Electronic Supplementary Material (ESI) for Catalysis Science & Technology.


# Mg-doped $SrTiO_3$ Photocatalyst with Ag−Co Cocatalyst for Enhanced Selective Conversion of $CO_2$ to CO Using $H_2O$ as the Electron Donor

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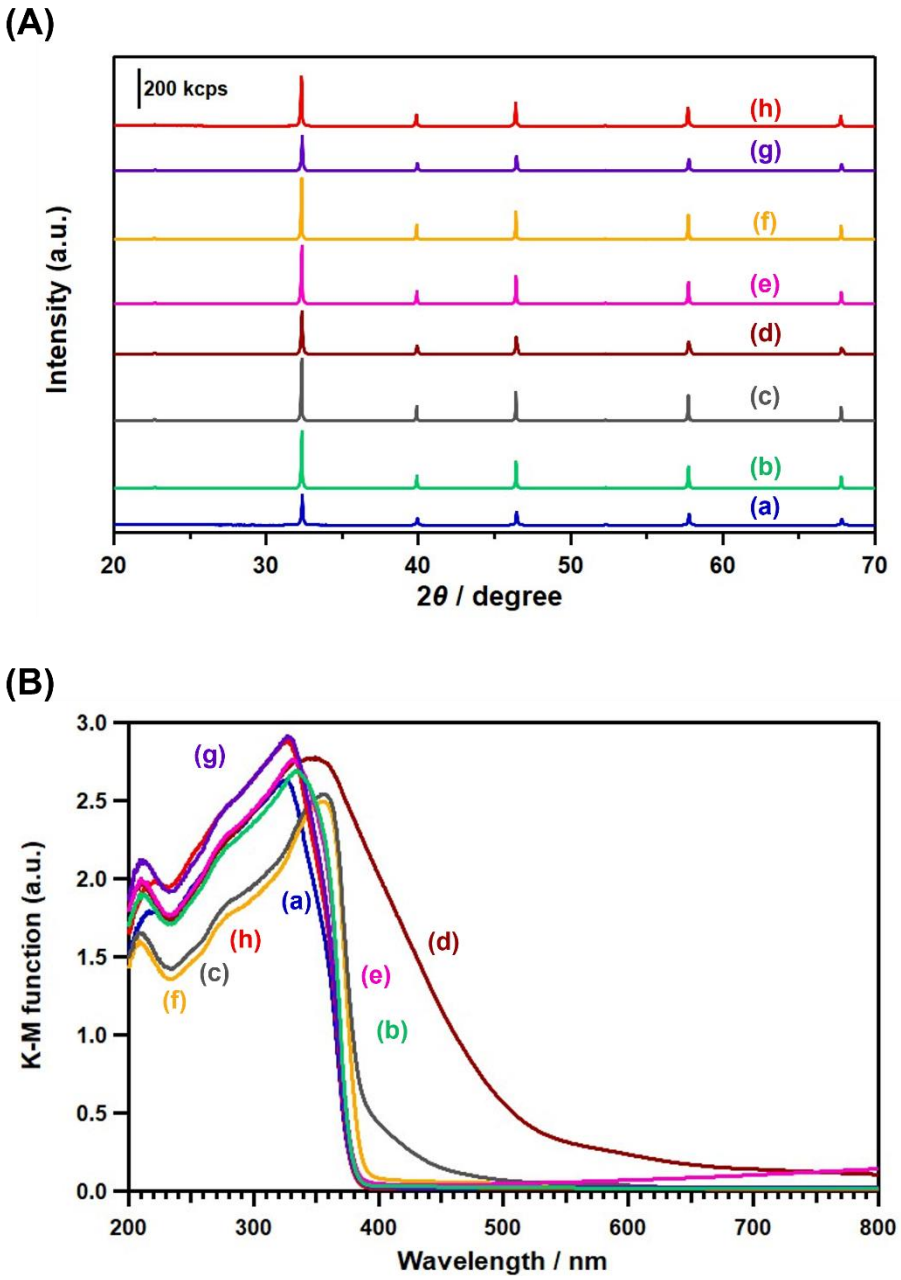



**Figure S1.** (A) XRD patterns and (B) UV-Vis DRS of (a) Al−$SrTiO_3$, (b) Zn−$SrTiO_3$, (c) Li−$SrTiO_3$, (d) Mn−$SrTiO_3$, (e) W−$SrTiO_3$, (f) Ca−$SrTiO_3$, (g) Y−$SrTiO_3$, and (h) Mg−$SrTiO_3$.

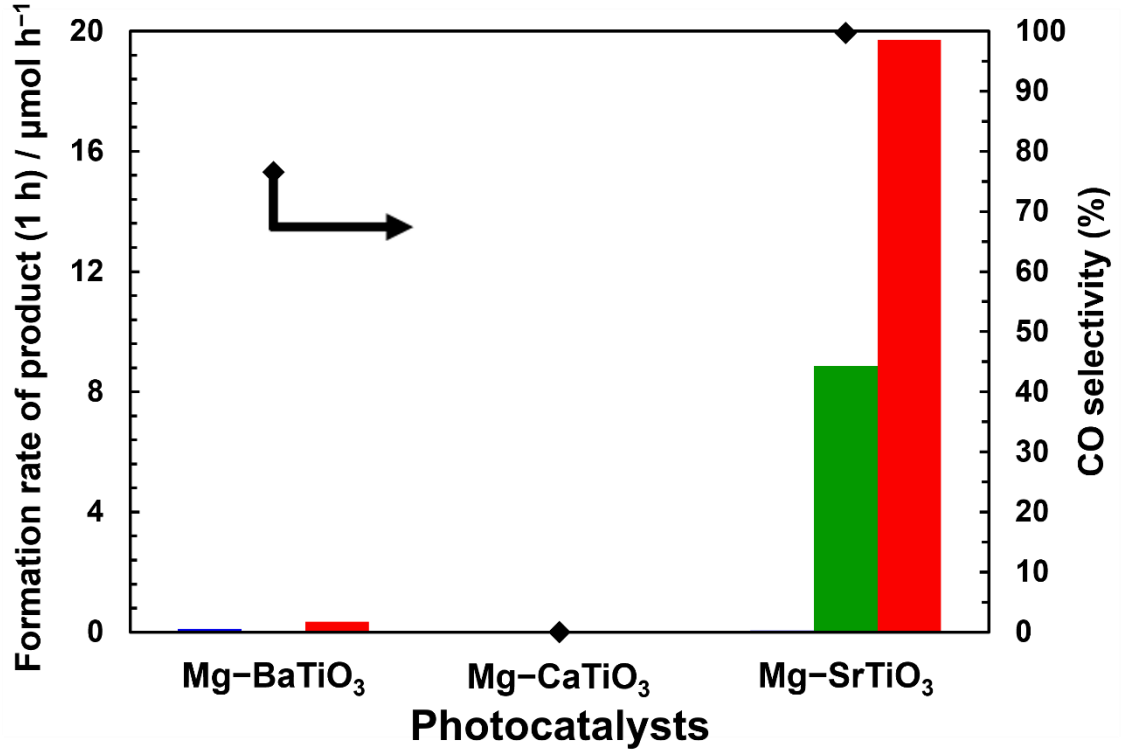



**Figure S2.** Formation rate of CO (red), $H_2$ (blue), and $O_2$ (green), and the selectivity toward CO evolution (black diamond) in the photocatalytic conversion of $CO_2$ by $H_2O$ over the Ag−Co/Mg−A$TiO_3$ photocatalysts (A = Ba, Ca, and Sr). Reaction conditions: Amount of photocatalyst: 0.2 g; Ag loading: 1 wt%; Co loading: 0.3 wt%; volume of reaction solution ($H_2O$): 0.2 L; additive: 0.1 M $NaHCO_3$; $CO_2$ flow rate: 30 mL $min^{-1}$; light source: monochromatic LED lamp at 365 nm; photoirradiation time: 1 h.

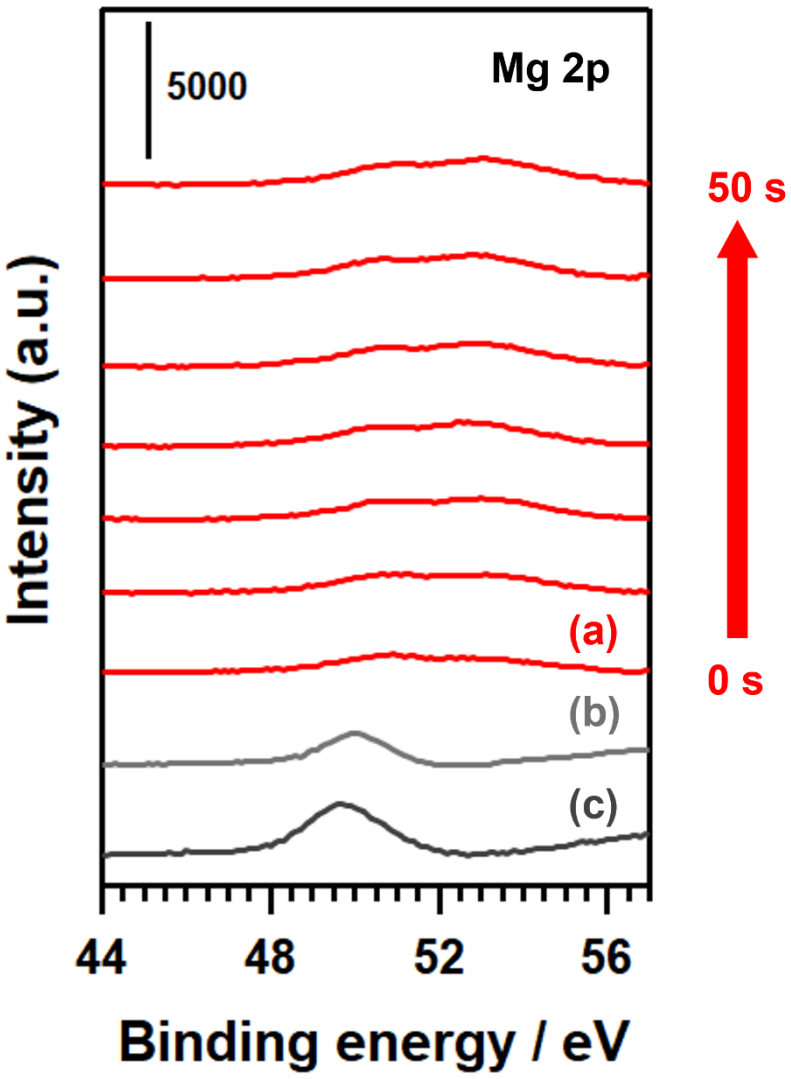



**Figure S3.** Mg 2p XPS spectra of (a) Mg−$SrTiO_3$ obtained at various Ar sputtering times, (b) $Mg(OH)_2$, and (c) MgO.

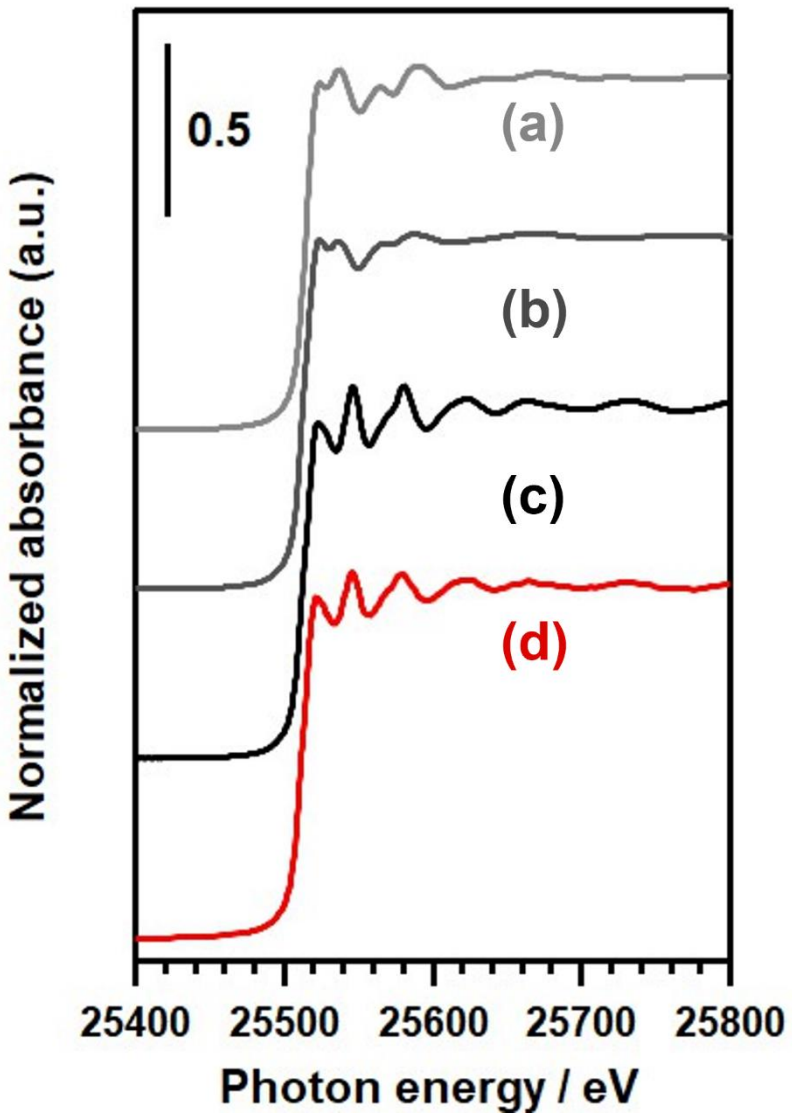



**Figure S4.** Ag K-edge X-ray absorption near edge structure (XANES) spectra of (a) AgO, (b) $Ag_2O$, (c) Ag foil, and (d) Ag−Co/Mg−$SrTiO_3$.

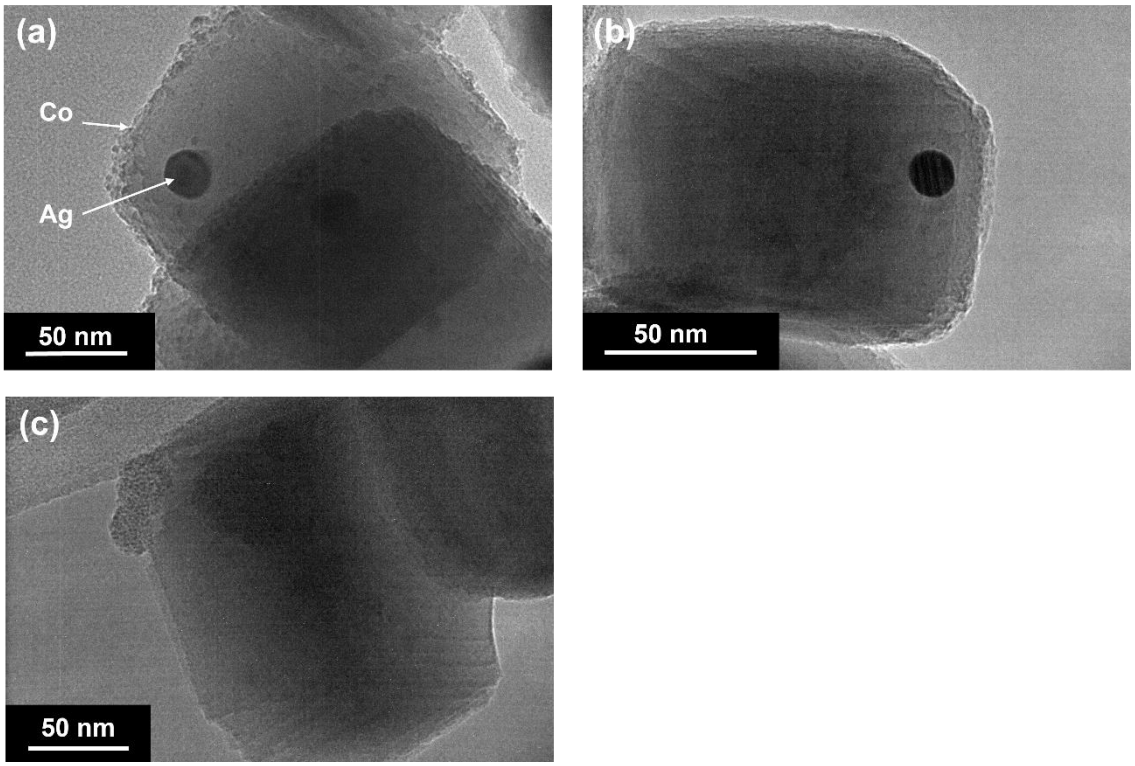



**Figure S5.** Transmission electron microscope (TEM) images of (a) Ag and Co-loaded Mg−$SrTiO_3$, (b) Ag-loaded Mg−$SrTiO_3$, and (c) Co-loaded Mg−$SrTiO_3$ by PD method.

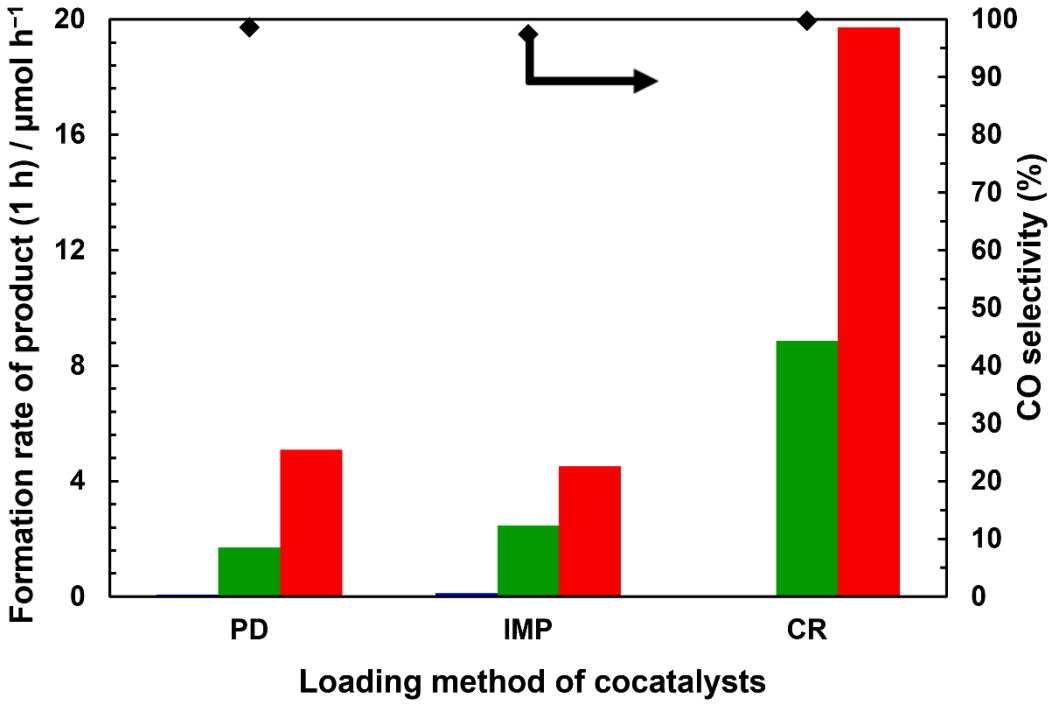



**Figure S6.** Formation rate of CO (red), $H_2$ (blue), and $O_2$ (green), and the selectivity toward CO evolution (black diamond) in the photocatalytic conversion of $CO_2$ by $H_2O$ over the Mg−$SrTiO_3$ photocatalysts in the presence of Ag−Co cocatalyst loaded by photodeposition (PD), impregnation (IMP), and chemical reduction (CR) method. Reaction conditions: Amount of photocatalyst: 0.2 g; Ag loading: 1 wt%; Co loading: 0.3 wt%; volume of reaction solution ($H_2O$): 0.2 L; additive: 0.1 M $NaHCO_3$; $CO_2$ flow rate: 30 mL $min^{-1}$; light source: monochromatic LED lamp at 365 nm; photoirradiation time: 1 h.

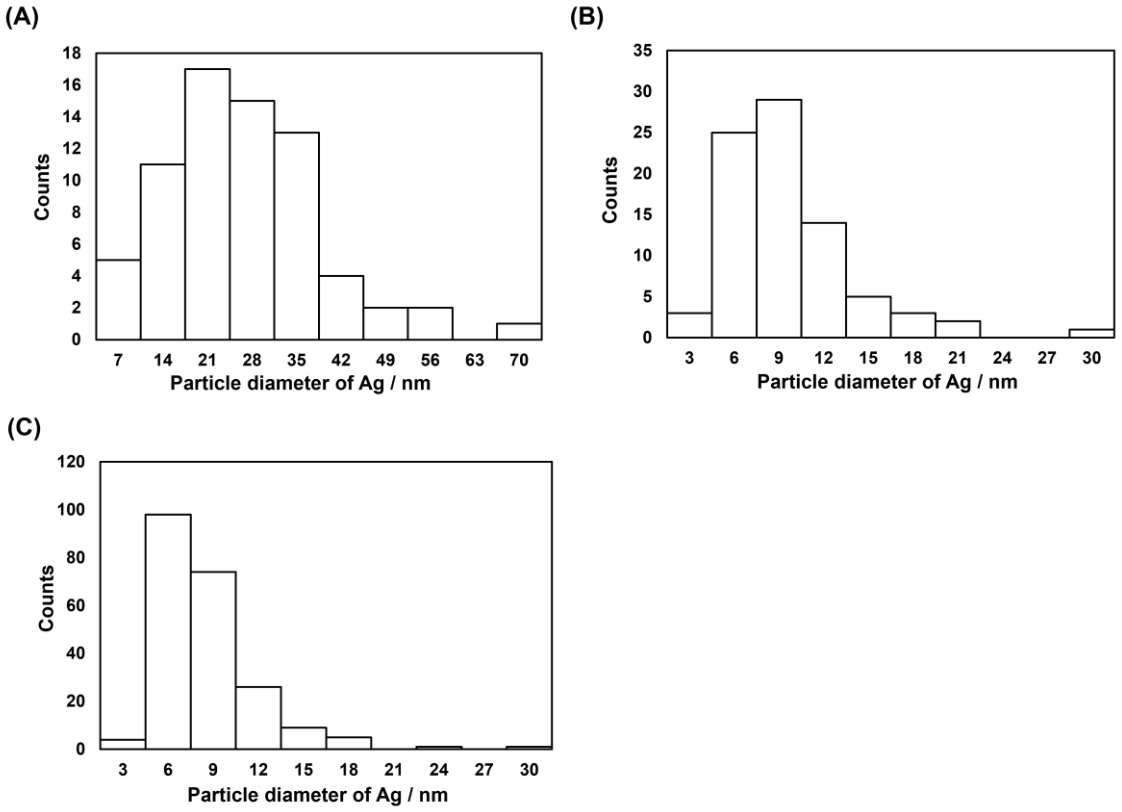



**Figure S7.** Particle diameter distributions of Ag loaded by (A) PD, (B) IMP, and (C) CR method on the surface of Mg−$SrTiO_3$.

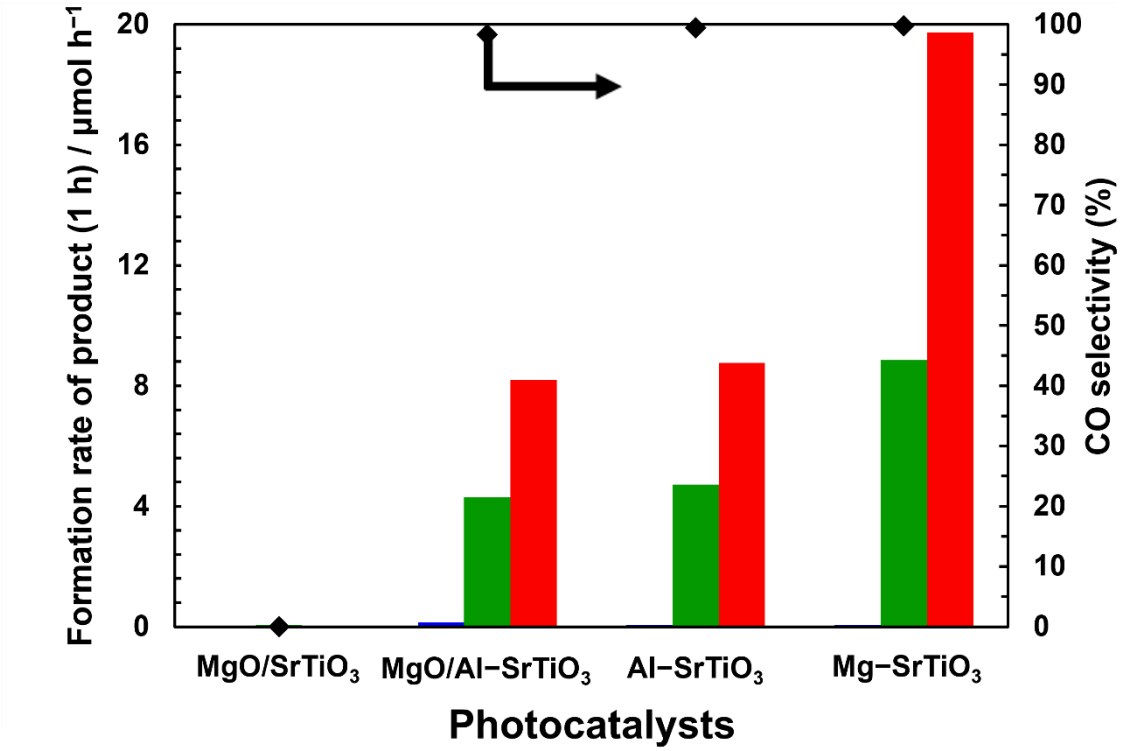



**Figure S8.** Formation rate of CO (red), $H_2$ (blue), and $O_2$ (green), and the selectivity toward CO evolution (black diamond) in the photocatalytic conversion of $CO_2$ by $H_2O$ over the Ag−Co/MgO/$SrTiO_3$, Ag−Co/MgO/Al−$SrTiO_3$, Ag−Co/Al−$SrTiO_3$ and Ag−Co/Mg−$SrTiO_3$ photocatalysts. Reaction conditions: Amount of photocatalyst: 0.2 g; Ag loading: 1 wt%; Co loading: 0.3 wt%; volume of reaction solution ($H_2O$): 0.2 L; additive: 0.1 M $NaHCO_3$; $CO_2$ flow rate: 30 mL $min^{-1}$; light source: monochromatic LED lamp at 365 nm; photoirradiation time: 1 h.

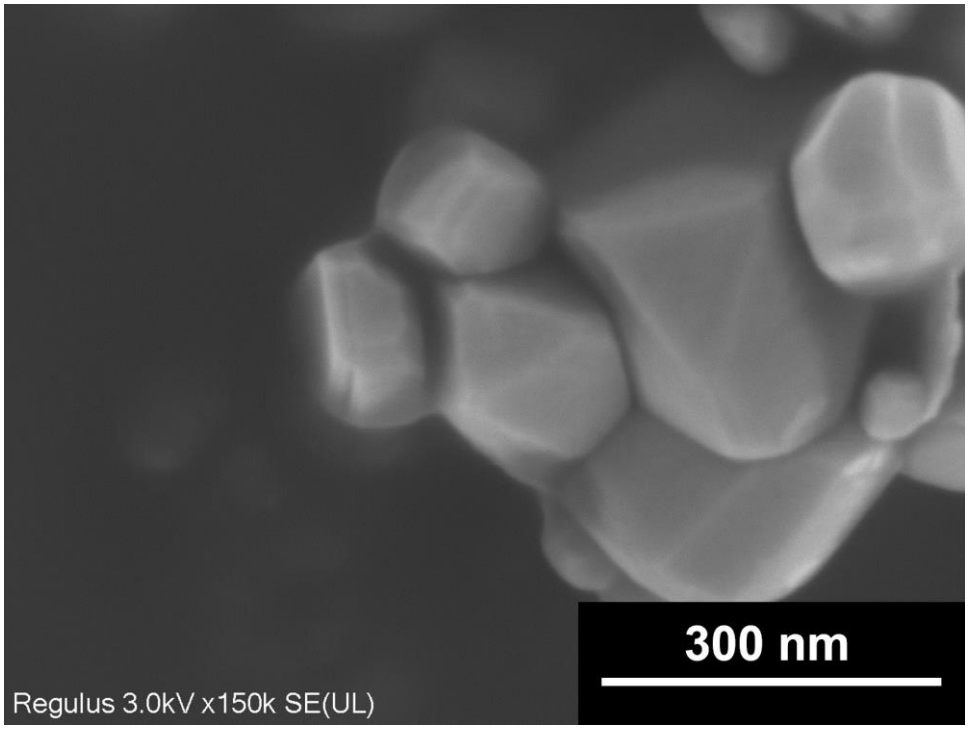



**Figure S9.** SEM image of Mg−$SrTiO_3$_1118 K.

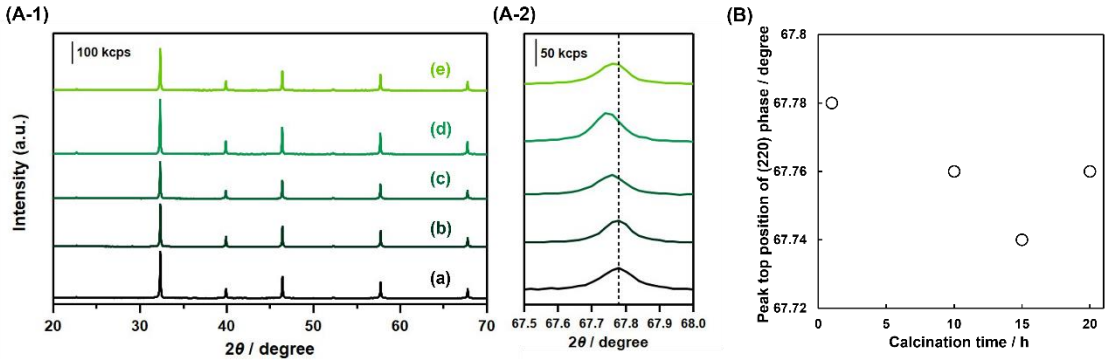



**Figure S10.** (A-1) XRD patterns of (a) pristine $SrTiO_3$, (b) Mg−$SrTiO_3$_1 h, (c) Mg−$SrTiO_3$_10 h, (d) Mg−$SrTiO_3$_15 h, and (e) Mg−$SrTiO_3$_20 h. (A-2) is the magnified view of (a)–(e) in (A-1). (B) Dependence of calcination time on the peak top position of (220) phase.

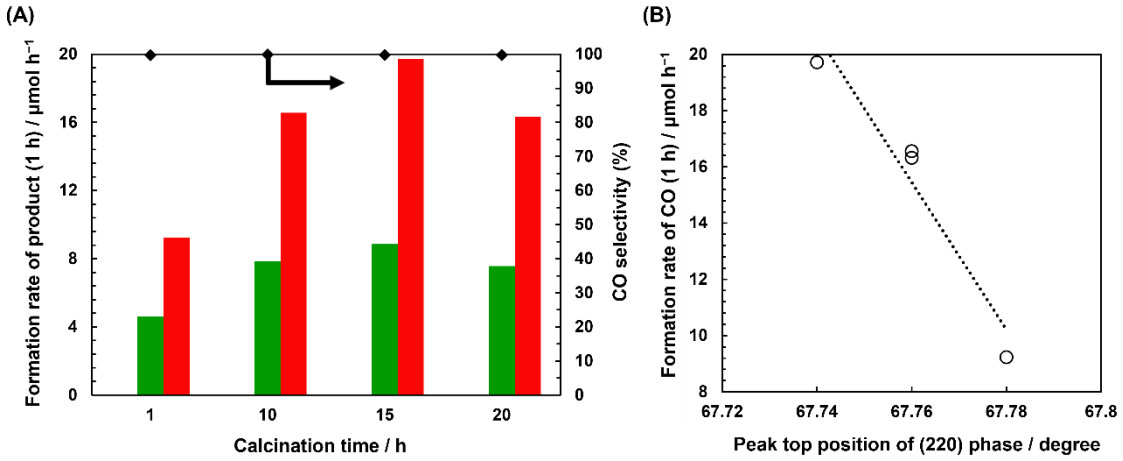



**Figure S11.** (A) Formation rate of CO (red), $H_2$ (blue), and $O_2$ (green), and the selectivity toward CO evolution (black diamond) in the photocatalytic conversion of $CO_2$ by $H_2O$ over the Ag−Co/Mg−$SrTiO_3$_***y*** h photocatalysts (***y*** = 1, 10, 15, and 20). Reaction conditions: Amount of photocatalyst: 0.2 g; Ag loading: 1 wt%; Co loading: 0.3 wt%; volume of reaction solution ($H_2O$): 0.2 L; additive: 0.1 M $NaHCO_3$; $CO_2$ flow rate: 30 mL $min^{-1}$; light source: monochromatic LED lamp at 365 nm; photoirradiation time: 1 h. (B) Dependence of peak top position on formation rate of CO.

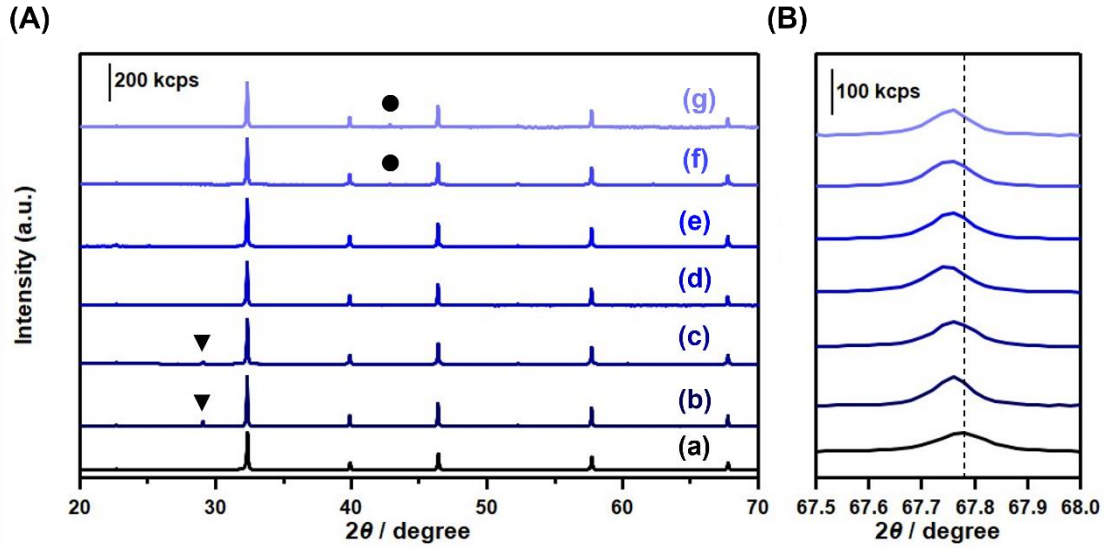



**Figure S12.** XRD patterns of (a) pristine $SrTiO_3$, (b) Mg(0)−$SrTiO_3$, (c) Mg(2)−$SrTiO_3$, (d) Mg(4)−$SrTiO_3$, (e) Mg(8)−$SrTiO_3$, (f) Mg(24)−$SrTiO_3$, and (g) Mg(100)−$SrTiO_3$ (▼ $Y_2O_3$, ● MgO).

**Table S1.** Actual contents of Mg, Ti, and Sr in the Mg−$SrTiO_3$, Mg−$SrTiO_3$_1268 K, and Mg(2)−$SrTiO_3$ using ICP measurements, which show characteristic photocatalytic activities as presented in the main text

| Samples | Formation rate of CO / μmol $h^{-1}$ | Atomic content | |
|---|---|---|---|
| | | Theoretical | Experimental |
| Mg−$SrTiO_3$ | 20 | $SrTi_{0.96}Mg_{0.04}O_3$ | $SrTi_{0.88}Mg_{0.029}O_{2.8}$ |
| Mg−$SrTiO_3$_1268K | 15 | $SrTi_{0.96}Mg_{0.04}O_3$ | $SrTi_{1.0}Mg_{0.025}O_3$ |
| Mg(2)−$SrTiO_3$ | 10 | $SrTi_{0.98}Mg_{0.02}O_3$ | $SrTi_{0.85}Mg_{0.017}O_{2.7}$ |

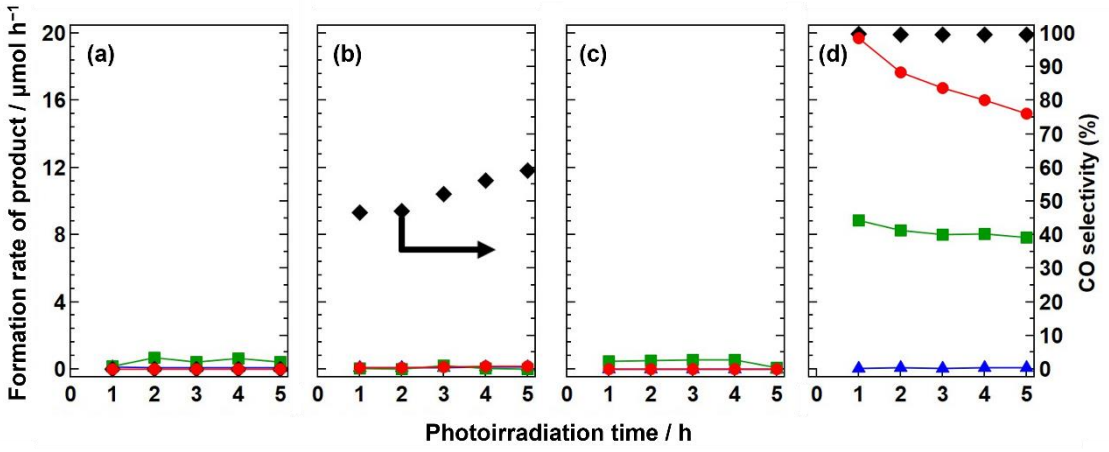



**Figure S13.** Formation rates of CO (red), $H_2$ (blue), and $O_2$ (green), and the selectivity toward CO evolution (black diamond) in the photocatalytic conversion of $CO_2$ by $H_2O$ over the Ag−Co/Mg−$SrTiO_3$ photocatalyst. (a) without photocatalyst (b) without additive (c) without photoirradiation (d) typical condition. Reaction conditions: Amount of photocatalyst: 0.2 g; Ag loading: 1 wt%; Co loading: 0.3 wt%; volume of reaction solution ($H_2O$): 0.2 L; additive: 0.1 M $NaHCO_3$; $CO_2$ flow rate: 30 mL $min^{-1}$; light source: monochromatic LED lamp at 365 nm; photoirradiation time: 5 h.

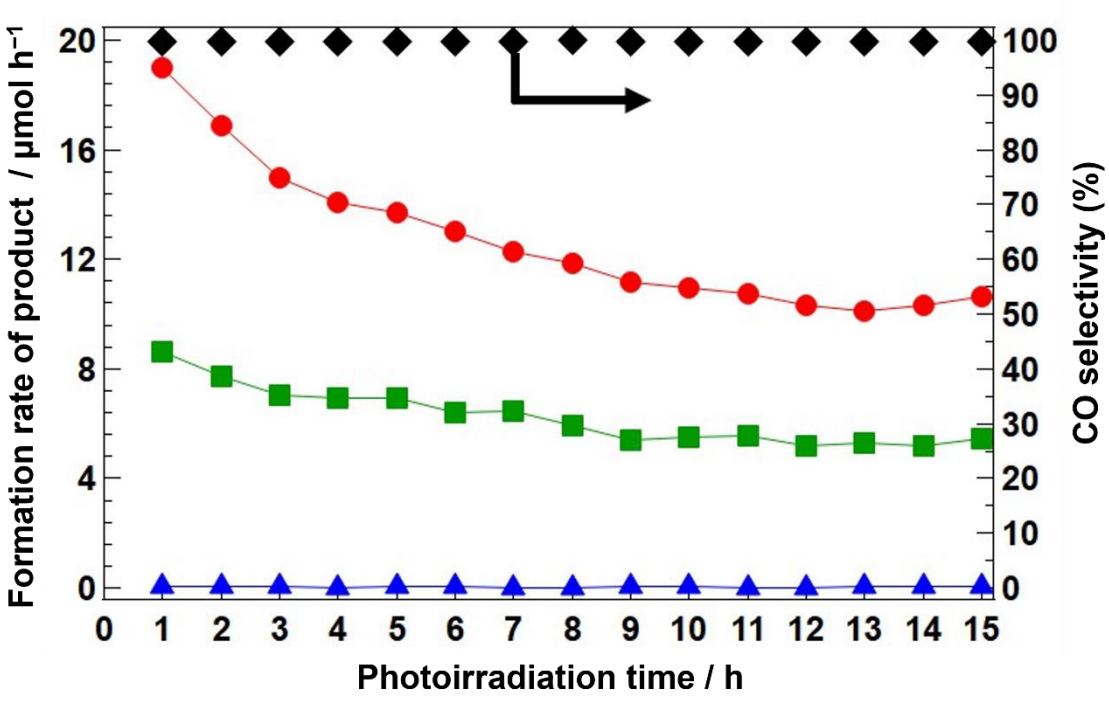



**Figure S14.** Formation rate of CO (red), $H_2$ (blue), and $O_2$ (green), and the selectivity toward CO evolution (black diamond) in the photocatalytic conversion of $CO_2$ by $H_2O$ over the Ag−Co/Mg−$SrTiO_3$ photocatalyst. Reaction conditions: Amount of photocatalyst: 0.2 g; Ag loading: 1 wt%; Co loading: 0.3 wt%; volume of reaction solution ($H_2O$): 0.2 L; additive: 0.1 M $NaHCO_3$; $CO_2$ flow rate: 30 mL $min^{-1}$; light source: monochromatic LED lamp at 365 nm; photoirradiation time: 15 h.

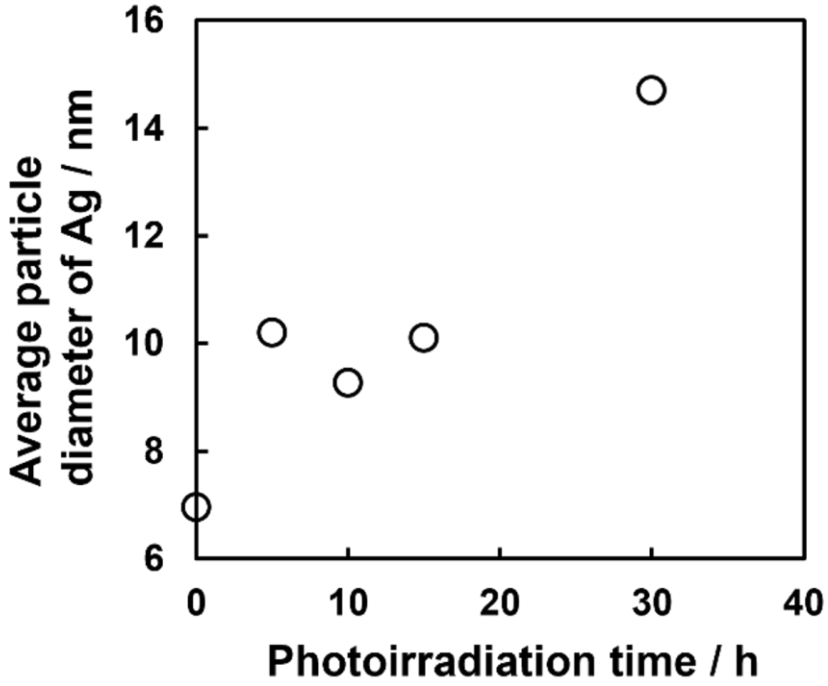
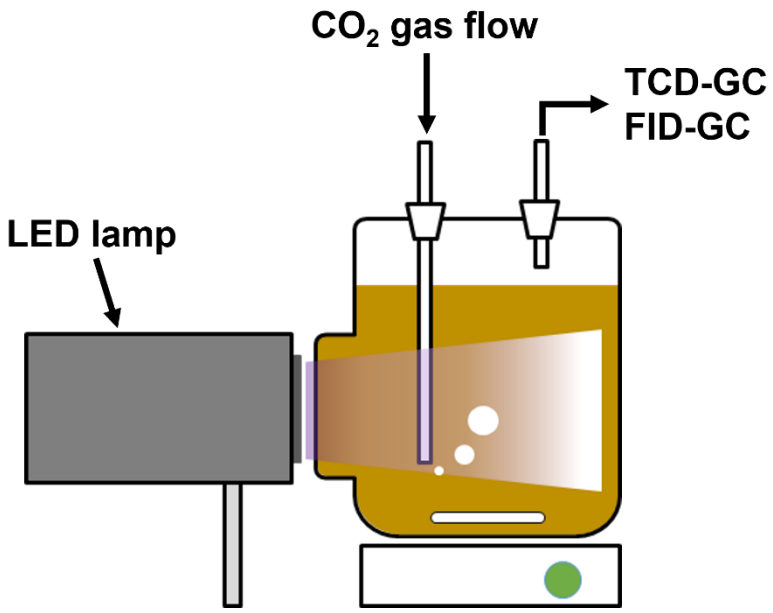



**Figure S15.** Dependency of average particle diameter of Ag cocatalyst on photoirradiation time.

**Scheme S1.** The scheme of the external-irradiation-type reaction vessel with the 365 nm monochromatic LED lamp




**The calculation of the apparent quantum efficiency (AQE)**

$$\text{AQE (\%)} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100$$

Number of reacted electrons

= 2 × total amount of substance of the photogenerated CO and $H_2$ during 1 h reaction

= $2 \times (20 + 0.057) \times 10^{-6} \times N_A$

Where $N_A$ is the Avogadro constant of $6.0 \times 10^{23}$ $mol^{-1}$.

Number of incident photons

= totally given light energy to photocatalyst for 1 h / energy per photon at 365 nm

$= W \times S \times 3600 / h \times c / (365 \times 10^{-9})$

Where $W$, $S$, $h$ and $c$ is the detected power of 400 mW $cm^{-2}$, the photo-irradiated area on reaction vessel of 20 $cm^{-2}$, Planck constant of $6.6 \times 10^{-34}$ J s and speed of light of $3.0 \times 10^{8}$.

Therefore, number of incident photons

$= 400 \times 10^{-3} \times 20 \times 3600 / (6.6 \times 10^{-34} \times 3.0 \times 10^{8}) / (365 \times 10^{-9}) = 5.3 \times 10^{22}$

From the above, AQE (%) $= 2 \times (20 + 0.057) \times 10^{-6} \times 6.0 \times 10^{23} / (5.3 \times 10^{22}) \times 100 =$ 0.045 %