Dual photocatalytic roles of light: Charge separation at the band gap and heat via localized surface plasmon resonance to convert CO₂ into CO above silver–zirconium oxide

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The intensity distribution of Xe arc lamp is shown in Figure S1.

A detailed time course of photocatalytic tests using ${}^{13}CO_2$, H₂, and Ag-ZrO₂ photocatalysts is shown in Figure S2. The dependence of the rate of CO formation on Ag content in the photocatalyst is also depicted in Figure S3. To understand the isotope ratio of ${}^{13}CO$ versus ${}^{12}CO$, the exchange reaction of ${}^{13}CO_2$ with photocatalysts was performed in the dark (Figure S4) as a control for that conducted under the influence of UV-visible light (Figure 2). Table S1 summarizes the formation rates of ${}^{13}CO$ and ${}^{12}CO$ obtained from various control tests in comparison to data from the light reaction (Table 1).



Figure S1. The intensity distribution of Xe arc lamp used in this study as a function of wavelength.



Figure S2. Time course of ¹³CO and ¹²CO formation during photocatalytic test exposed to ¹²CO₂ (2.3 kPa) and H₂ (21.7 kPa) using (A) ZrO₂, (B) Ag (0.50 wt. %)–ZrO₂, (C) Ag (3.0 wt. %)–ZrO₂, (D) Ag (5.0 wt. %)–ZrO₂, (E) Ag (10 wt. %)–ZrO₂, and UV-visible light. Amount of catalyst used was 0.100 g.



Figure S3. Dependence of ¹³CO and ¹²CO formation rates on the Ag content in the Ag-ZrO₂ photocatalysts (0.100 g) using ¹³CO₂ (2.3 kPa), H₂ (21.7 kPa), and UV-visible light.



Figure S4. Time course of ${}^{13}CO_2$ (0.67 kPa) exchange reaction exposed to dark conditions using (A) ZrO_2 and (B) Ag (5.0 wt. %)-ZrO₂. The quartz reactor was completely wrapped by Al foil. Amount of catalyst used was 0.100 g.

TABLE S1. Summary of kinetic data on CO_2 conversion using the ZrO_2 -based photocatalyst (control tests). (A) ¹³CO₂ (2.3 kPa) and H₂ (21.7 kPa) under dark conditions

Entry	Catalyst	Formation rate (μ mol h ⁻¹ g _{cat} ⁻¹)			
		¹³ CO	¹² CO		
a	ZrO ₂	0.0038	0.0025		
b	Ag 5.0%-ZrO ₂	0.0089	0.0036		

(B) ¹³CO₂ (2.3 kPa) under UV-visible light

Entry	Catalyst	Formation rate (µmol h ⁻¹ g _{cat} ⁻¹)				
		¹³ CO	¹² CO	H ₂		
a	Ag 5.0%-ZrO ₂	<0.000 9	<0.001	<0.002		

(C) ¹³CO₂ (2.3 kPa) and H₂O (2.7 kPa) under dark conditions

Entry	Catalyst	Formation rate (μ mol h ⁻¹ g _{cat} ⁻¹)				
		¹³ CO	¹² CO	H ₂		
a	Ag 5.0%-ZrO ₂	<0.0009	<0.001	<0.002		
a' ^{*1}		0.0060	0.0028	0.052		

^{*1} Monitored in dark conditions followed by tests during exposure to UV-visible light.

Table S2. Ag temperature changes in the Ag-ZrO₂ photocatalysts monitored by EXAFS under various photocatalytic reaction conditions.

				Maximum σ		Minimum σ		
Entry	Ag content (wt. %)	Ambient gas	Light irradiated	Т (К)	Irradiatio n time (min)	Т (К)	Time after light was off (min)	Note
а	3.0	CO ₂ + H ₂	UV-visible (full)	392	90	290	12	Figure 5
b		Ar		367	50	302	10	Figure S6
с	5.0		(Iuli)	363	90	297	<35	
d		5.0 CO ₂ + H ₂	UV-visible (λ> 320 nm)	365	90	298	<35	
e			UV-visible (λ> 580 nm)	329/ 317	50/ 90	296	15	



Figure S5. (A) Fluorescence spectra of ZrO_2 with excitation at 200 nm (a) and 240 nm (b) and (B) excitation spectra of the fluorescence detection at 370 nm (a) and 396 nm (b). 2 mg of ZrO_2 sample powder was suspended in 3 mL of water.



Figure S6. The change of N(A) and σ values (B) and FT obtained from k^3 weighted Ag K-edge EXAFS χ function (C) for Ag (3.0 wt. %)-ZrO₂ sample irradiated under argon (90 kPa) and UV-visible light for 60 min is followed under dark.

Surface Debye temperature was reported for vertical displacement at the Ag(1 1 1) (155 K), Ag(1 1 0) (152 K), and Ag(1 0 0) (104 K) surfaces. We took this effect into account for one of the three degrees of freedom (one vertical, two lateral) for surface Ag atoms, e.g., the mean N value for Ag (3.0 wt. %)- ZrO_2 (9.5 based on Figure 5A) corresponds to a dispersion of 0.45. If the surface Ag atoms on the Ag nanoparticle hemisphere are free for the enhanced degree of freedom, a

portion, i.e., $0.45 \le \frac{1}{2} \le \frac{1}{3} = 0.075$, is enhanced at the surface versus the rest, $0.55 + 0.45 \le \frac{1}{2} + 0.45 \le \frac{1}{2} \le \frac{2}{3} = 0.925$, which behaves as a bulk site.

If we assume that there is a homogeneous intensity distribution wavelength for the Xe arc lamp (200–1100 nm, 90 mW cm⁻²)¹ and that the portion between 360 and 480 nm (Figure 4) effectively induced Ag LSPR in Ag (3.0 wt. %)–ZrO₂ (125 mg of disk with diameter of 1.0 cm), then this results in an effective energy of 9.42 mJ s⁴. The standard heat capacity for Ag and ZrO₂ is 25.350 and 56.123 J K⁴ mol⁴,^{2,3} respectively, which results in 56.1 mJ K⁴ for 125 mg of a Ag–ZrO₂ disk. Therefore, the rate of increase in the sample's temperature was calculated as 10.1 K min⁴, which is consistent with observed initial ramping rates (3.9–5.3 K min⁴; Figures 5B and S6B) if Ag light absorption efficiency ranged from 39% to 52% for absorption, scattering, and light reflection.

The time course for Ag-Ag peak intensity and the N and σ values under CO₂ and H₂ (Figure 5A-C) were compared with those in the Ag K-edge EXAFS monitored under argon (90 kPa; Figure S6). The Ag-Ag peak intensity in the FT significantly decreased under UV-visible light but recovered after the light was turned off (panel C), whereas the N value remained between 8.8 and 10.2 during monitoring (panel A). Based on the σ values, the Ag temperature increased from 286 K to 355 K during a 13 min period of light irradiation and progressively reached 367 K in 50 min (panel B and Table S2b). These trends agree with trends under CO₂ and H₂ (Figure 5B), which demonstrate that changes in the σ value were due to heat converted from LSPR.

Scheme S1. Proposed intermediate species starting from CO_2 and moisture to H_2 .





Figure S7. Time course of ¹³CO and ¹²CO formation during photocatalytic tests when exposed to ¹²CO₂ (2.3 kPa) and H₂O (2.7 kPa) using Ag (5.0 wt. %)-ZrO₂ and UV-visible light. Amount of catalyst used was 0.100 g.

The time course of photocatalytic test using $^{13}CO_2$, moisture, and Ag 5.0 wt. %-ZrO₂ is illustrated in Figure S7 showing 3 days under UV-visible light followed by 3 days under dark conditions. The proposed mechanism beginning from CO₂ and moisture is illustrated in Scheme S1.

References

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