ZrO₂(1 0 0) lattice fringe (i.e., the interval 0.364 nm versus the theoretical 0.364 nm; Figure 6).⁴² The EXAFS FT peak intensity was significantly sup-

pressed, i.e., by as much as 31%, during a 100 min period of light irradiation (Figure 5C). On the contrary, peak intensity quickly recovered when the light was turned off.

Such light-induced changes in the FT were quantitatively evaluated using a curve fit analysis based on the plane-wave approximation for amplitude $A_i(k)$, backscattering amplitude f_i , Debye–Waller factor σ_i , and mean free photoelectron path λ for shell i⁴³ using a XDAP 2.2.7 code:²⁹



Figure 5. The time course changes of (A) coordination number N values, (B) Debye–Waller factor σ values, and (C) FT obtained from angular photoelectron wave number k^3 -weighted Ag K-edge EXAFS χ -function for Ag (3.0 wt. %)–ZrO₂ under CO₂ (2.3 kPa) and H₂ (21.7 kPa) irradiated by UV–visible light for 100 min followed by dark conditions for 20 min. (D) The change in the FT of the Ag K-edge EXAFS for fresh Ag–ZrO₂: 3.0, 5.0, and 10 wt. % Ag. (E) The correlation between the σ value and temperature for bulk sites (circle, \bigcirc) and surface sites (vertical motion; square, \Box) in/on the Ag metal generated by the correlated Debye model using a FEFF8 code.



Figure 6. HR-TEM image of Ag (5.0 wt. %)-ZrO₂.

$$A_{i}(k) = \frac{N_{i}}{kR_{i}^{2}} \left| f_{i}(k) \right| \exp\left[-2\left(\sigma_{i}^{2}k^{2} + \frac{R_{i}}{\lambda}\right) \right], i = Ag$$
(12).

The *N* value was 9.0 ± 0.7 before light irradiation and did not change significantly during both light irradiation (8.3–10.0) and after the light was off (10.1 ± 0.7; Figure 5A). *N* values of 9–10 correspond to a particle size (*d*) of 2.5–3.7 nm assuming the spherical face-centered cubic (fcc) nanoparticle model and that surface dispersion (*D*) is 0.54–0.36 (mean value = 0.45).^{44,45}

The σ value was calculated to be 0.00995 nm for Ag metal at 290 K using the correlated Debye model^{46,47} with the *ab initio* multiplescattering calculation code, FEFF8⁴⁸ and the Debye Ag temperature [$\theta_{D(Bulk)}$ 225 K].⁴⁹ The XDAP code provides an experimental difference for the σ^2 value from that of the Ag metal (model) based on equation 12. Initial σ values of 0.0101 nm for Ag (3.0 wt. %)– ZrO₂ before light irradiation quickly increased to 0.0107 nm (10 min irradiation) and progressively increased to 0.0117 nm (90 min light irradiation, shown in Figure 5B). Then, the value quickly decreased to 0.0101 nm after the light was turned off at 112 min.

Furthermore, we evaluated the temperature at the Ag site based on the σ values. The σ value temperature dependence derives from the FEFF8 combined with the correlated Debye model ^{46,47} for both bulk and surface Ag sites using the bulk and surface Debye temperature (Figure 5E-a and b, respectively). We assumed that the thermodynamically stable fcc(1 1 1) face had preferable exposure for latter value [$\theta_{D(Surf, \perp)}$ 155 K].⁵⁰ We also approximated the mean Ag nanoparticle temperature as the arithmetic mean temperature based on the $\theta_{D(Surf, \perp)}$ weighted by 1/2·1/3D [D: dispersion of nanoparticles (0.45), for an effective vertical degree of freedom at a free hemisphere surface] and that based on the $\theta_{D(Bulk)}$ weighted by (1–D) + 1/2D + 1/2·2/3D (bulk site, non-free hemisphere in contact with ZrO₂, and two lateral degrees of freedom at a free hemisphere surface) (see Supporting Information for the detail).

As a result, the initial temperature of 286 K before irradiation rose to 325 K after 10 min of irradiation and progressively increased to 392 K after 90 min of light irradiation (Figure 5B and Table S2a). The temperature quickly dropped to 290 K after the light was turned off. Such rise/drop in temperature is possibly due to LSPR heat transformation.⁵¹ Similarly to the result using Ag (3.0 wt.%)– ZrO₂ above, the initial temperature increased to 363 K after a 90 min UV–visible light irradiation and quickly dropped to 297 K once the light was off using the Ag (5.0 wt. %)–ZrO₂ sample (Table S2c). Related to the EXAFS method, the nanoparticle temperature was also monitored based on surface-enhanced Raman scattering for the N=C stretching vibration of adsorbed probe molecules.⁵² The method based on the σ value used in this study via EXAFS is common and can directly probe for all nanoparticles to expose LSPR, e.g., Au and Ag. Three-dimensional mapping of Ag nanoparticles was performed via electron energy loss spectroscopy as a function of energy loss.⁵³

Furthermore, we also observed increases or decreases in temperature under argon and UV-visible light (367 K at 50 min of light, 302 K 10 min after light had been turned off; Figure S6B and Table S2b), demonstrating that the ambient gas was not a major factor for temperature up/down. The σ value/temperature negligibly changed until 329 K when the incident light wavelength was filtered at more than 580 nm (Table S2e), whereas an essentially identical rise/drop during full light (365 K at 90 min, 298 K when light was off) for the σ value/temperature was observed when λ was more than 320 nm (Table S1d), demonstrating the heating effect by infrared portion of light were marginal in comparison to that by light whose wavelength was in the range $320 < \lambda < 580$ nm via LSPR of Ag (Figures 4 and S1). Reaction heat was not a factor in this study because the reaction that reduces CO₂ to CO (equation 2) is endothermic. The heating and reaction promotion was reported for the exothermic formation of methane from CO₂ using Ni-based photocatalysts.³¹ The temperature dropped to the same level (i.e., 290-302 K) essentially in 10-35 min after UV and/or visible light turned off (Table S2a-e) in comparison to 286 K before UV and/or visible light irradiation. This fact guarantees that the heat originating from probe synchrotron X-ray was negligible in this study.

Ag nanoparticles were always metallic for the Ag–ZrO₂ samples (Figure 5D), and N values for the fresh Ag–ZrO₂ samples gradually increased from 9.0 \pm 0.7, 9.6 \pm 0.6, and 10.7 \pm 0.8 for 3.0, 5.0, and 10 wt. % Ag, respectively, which corresponds to (d, D) sets of (2.5)nm, 0.54), (3.1 nm, 0.43), and (4.2 nm, 0.28).44,45 Thus, Ag surface atoms increase from 0.15 to 0.20 and finally to 0.26 mmol g_{cat}^{-1} , respectively, whereas the CO formation rates reached maximum values at 5.0 wt. % Ag (Table 1A and Figure S3), which indicates that the ZrO₂ sites were primarily responsible for CO₂ reduction and were assisted by heated neighboring Ag sites via LSPR that activated and supplied H to move forward equation 2 (Scheme 1d). The close correlation between Au LSPR and H₂ activation was reported using the Au-SiO₂ photocatalyst due to the charge excitation to the untibonding H₂ orbital from LSPR.⁵⁴ H₂ activation via the Ni-H species above the Ni/SiO₂·Al₂O₃ photocatalyst³¹ relates to the mechanisms discussed in this study, i.e., endothermic CO formation, versus exothermic methane formation.³¹

In the Ag–ZrO₂ UV–visible absorption spectrum, peaks appear centered at 428 and 368 nm (2.90–3.37 eV) due to a LSPR at Ag (Figure 4). The Ag work function is 4.52–4.74 eV,⁵⁵ i.e., a Fermi level (E_F) of 0.08–0.30 V for a standard hydrogen electrode versus the reduction potential from CO₂ to CO (–0.11 V)¹ or ZrO₂ conduction band minimum (–1.0 V).¹³ For nanoparticles to exhibit LSPR behavior, previous reported that the following mechanisms need to occur: (i) charge excitation to an unoccupied adsorbate state,^{54,56} (ii) hot electron injection that originates from LSPR for support, ^{19,57-60} (iii) electron trapping from the support to the Schottky barrier, ⁵⁹ and (iv) plasmonic resonant energy transfer (PRET).⁵⁹⁻⁶¹ However, for cases i–iii it is often difficult to explain how holes remained react after electron activation/reaction because the O moiety that derives from CO_2 must transfer to the LSPR nanoparticles for oxidation. In this study, H₂ oxidizes based on its association with the reduction of bicarbonate species above ZrO₂. Therefore, holes react with H₂ to form H⁺ and must further react with O that derives from CO_2 to form water above the Ag surface. Thus, Ag thermally contributes for CO generation when heated to 325 K–392 K (Figure SB), i.e., converted from LSPR (H₂ easily dissociates on the heated Ag surface and spills over the ZrO₂ surface) (Scheme 1d, e).

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The conversion of LSPR over Ag and Au owing to heat preceded phenol decomposition⁶² and thiosulfate oxidation,⁶³ whereas previous studies considered that short-lived heat converted from LSPR over Ag promotes reactant diffusion in the aqueous solution.⁶⁴ This study is the first to report the conversion of CO₂ assisted by heat that was converted via LSPR. Peaks due to formate species were not detected in our FTIR spectra, and we are unable to find evidence that the formate was an intermediate to CO.^{14,65} The H and bicarbonate species coupled with the hole and electron, respectively, and combine to form CO and water, which is enhanced by a factor of 3.9 due to Ag (Table 1A-a, d). The rise in the Ag temperature in the ~0.5 h experiment via LSPR (Figure SB) and H₂ activation effects (Scheme 1) agree with the ~0.5 h induction period for CO formation using Ag-containing photocatalysts (Figure S2, Left).

Finally, we tested the photocatalytic conversion of CO₂ using moisture (equation 3). Using ZrO₂, ¹³CO₂ (2.3 kPa), moisture (2.7 kPa), and UV-visible light, the CO generation rate increased by a factor of 1.2 compared with using ¹³CO₂ and H₂ (Table 1A-a, B-a). However, the molar ratio of the newly formed CO:H₂ was 1:0.41 rather than 1:1 based on equation 3. Since 90% of the newly formed CO was ¹²CO, the bidentate bicarbonate species c was more stable above ZrO₂ (Scheme 1), forming CO gas and a hydroxy group. Conversely, using the Ag (5.0 wt. %)-ZrO₂ photocatalyst, the CO formation rate was suppressed by 96% compared with the formation rate when using ZrO_2 (Table 1B-a, b) and by 99% when using CO_2 and H_2 (Table 1A-d). Instead, H_2 preferably formed at 0.15 μ mol h⁻¹ g_{cat}⁻¹. Based on the effects of Ag, H₂ selectivity in the reduced products increased from 29% to 95% with equation 1 (water splitting) rather than equation 3 due to the preferential adsorption of water versus CO2 on ZrO2 and H2 desorption above Ag (Scheme S1). Water that blocks the O vacancy site is also plausible. Once reaction intermediates, i.e., H and bicarbonate form under light, CO and H₂ are slowly formed via thermal energy under dark at 295 K (Table S1C-a'). In contrast that ¹²CO was preferably formed among total CO under light (61%; Table 1B-b and Figure S7, Left column), ¹³CO became a major product (68%, Table S1C-a' and Figure S7, Right column) under dark due to the gradual consumption of preadsorbed bicarbonate (12C 98.9%) that is in the equilibrium with gas-phase ¹³CO₂ (Figure 2B). The addition of Mg^{2+} onto the Ag (5.0 wt. %)–ZrO₂ to attract CO₂ to the surface mitigated the water blocking problem. Therefore, the CO formation rate increased from 0.0080 to 0.093 $\mu mol \; h^{-1} \; g_{cat}{}^{-1}$, i.e., a factor of 11.7, via the addition of Mg²⁺ similar to the MgO-Pt-TiO₂ photocatalysts (Table 1B-c).⁶⁶

4. CONCLUSIONS

In this study, the Ag (5.0 wt. %)–ZrO₂ photocatalyst was the most active during ¹³CO₂ reduction using H₂ and UV–visible light at a rate of 0.66 μ mol h⁻¹ g_{cat}⁻¹. The product included 5.5–8.6% ¹²CO. However, this CO derives from preadsorbed CO₂ from the air that exchanged with gas-phase ¹³CO₂ at a rate constant of 2.0 h⁻¹. FTIR spectra demonstrated bridging and monodentate bicarbonate species via ZrO₂ surface hydroxy group consumption under photoreaction CO₂ and/or H₂ conditions. The bridging bicarbonate species were exchangeable with the gas-phase CO₂ and O vacancy on the ZrO₂ surface should have participated in its formation. Under H₂ and UV–visible light with the expense of bridging bicarbonate, 15% was directed to ¹³CO₂.

The charge separation contribution at the ZrO_2 BG and the Ag contribution characterized by LSPR were evaluated based on inprofile kinetic data measurements using sharp-cut filters: 70 and 28%, respectively. We further investigated the contribution of the mean 2.5–3.7 nm Ag nanoparticles using in situ EXAFS. A rise in temperature from 286 to 392 K when exposed to UV–visible light irradiation and a rapid drop to 290 K under dark conditions were directly monitored based on the Debye–Waller factor change for a Ag–Ag interatomic pair interference. H₂ should oxidize based on its association with bicarbonate species reduction above ZrO_2 , but no evidence for available O on Ag was found in this study. Thus, the heated Ag surface activated H₂, and the H atoms spill over to the bicarbonate species above ZrO_2 rather than hot electron injection or PRET to/with ZrO₂.

Such dual roles for light during charge separation at the BG and heat via LSPR were remarkably effective when using CO_2 and H_2 . Instead, we found that using CO_2 and moisture disadvantageously yielded reversely formed H_2 over Ag. However, H_2 formation was redirected toward CO formation via the addition of Mg^{2+} as the CO_2 -anchor sites. The combination of alkaline [earth] metal ion– LSPR metal (Ag, Au)–ZrO₂ is required for artificial photosynthesis free from C-impurity problems and using the dual roles of light: charge separation and heat via LSPR.

ASSOCIATED CONTENT

Supporting Information

Supporting Information includes intensity distribution of Xe arc lamp, detailed data from the photocatalytic tests and data from control experiments, absorption–fluorescence spectra, theoretical details and synchrotron X-ray experiments under Ar, a summary of the Ag temperature evaluation based on the Debye–Waller factor, and time course as well as the proposed reaction mechanisms under CO_2 and moisture. The Supporting Information is available free of charge on the ACS Publication website.

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Author Contributions

The authors declare no competing financial interest. YI, HZ, TI, and TK contributed equally. The manuscript was written by all.

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