Supporting information

Dual Ag/Co cocatalyst synergism for the highly effective photocatalytic conversion of CO_2 by H_2O over Al-$SrTiO_3$

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Experimental

Preparing Al-$SrTiO_3$

Perovskite-structured $SrTiO_3$ was fabricated using a solid-state reaction, with stoichiometric $SrCO_3$ (3.10 g) and TiO_2 (1.59 g) as the Sr and Ti sources.[1] The $SrCO_3$:TiO_2 molar ratio was 1.05 because $SrCO_3$ was observed to evaporate. After grinding for 10 min, the mixture was transferred to an alumina crucible and calcined at 1373 K for 10 h in air, after which the sample was washed at 353 K with ultrapure deionized water several times and dried at 298 K overnight. A facile flux method was used to fabricate Al-$SrTiO_3$ using the prepared $SrTiO_3$.[2, 3]

Loading the catalyst onto the Al-$SrTiO_3$

The Ag and Co dual cocatalyst was simultaneously used to modify the surface of the as-prepared Al-$SrTiO_3$ photocatalyst using a chemical-reduction (CR) method. Al-$SrTiO_3$ (0.75 g) was dispersed in ultrapure deionized water (50 mL) and 0.1 M aqueous solutions of $AgNO_3$ (0.695 mL) and $Co(NO_3)_2$ (0.347 mL), and a 0.4 M aqueous solution of NaH_2PO_2 (1.50 mL) were added to the suspension in a stepwise manner. After the suspension was maintained at 353 K for 1.5 h, it was filtered and the collected powder was dried in air at 298 K overnight. Meanwhile, the Ag and Co dual cocatalyst was also singly loaded on Al-$SrTiO_3$ using the CR method. The Ag and Co-loaded Al-$SrTiO_3$ sample are referred to as "Ag(*x*)Co(*y*) Al-$SrTiO_3$", where *x* is the Ag cocatalyst loading (0.0, 0.5, 1.0, 1.5, 1.7, 2.0m and 2.5 mol%) and *y* is the Co cocatalyst loading (0.0, 0.425, 0.85, 1.275, 1.7, and 2.5 mol%).

For the impregnation (IMP) method, an aqueous solution of $AgNO_3$ (0.695 mL, 0.1M) and $Co(NO_3)_2$ (0.347 mL, 0.1M) was dispersed into 20 mL of an aqueous suspension of Al-$SrTiO_3$ (0.75 g). After aging at 353 K for 0.5 h, the mixture was evaporated at 353 K for 1.0 h with stirring, after which the dried mixture was ground and calcined at 723 K for 2 h in air.

The various cocatalysts were used to modify the surfaces of Al-$SrTiO_3$ photocatalysts using the photodeposition (PD) method, in which 0.75 g of Al-$SrTiO_3$ was dispersed in ultrapure deionized water (1000 mL), and a 0.1 M aqueous solution of $AgNO_3$, H_2PtCl_6, or $HAuCl_4$ (0.695 mL) was added into the suspension. In addition, a stoichiometric amount of $NaIO_3$ was added into the suspension as the hole donor when MnO_2, PbO_2, or Co_3O_4 catalysts were loaded onto Al-$SrTiO_3$ using $Mn(NO_3)_2$, $Pb(NO_3)_2$, or $Co(NO_3)_2$ (0.347 mL, 0.1 M aq.) as the metal source. After purging the air from the reactor with flowing Ar, the suspension was irradiated using a 400-W high-pressure Hg lamp with a quartz jacket connected to a water-cooling system, while Ar was bubbled through the suspension at 30 mL min^{-1}. The cocatalyst-loaded Al-$SrTiO_3$ samples were then vacuum filtered, washed, and dried at 298 K in air overnight.

Characterization

The crystalline properties of $SrTiO_3$ and Al-$SrTiO_3$ were characterized by X-ray diffractometry (XRD) using a Rigaku Ultima IV powder diffractometer equipped with a Cu Kα (λ = 0.154056 nm) radiation source operating at 30 kV and 30 mA. UV-visible diffuse reflectance (UV-vis DR) spectroscopy on a JASCO V-670 instrument equipped with an integrating sphere was used to acquire absorption spectra of the samples. Spectralon® (Labsphere Inc.) was used as the standard reflection sample. In addition, the microstructure and morphology of each sample was examined by field-emission scanning electron microscopy (SEM; SU-8220, Hitachi High-Technologies, Japan), augmented by energy dispersive X-ray spectroscopy (EDS) (15.0 kV). Meanwhile, transmission electron microscopy (TEM, JEM-2100F, Japan) was used to examine the morphologies of the AgCo/Al-$SrTiO_3$ photocatalysts. The actual amounts of the Ag and Co species loaded on the AgCo/Al-$SrTiO_3$ samples were determined by X-ray fluorescence (XRF) with an energy-dispersive X-ray (EDX-8000, Shimadzu, Japan) spectrometer. Co 2p X-ray photoelectron spectra of AgCo/Al$SrTiO_3$ were acquired to determine the valences of the Co cocatalysts (XPS, ESCA 3400, Shimadzu Corp., Japan). The X-ray absorption fine structure (XAFS) of the Ag K-edge (beam line BL01B1) and Co K-edge (beam line BL37XU) were examined at the SPring-8 synchrotron facility. The liquid products in the reaction solution was analysed using the high-performance liquid chromatography (HPLC 4000, JASCO Corp., Japan)

Photocatalytic reactions

CO_2 was photocatalytically converted with H_2O as the electron donor using a quasi-flow batch system with an internal-irradiation-type reaction vessel at 298 K and under ambient pressure. AgCo/Al-$SrTiO_3$ (0.5 g) was added to an aqueous solution of $NaHCO_3$ (0.1 M, 1.0 L) and CO_2 (99.999%, 30 mL min^{-1}) was bubbled through the suspension. A 400-W high-pressure Hg lamp with a water-cooled Pyrex® jacket (to cut off light at $\lambda < 300$ nm) was used to irradiate the sample. The gaseous products that evolved from the photoreaction system (i.e., H_2, and O_2) were analyzed by gas chromatography with a thermal conductivity detector (TCD–GC; Model: GC-8A, Shimadzu Corporation, Japan) with a 5A molecular sieve (MS 5A) column, and Ar as the carrier gas. In addition, the photocatalytic CO product was analyzed using a flame-ionization detector (FID–GC; Model: GC-8A, Shimadzu Corporation, Japan) with a methanizer, and a Shincarbon ST column, and N_2 as the carrier gas.

The photocatalytic reaction was also carried out in a quasi-flow batch system in a 200 mL reactor with external irradiation at 365 nm to determine the apparent quantum efficiency (QE). AgCo/Al-$SrTiO_3$ (0.1 g) was dispersed in $NaHCO_3$ (0.1 M, 0.2 L) with CO_2 (99.999%, 30 mL min^{-1}) bubbling. The suspension was then irradiated at 365 nm using an LED controller (Model: IRS-1000, CELL System Co., Ltd., Japan). The photoirradiation area was a 5-cm-diameter circle. The gaseous products were analyzed using the same TCD–GC and FID–GC systems detailed above.

Table S1. The XRF data of the different amount of Ag and Co loaded Al-$SrTiO_3$ prepared by CR, PD, IMP method.

Sample	Ag mol%	Co mol%
Ag(0)Co(0)	0.00	0.00
Ag(1.7)Co(0)_CR	1.78	0.00
Ag(1.7)Co(0.425)_CR	1.68	0.35
Ag(1.7)Co(0.85)_CR	1.82	0.76
Ag(1.7)Co(1.275)_CR	1.72	0.69
Ag(1.7)Co(1.7)_CR	1.84	1.06
Ag(0)Co(0.85)_CR	0.00	0.75
Ag(0.5)Co(0.85)_CR	0.53	0.89
Ag(1.0)Co(0.85)_CR	1.02	0.83
Ag(1.5)Co(0.85)_CR	1.62	0.91
Ag(2.0)Co0.85)_CR	2.13	0.76
Ag(0.5)Co(0.25)_CR	0.45	0.29
Ag(1.0)Co(0.5)_CR	1.03	0.49
Ag(1.5)Co(0.75)_CR	1.82	0.68
Ag(1.7)Co(0.85)_CR	1.82	0.76
Ag(2.0)Co(1.0)_CR	1.97	0.61
Ag(2.5)Co(1.25)_CR	2.57	0.53
Ag(1.7)Co(0.85)_PD	1.75	0.86
Ag(1.7)Co(0.85)_IMP	1.67	0.87
Ag(1.7)Co(0.85)_CR_hv 5h	1.71	0.77

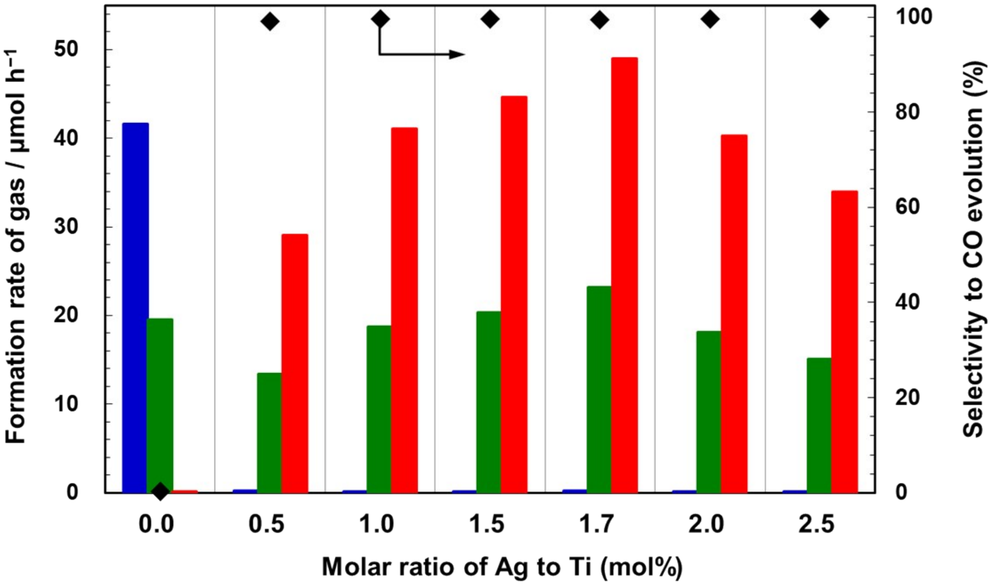


Figure S1. Formation rates of H_2 (blue), O_2 (green), and CO (red) for the photocatalytic conversion of CO_2 by H_2O over the 0.85 mol% Co and various amounts of the 0.00, 0.50, 1.0, 1.5, 2.00, and 2.5 mol% Ag cocatalyst loaded Al-$SrTiO_3$ prepared by CR method.

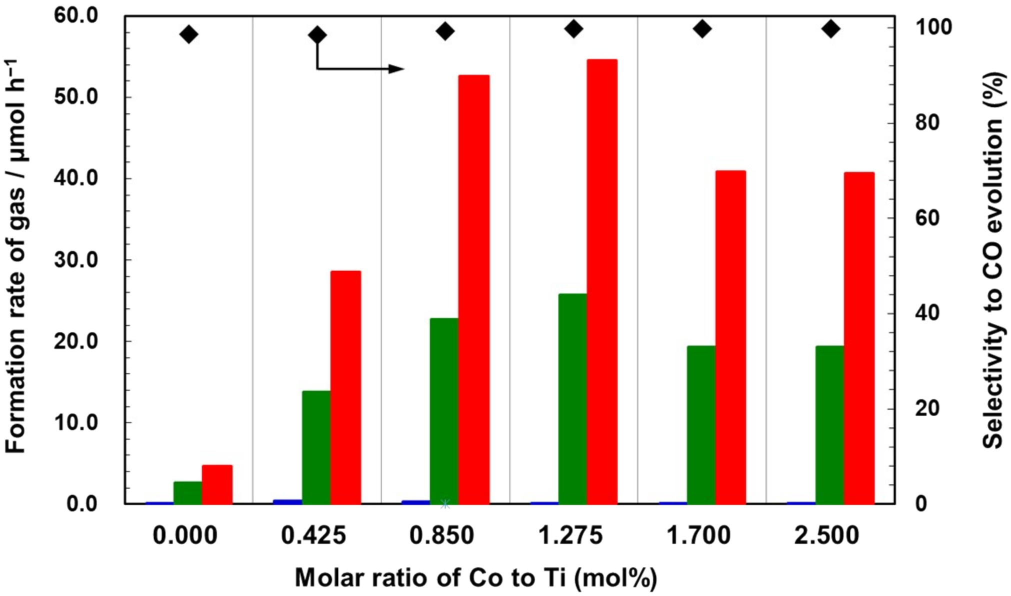


Figure S2. Formation rates of H_2 (blue), O_2 (green), and CO (red) for the photocatalytic conversion of CO_2 by H_2O over the 1.7 mol% Co and various amounts of the 0.00, 0.425, 0.850, 1.275, 1.7, and 2.5 mol% Co cocatalyst loaded Al-$SrTiO_3$ prepared by CR method.

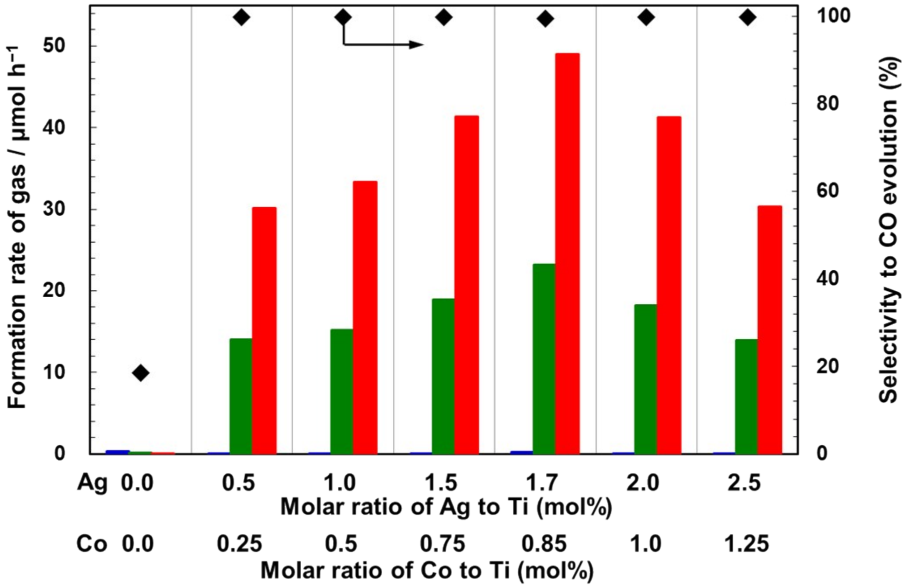
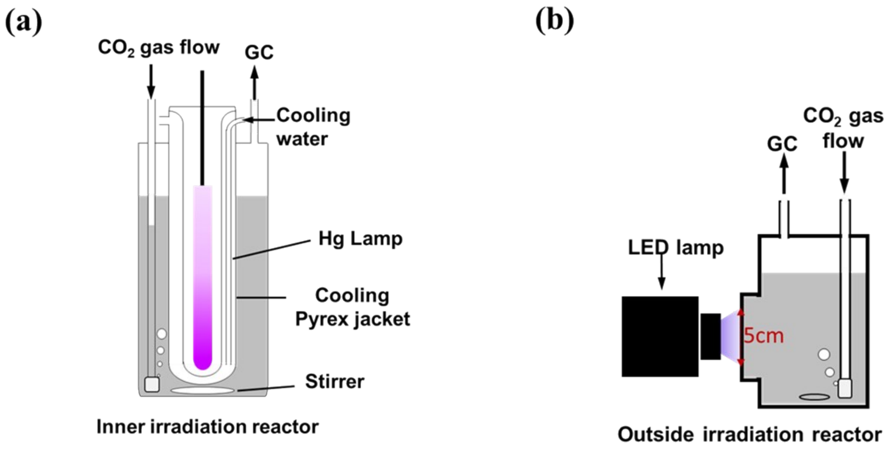


Figure S3. Formation rates of H_2 (blue), O_2 (green), and CO (red) for the photocatalytic conversion of CO_2 by H_2O over the different amount of Ag and Co loaded Al-$STiO_3$ prepared by CR method.

Scheme S1. The scheme of the (a) inner irradiation reactor with the high-pressure Hg lamp $\lambda \geq 300$ nm, (b) the outside irradiation reactor with the LED light $\lambda = 365$ nm nm[*]



[*] Photocatalytic reaction conditions: Amount of photocatalyst, (a) 0.5 g and (b) 0.1 g; amount of Ag loaded, 1.7 mol%; amount of Co loaded, 0.85 mol%; volume of the reaction solution (H_2O), (a) 1.0 L and (b) 0.2 L; additive, 0.1 M $NaHCO_3$; CO_2 flow rate; 30 mL min^{-1}.

The calculation of the apparent quantum efficiency in the outside irradiation reactor.

AQE (%) = (number of reacted electrons/number of incident photons (*Np*)) × 100 %

= (number of the evolved ($CO + H_2$) molecules * 2 / *Np*) × 100 %

The number of the evolved ($CO + H_2$) molecules for 1 h: (7.45 μmol h^{-1}+ 0.11 μmol h^{-1}) *1 h* N_A

Where N_A represents the Avogadro constant

Luminous power:

$W = (I / C * S = (32.77 \text{ mA/cm}^2)/(155 \text{ mA W}^{-1})\ 19.625 \text{ cm}^2 = 4.15 \text{ W}$

Where the I represents the detected photocurrent at 32.77 mA/cm^2, C represents the conversion efficiency of the detector used at 155 mA W^{-1}, S represents the area of the irradiation area of the reaction system (Scheme S1(b)): 2.5*2.5*π cm^2

$Np = (W * t * \lambda) /(h * c) = 2.74*10^{22}$

Where t represents the photoirradiation time 3600 s, λ represents the light wavelength at 365 nm, h represents the Planck constant, c represents the speed of the light,

Thus, *AQE* (%) = (number of the evolved ($CO + H_2$) molecules * 2/ *Np*) × 100% = 0.033%

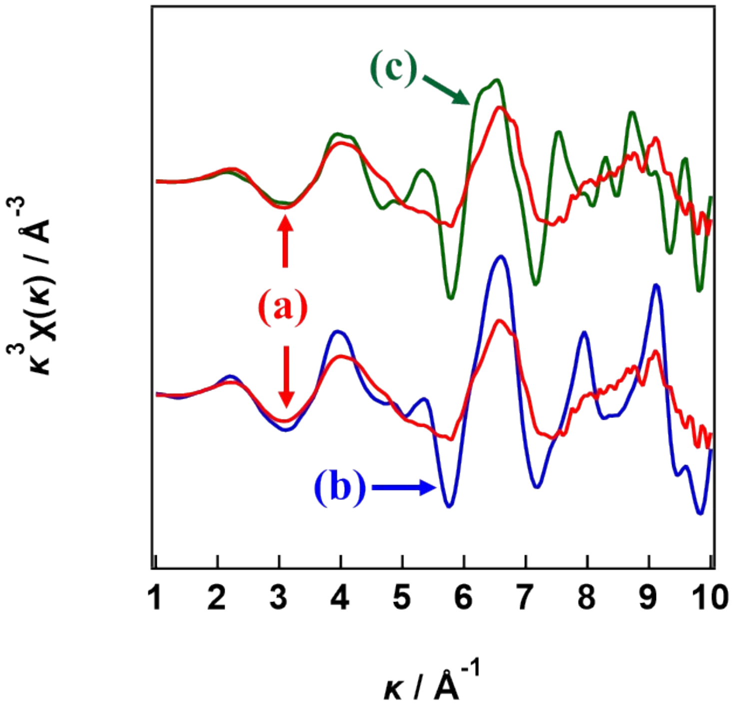
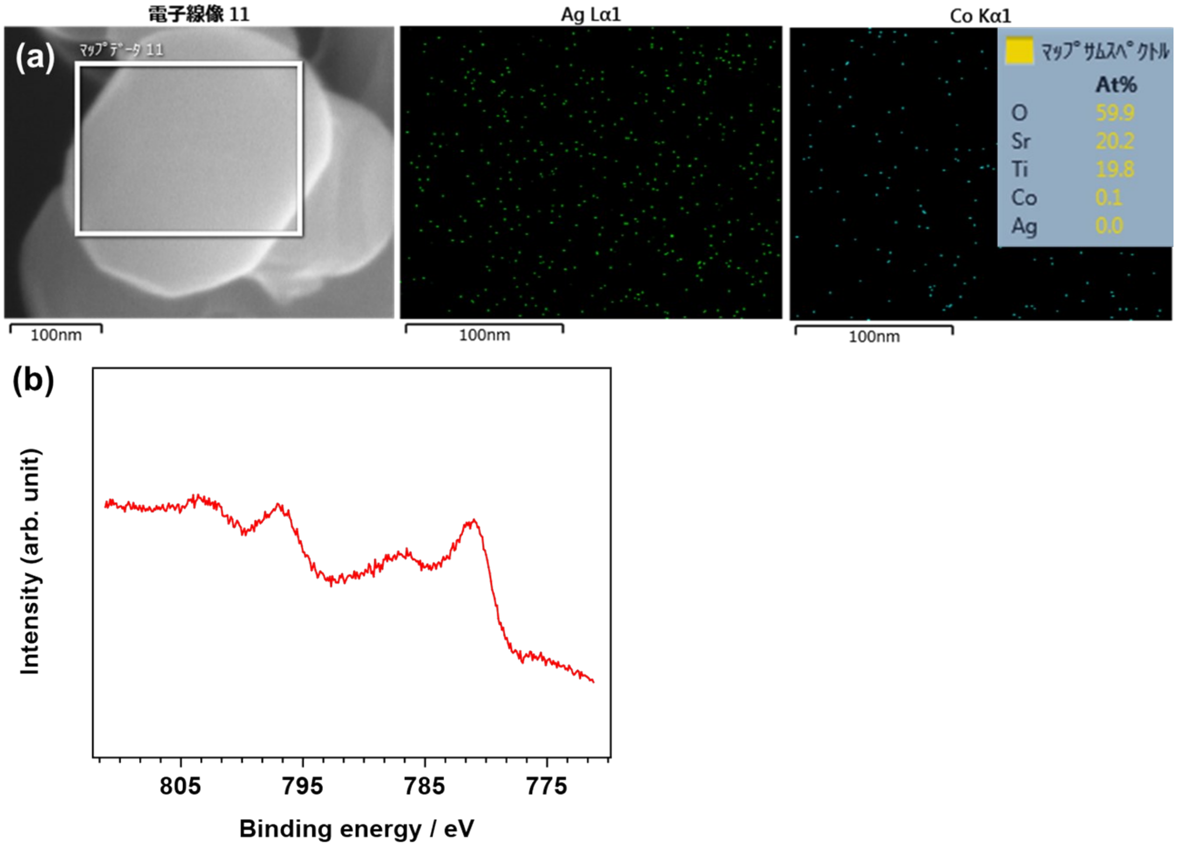


Figure S4. Co K−edge EXAFS oscillations of (a) AgCo/Al-SrTiO$_3$_CR (red), (b) CoOOH (green), and (c) Co$_3$O$_4$ (blue)



	At%
O	59.9
Sr	20.2
Ti	19.8
Co	0.1
Ag	0.0

Figure S5. (a) The EDX mapping and spectra of the Co/Al-$SrTiO_3$, (b) XPS spectra of Co 2p of Co/Al-$SrTiO_3$.

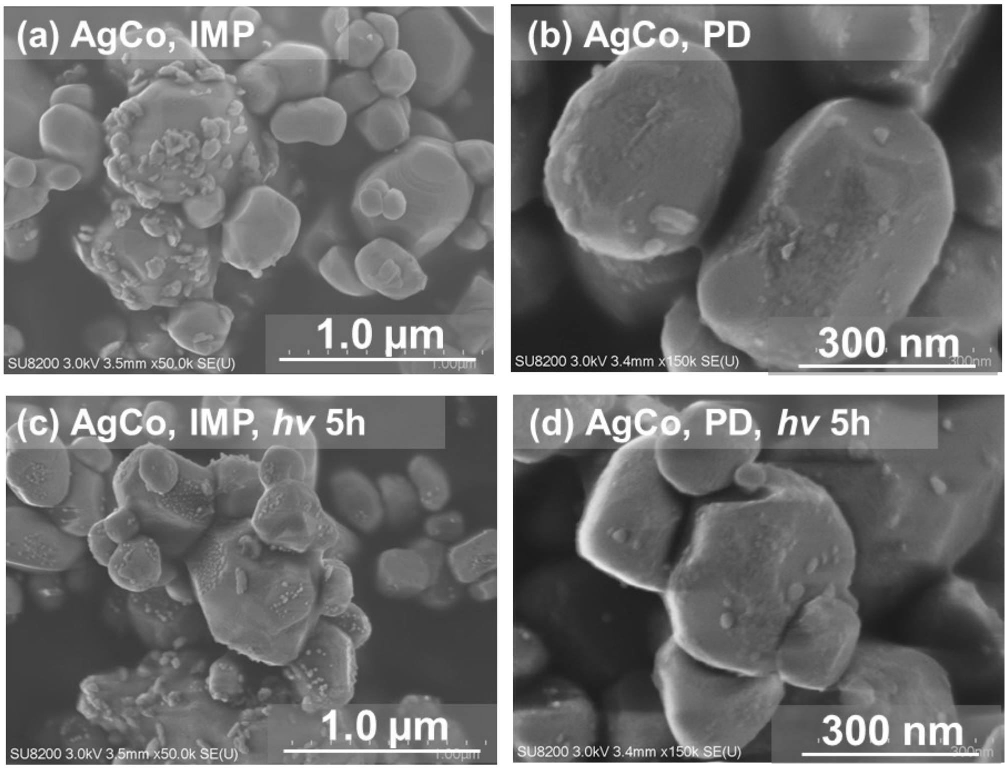


Figure S6. SEM image of the different cocatalyst loaded Al-$SrTiO_3$ prepared by different methods (a) and (c) AgCo prepared by IMP method, (b) and (d) Ag prepared by PD method, (a-b) before photocatalytic reaction, (c-d) after 5 h photocatalytic reaction.

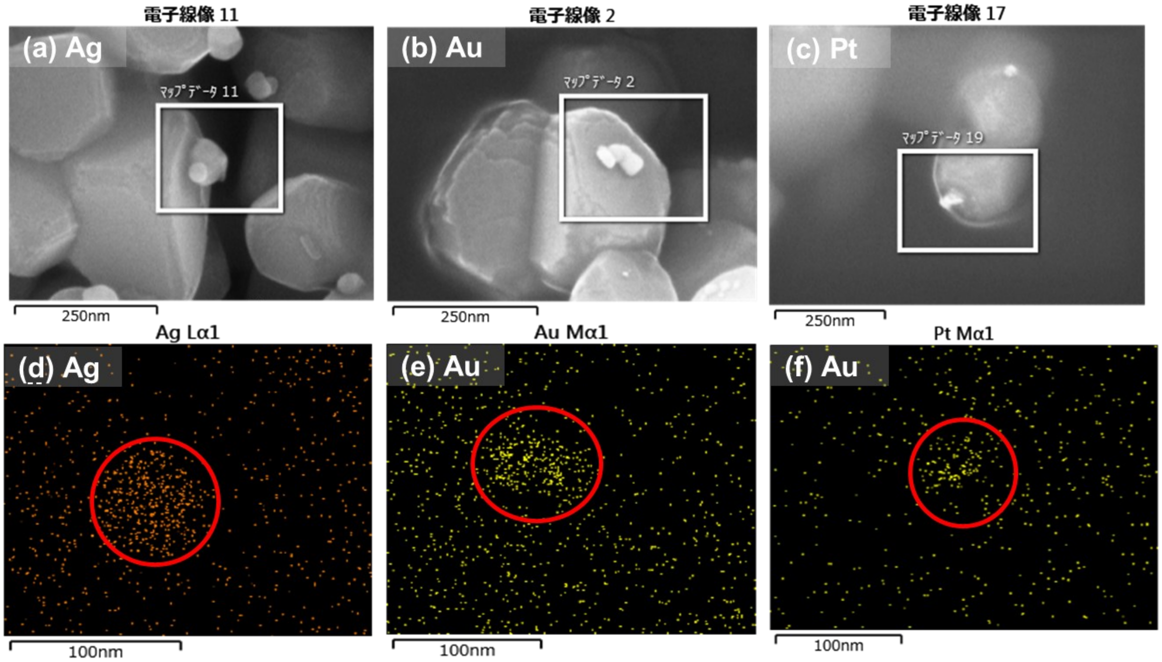


Figure S7. SEM images and EDS mappings of the different cocatalysts loaded Al-SrTiO$_3$ (a) and (d) Ag, (b) and (d) Au, (c) and (f) Pt

Table S2. Photocatalytic reduction of CO_2 into CO by H_2O over different cocatalyst loaded photocatalysts prepared by PD method [a]

Photocatalyst	Formation rates of products (μmol h^{-1})			Selec. toward CO (%)	Consumed e /h+
	H_2	O_2	CO		
Ag/Al-$SrTiO_3$	0.27	1.58	3.18	92.2	1.09
Pt/Al-$SrTiO_3$	96.7	48.9	0.00	0.00	0.99
Au/Al-$SrTiO_3$	17.2	8.52	0.25	1.43	1.02
MnO_2/Al-$SrTiO_3$	2.13	0.96	0.00	0.00	1.11
PbO_2/Al-$SrTiO_3$	Trace	Trace	Trace		
Co_3O_4/Al-$SrTiO_3$	9.28	4.92	0.04	0.47	0.95

[a] Photocatalytic reaction condition: 0.5g photocatalyst; 1.0 L $NaHCO_3$ (0.1 M) aqueous solution; 1.7 mol% Ag cocatalyst loading; 0.85 mol% Co cocatalyst loading; CO_2 flow (30 ml min^{-1}), 400 W high-pressure Hg lamp.

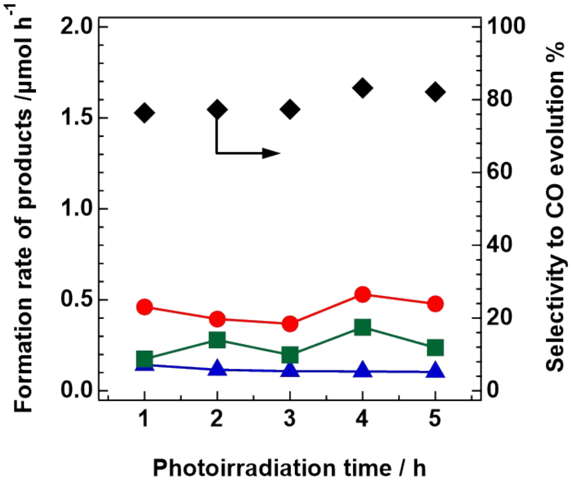


Figure S8. The formation rate of CO (red circle), O_2 (green square), and H_2 (blue triangle), and selectivity toward CO evolution (black diamond) over the AgCo/Al-$SrTiO_3$_CR in pure water under photoirradiation and CO2 bubbling for 5 h.

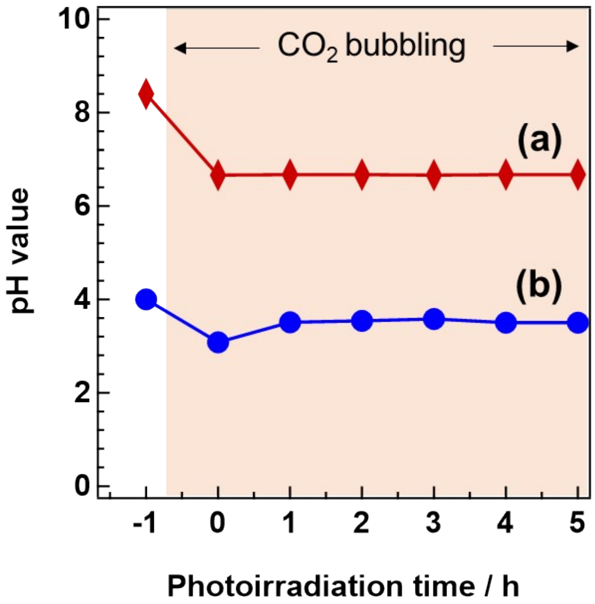


Figure S9. pH value of suspension before and after CO_2 bubbling (a) under typical conditions, (b) without $NaHCO_3$ additive.

Reference

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2. Y. Ham, T. Hisatomi, Y. Goto, Y. Moriya, Y. Sakata, A. Yamakata, J. Kubota and K. Domen, *J. Mater. Chem. A*, 2016, **4**, 3027-3033.
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