Mg-doped SrTiO$_3$ Photocatalyst with Ag–Co Cocatalyst for Enhanced Selective Conversion of CO$_2$ to CO Using H$_2$O as the Electron Donor

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Abstract

Photocatalytic conversion of CO$_2$ by H$_2$O is a promising method for solving energy and environmental problems. In this context, efficient photocatalysts that facilitate the selective conversion of CO$_2$ to the value-added chemical CO are essential. In this study, for the first time in the literature, we used an Mg-doped SrTiO$_3$ photocatalyst (Mg–SrTiO$_3$) for the photocatalytic conversion of CO$_2$ to CO using H$_2$O as the electron donor under monochromatic UV-light irradiation at 365 nm. Compared to pristine SrTiO$_3$, Mg–SrTiO$_3$, which is prepared via a flux method, exhibited dramatically enhanced conversion of CO$_2$ to CO in the presence of Ag–Co cocatalyst. Moreover, the selectivity toward CO evolution was greater than 99%, indicating suppression of the unnecessary and competitive H$_2$ evolution. Scanning electron microscopy of Mg–SrTiO$_3$ revealed edge-shaved cubic particles, which were correlated to the anisotropic distribution of photogenerated electrons and holes and the consequent enhancement of photocatalytic activity. Furthermore, the Mg-doping temperature and amount used to prepare Mg–SrTiO$_3$ influenced the substitution of Ti$^{4+}$ sites in the bulk of SrTiO$_3$ by Mg$^{2+}$, thereby affecting the CO evolution. The apparent quantum efficiency of optimal Mg–SrTiO$_3$ in the photocatalytic conversion of CO$_2$ was determined to be 0.05%.
Introduction

Climate change is a serious and escalating problem globally. \(^1\) \(^2\) It is primarily attributed to the greenhouse effect of atmospheric CO\(_2\). \(^3\) The concentration of atmospheric CO\(_2\) has reached over 400 ppm by 2013 and has been predicted to further increase in the near future. \(^4\) Among the many approaches to reduce CO\(_2\) emissions, \(^5\) \(^6\) \(^7\) photocatalysis has attracted significant attention owing to several reasons.

In 1972, Honda and Fujishima reported that photoirradiation of TiO\(_2\) electrodes can shift the anode potential for water oxidation to a more negative in electrochemical water splitting. \(^8\) This study promoted the development of photocatalysis for degradation of organic compounds and overall water splitting. A promising photocatalyst that is widely used for generating clean energy is the perovskite oxide SrTiO\(_3\). \(^9\) \(^10\) \(^11\) \(^12\) Domen et al. reported that Al-doped SrTiO\(_3\) (Al–SrTiO\(_3\)) is an excellent photocatalyst for efficient photocatalytic H\(_2\)O splitting, \(^13\) where it showed a near 100\% internal quantum efficiency. This efficiency was attributed to the particle shape of the photocatalyst, which promoted the charge separation as suggested by the electrical simulation. \(^14\) Yamakata et al. demonstrated that doping Na\(^+\) into SrTiO\(_3\) improved the photocatalytic activity for water splitting. They concluded that the generated oxygen vacancies act as trapping sites for the photogenerated electrons, consequently extending their lifetimes. \(^15\) \(^16\)
Even though photocatalytic water splitting has been extensively studied, the photocatalytic conversion of CO\textsubscript{2} by water, which is known as “artificial photosynthesis”, requires further improvement.\textsuperscript{17–19} Conversion of the emitted CO\textsubscript{2} into value-added chemicals such as CO, HCOOH, CH\textsubscript{3}OH, and CH\textsubscript{4} using solar light could promote a sustainable society built on energy recycling. In particular, CO is considered as a useful and important product as it can be converted into a liquefied hydrocarbon, which is a raw material in core industries, through the Fischer–Tropsch process.\textsuperscript{20} Our research group has previously reported the photocatalysts Ag/SrO/Ta\textsubscript{2}O\textsubscript{5}, Ag/La\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}, Ag/ZnTa\textsubscript{2}O\textsubscript{6}, and Ag/SrNb\textsubscript{2}O\textsubscript{6} for the selective conversion of CO\textsubscript{2} by water under UV-light irradiation (< 300 nm).\textsuperscript{21–24} These photocatalysts use water as both an electron donor and a proton source, which is favourable because water is abundant, cheap, easy to use, and non-toxic. Moreover, we demonstrated that Ag/Sr\textsubscript{2}KTa\textsubscript{5}O\textsubscript{15} and Ag/ZnGa\textsubscript{2}O\textsubscript{4}/Ga\textsubscript{2}O\textsubscript{3} facilitated a sufficiently high selectivity toward CO\textsubscript{2} conversion via the complete suppression of H\textsubscript{2} evolution.\textsuperscript{24,25} Even though H\textsubscript{2} evolution (H\textsuperscript{+}/H\textsubscript{2}: −0.41 V vs NHE at pH = 7.0) proceeds preferentially over CO\textsubscript{2} reduction owing to the more negative standard redox potential of the latter reaction (CO\textsubscript{2}/CO: −0.51 V vs NHE at pH = 7.0),\textsuperscript{26} the modification of photocatalysts with appropriate cocatalysts enabled selective CO formation. Furthermore, a recent study reported that Ag–Co/Al–SrTiO\textsubscript{3} is the only effective photocatalyst for the
photocatalytic conversion of CO₂ under an irradiation of 365 nm. This was attributed to the bandgap energy of Al-doped SrTiO₃ is 3.2 eV, which is smaller than that of the previously reported Ga-based and Ta-based photocatalysts. The Ag–Co dual cocatalyst was more effective than single Ag and Co cocatalysts for CO evolution when paired with Al–SrTiO₃, where Ag and Co are active sites for CO₂ conversion and H₂O oxidation, respectively. The formation rate of CO over Ag–Co/Al–SrTiO₃ was approximately seven times higher than that of Ag/Al–SrTiO₃. In a continuation of our efforts to identify effective photocatalysts for the photocatalytic conversion of CO₂ to CO in water, in this study, we investigated metals other than Al as dopants for SrTiO₃ and optimized the doping process. Subsequently, we evaluated the photocatalytic activity of the doped SrTiO₃ photocatalysts in the conversion of CO₂ to CO under UV-LED-light irradiation at 365 nm.

Experimental Section

Preparation of the photocatalysts

The perovskite-structured SrTiO₃ photocatalyst was fabricated via a previously reported solid-state method. SrCO₃ (21 mmol) and TiO₂ (20 mmol) were ground for 15 min in a mortar and pestle, and the mixture was transferred to an alumina crucible to
calcine at 1373 K for 10 h in air. The resulting powder was washed three times with hot ultrapure water and dried overnight at room temperature. BaTiO$_3$ and CaTiO$_3$ were synthesised via the same procedure using BaCO$_3$ and CaCO$_3$ as precursors, respectively.

M-doped SrTiO$_3$ (M–SrTiO$_3$, M = Al, Zn, Li, Mn, W, Ca, Y, and Mg) was synthesised via a flux method.$^{33}$ SrCl$_2$ flux (100 mmol) was added to a mixture of the prepared SrTiO$_3$ (10 mmol) and a metal oxide (0.4 mmol). The mixture was ground for 15 min in a mortar and pestle, transferred to an yttria crucible, and calcined at 1418 K for 15 h. The obtained powder was washed three times with hot ultrapure water and dried overnight at 353 K. Next, we fabricated a series of Mg–SrTiO$_3$ photocatalysts, termed as Mg–SrTiO$_3$$_{x}$ K, Mg–SrTiO$_3$$_{y}$ h, and Mg(z)–SrTiO$_3$, where x, y, and z are the calcination temperature ($x$ = 1118, 1268, 1318, 1368, and 1418 K), calcination time ($y$ = 1, 10, 15, and 20 h), and molar ratio (mol%) of Mg to Ti ($z$ = 0, 2, 4, 8, 24, and 100), respectively. Mg-doped BaTiO$_3$ (Mg–BaTiO$_3$) and Mg-doped CaTiO$_3$ (Mg–CaTiO$_3$) were also fabricated via the same method using BaCl$_2$ and CaCl$_2$ as fluxes, respectively.

**Loading of the cocatalysts**

A conventional chemical reduction (CR) method was used to load Ag and Co cocatalysts onto the surface of M–SrTiO$_3$. A conventional chemical reduction (CR) method was used to load Ag and Co cocatalysts onto the surface of M–SrTiO$_3$. $^{33}$M–SrTiO$_3$ (0.75 g) was dispersed in ultrapure
water (50 mL), and the suspension was maintained at 353 K. Aqueous solutions of AgNO₃ (0.1 M, 0.695 mL), Co(NO₃)₂ (0.1 M, 0.347 mL), and NaH₂PO₄ (0.4 M, 1.5 mL) were added to the suspension while continuously stirring. The resultant suspension was maintained at 353 K for 1.5 h, following which the powder was via vacuum filtration and dried overnight at room temperature.

Furthermore, MgO/SrTiO₃ and MgO/Al−SrTiO₃ were prepared by an impregnation method as reference materials.²⁷ SrTiO₃ or Al−SrTiO₃ (0.92 g) was added to an acetone solution of Mg(NO₃)₂·6H₂O (0.051 g). The solvent was completely evaporated by heating the suspension while vigorously stirring, and the resultant powder was calcined at 773 K for 5 h.

**Characterization**

The crystalline properties of the fabricated photocatalysts were evaluated by X-ray diffraction (XRD) using a Rigaku SmartLab SE equipped with CuKα radiation (λ = 0.154 nm). UV-visible diffuse reflectance spectroscopy (UV-Vis DRS) was performed using the JASCO V-670 spectrometer equipped with an integrating sphere. A BaSO₄ plate was used as a standard reflection sample. Scanning electron microscopy (SEM) images were obtained at an acceleration voltage of 3.0 kV using a field-emission scanning
electron microscope (SU-8220, Hitachi High-Technologies) equipped with an energy-dispersive X-ray spectroscopy (EDS) unit for elemental mapping.

**Photocatalytic reactions**

The photocatalytic conversion of CO\(_2\) by H\(_2\)O as the electron donor was conducted using an external irradiation-type reaction vessel (Scheme S1) in a quasi-flowing batch system. Ag–Co/M–SrTiO\(_3\) (0.2 g) was dispersed in a 0.1 M aqueous solution of NaHCO\(_3\) (200 mL). A high purity CO\(_2\) gas (99.999%) was bubbled into the resultant suspension at a flow rate of 60 mL min\(^{-1}\) for 1 h to remove the dissolved air in the reaction solution. The suspension was then irradiated using a monochromatic UV-LED lamp at 365 nm (IRS-1000, CELL System Co., Ltd., Japan) with continuous CO\(_2\) gas flow at a flow rate of 30 mL min\(^{-1}\). The generated gases were analysed using online gas chromatographs equipped with a thermal conductivity detector (TCD–GC; GC-8A, Shimadzu Corporation, Japan; Ar carrier gas; molecular sieve 5A column) and a flame-ionisation detector with a methanizer (FID–GC; GC-8A, Shimadzu Corporation, Japan; N\(_2\) carrier gas; Shincarbon ST column). The CO selectivity and balance of consumed electrons and holes (\(e^-/h^+\)) were calculated using Eqs (1) and (2) as follows:

CO selectivity (\%) = \(\frac{R_{CO}}{R_{CO} + R_{H_2}}\) × 100  \hspace{1cm} (1)
\[ e^-/h^+ = \frac{(2R_{CO} + 2R_{H_2})}{4R_{O_2}} \]  \hspace{1cm} (2)

where \( R_{CO} \), \( R_{H_2} \), and \( R_{O_2} \) are the formation rates of CO, H\(_2\), and O\(_2\) (\( \mu \text{mol h}^{-1} \)), respectively.

The apparent quantum efficiency (AQE, \%) of the photocatalysts was calculated from the formation rate of the product and the light intensity measured using a power meter (OPHIR Photonics, A Newport Company) using Eq (3).

\[ \text{AQE} \ (%) = \left( \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \right) \times 100 \hspace{1cm} (3) \]

Number of reacted electrons was calculated using Eq (4):

\[ \text{Number of reacted electrons} = 2 \times (R_{CO} + R_{H_2}) \times 10^{-6} \times N_A \hspace{1cm} (4) \]

where \( N_A \) is the Avogadro constant \((6.0 \times 10^{23} \text{ mol}^{-1})\).
Results and discussion

Figure S1 shows the XRD patterns and UV-Vis DR spectra of $M$–SrTiO$_3$ ($M$ = Al, Zn, Li, Mn, W, Ca, Y, or Mg). Well-ordered diffraction patterns corresponding to the perovskite structure were observed in all the cases. Moreover, the dopant metals did not alter the absorption wavelength, whereas the DR spectrum of Mn–SrTiO$_3$ shows a typical absorption corresponding to d-d transition of Mn species. Figure 1 shows the formation rates of gaseous products (CO, H$_2$, and O$_2$) and selectivity toward CO evolution in the photocatalytic conversion of CO$_2$ in the presence of the Ag–Co/M–SrTiO$_3$ photocatalysts ($M$ = Al, Zn, Li, Mn, W, Ca, Y, and Mg) upon photoirradiation for 1 h. Zn–SrTiO$_3$, Li–SrTiO$_3$, Mn–SrTiO$_3$, W–SrTiO$_3$, Ca–SrTiO$_3$, and Y–SrTiO$_3$ exhibited extremely low photocatalytic activities for the conversion of CO$_2$, whereas Al–SrTiO$_3$ and Mg–SrTiO$_3$ showed moderate activities. Mg–SrTiO$_3$ exhibited the highest activity for CO evolution, which has been observed as a CO formation rate of ~20 μmol h$^{-1}$. A previous study reported that Al–SrTiO$_3$ showed excellent activity in the presence of Rh/Cr$_2$O$_3$/CoOOH cocatalysts during photocatalytic H$_2$ evolution.$^{14}$ However, H$_2$ evolution was drastically suppressed (0.055 μmol h$^{-1}$) in the presence of Ag–Co/Mg–SrTiO$_3$, where the selectivity toward CO evolution was greater than 99%, indicating that Mg-doping into SrTiO$_3$ improved the photocatalytic activity for the conversion of CO$_2$. Moreover, the CO
formation rate over Mg–SrTiO$_3$ was two or more times higher than that over the previously reported Al–SrTiO$_3$ photocatalyst.$^{27}$ Furthermore, stoichiometric O$_2$ evolution (8.9 μmol h$^{-1}$) was observed in the presence of Mg–SrTiO$_3$ ($e^-/h^+ = 1.1$), suggesting that H$_2$O acts as both an electron donor and a proton source for the photocatalytic conversion of CO$_2$ in water. Figure S2 shows the photocatalytic activities of Ag–Co/Mg–ATiO$_3$ photocatalysts (A = Ba, Ca, and Sr) in the conversion of CO$_2$. Mg–BaTiO$_3$ and Mg–CaTiO$_3$ showed extremely low and no photocatalytic activity, respectively, indicating that other perovskite photocatalysts are not effective in this reaction. Therefore, we focused on the effect of Mg-doping into SrTiO$_3$ on the photocatalytic conversion of CO$_2$ in water.
Figure 1. 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\(_2\) in H\(_2\)O over the pristine and the doped Ag–Co/M–SrTiO\(_3\) photocatalysts (M = Al, Zn, Li, Mn, W, Ca, Y, and Mg). Reaction conditions: Amount of photocatalyst: 0.2 g; Ag loading: 1 wt%; Co loading: 0.3 wt%; volume of reaction solution (H\(_2\)O): 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.
As shown in Figure 2(A), the XRD patterns of pristine SrTiO$_3$, Mg–SrTiO$_3$, and Ag–Co/Mg–SrTiO$_3$ revealed that the diffraction patterns of both SrTiO$_3$ and Mg–SrTiO$_3$ can be assigned to the pure phase of the perovskite structure with a $Pm3m$ (211) space group (ICSD 23076). Peaks corresponding to the Ag or Co species were not observed in the XRD pattern of Ag–Co/Mg–SrTiO$_3$, suggesting that the Ag–Co cocatalyst was loaded on the surface of Mg–SrTiO$_3$ with high dispersion. The peak at approximately $2\theta = 67.8^\circ$ in the pattern of Mg–SrTiO$_3$, shown in Figure 2(A–2), is ascribed to the (220) phase. This peak shifted to a lower angle than that of SrTiO$_3$, which indicates that replacing Ti$^{4+}$ in the bulk of SrTiO$_3$ with Mg$^{2+}$ dopant extends the lattice plane distance. The ionic radii of six-coordinated Sr$^{2+}$, Ti$^{4+}$, and Mg$^{2+}$ were 1.18, 0.605, and 0.720 Å, respectively.\textsuperscript{35} Figure 2(B) shows the UV-Vis DR spectra of SrTiO$_3$, Mg–SrTiO$_3$, and Ag–Co/Mg–SrTiO$_3$. The absorption edge of SrTiO$_3$ was estimated to be 390 nm, which confirms the suitability of the monochromatized UV-LED irradiation at 365 nm. The UV-Vis DR spectrum of Mg–SrTiO$_3$ ((b) in Figure 2(B)) shows that Mg$^{2+}$ doping did not influence the absorption wavelengths of SrTiO$_3$. The Tauc plot (Figure 2(C)) revealed that the band gap energy of pristine SrTiO$_3$ and Mg–SrTiO$_3$ is 3.2 eV, which is consistent with previous reports.\textsuperscript{36–38} In the case of Ag–Co/Mg–SrTiO$_3$ ((c) in Figure 2(B)), a broad absorption was observed in the visible-light region. This broad peak could be ascribed to the plasmonic absorption
of Ag nanoparticles. These results confirm that the Ag nanoparticles from the Ag–Co dual cocatalyst were loaded onto Mg–SrTiO₃. Moreover, the Ag K-edge XANES spectrum of Ag–Co/Mg–SrTiO₃ is in good agreement with that of the Ag foil, indicating that Ag particles with a valence number of 0 were loaded onto Mg–SrTiO₃ as a cocatalyst (Figure S3).
Figure 2. (A) X-ray diffraction (XRD) patterns, (B) UV-visible diffuse reflectance spectra, and (C) Tauc plots of (a) pristine SrTiO$_3$, (b) Mg–SrTiO$_3$, and (c) Ag–Co/Mg–SrTiO$_3$. (A-2) is the magnified view of (a) and (b) in (A-1).
The SEM images in Figure 3(a) show that the pristine SrTiO$_3$ has an irregular shape. In the absence of Mg dopant, the shape of the SrTiO$_3$ particle is regulated by the calcination with SrCl$_2$ flux, resulting in cubic particles with $\{100\}$ facets (Figure 3(b)). However, Mg–SrTiO$_3$ has edge-shaved cube particles with $\{110\}$ facets in addition to the $\{100\}$ facets, as shown in Figure 3(c). A similar change was observed for Al–SrTiO$_3$ in the previous studies.$^{13,40}$ Takata et al. have performed calculations to determine the distribution of photogenerated electrons and holes of SrTiO$_3$ in the $\{100\}$ and $\{110\}$ facets. They observed that the concentration of electrons around the $\{100\}$ facets was relatively high, whereas the holes were easily transferred to the $\{110\}$ facets.$^4$ To confirm this anisotropic charge distribution, we investigated the photodeposition of Ag and Co cocatalysts on the surface of Mg–SrTiO$_3$ in this study. As shown in Figure S4, the Ag and Co cocatalysts were deposited on the $\{100\}$ and $\{110\}$ facets, respectively. This result indicates that photoexcited electrons and holes are selectively distributed in Mg–SrTiO$_3$ based on the facets. This distribution suppresses the electron-hole recombination, thus contributing to the high photocatalytic activity. We used the CR method to load Ag and Co cocatalysts on Mg–SrTiO$_3$ as it is regarded as the optimal method for the photocatalytic conversion of CO$_2$ (Figure S5). As shown in Figure 3(d), the cocatalysts loaded by the CR method were not facet-selective but were highly dispersed on the
surface of the Mg–SrTiO$_3$ particles. The average diameter of the Ag cocatalyst was estimated to be 7.0 nm based on the diameter distribution in the TEM images. This diameter is smaller than that of the Ag cocatalysts loaded via the photodeposition and impregnation methods (Figure S6).

**Figure 3.** SEM images of (a) pristine SrTiO$_3$; (b) flux-treated SrTiO$_3$; (c) Mg–SrTiO$_3$; and (d) Ag–Co/Mg–SrTiO$_3$. 

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Several previous reports have demonstrated that the modification of photocatalysts with metal oxides or hydroxides such as SrO, Cr(OH)$_3$, Pr(OH)$_3$, and layered double hydroxides, which can provide adsorption sites for CO$_2$, improves the photocatalytic activity in the selective conversion of CO$_2$.$^{21,41-45}$ However, we observed that the CO formation rate and CO selectivity are higher for Mg–SrTiO$_3$ than those for MgO/SrTiO$_3$ and MgO/Al–SrTiO$_3$ (fabricated via the conventional impregnation method) in the presence of the Ag–Co cocatalyst, as shown in Figure S7. These results clearly indicate that the residual MgO or Mg(OH)$_2$ on the surface of Mg–SrTiO$_3$ does not significantly improve the photocatalytic activity. Therefore, Mg$^{2+}$-doping into the bulk structure of SrTiO$_3$ is essential for good photocatalytic conversion of CO$_2$ in water.
Figure 4 shows the XRD patterns of the Mg–SrTiO$_3$ fabricated by calcination at 1118, 1268, 1318, 1368, and 1418 K. These diffraction patterns correspond to the perovskite structure of SrTiO$_3$, and no impurity phases were observed in any of the cases. The position of the diffraction peak at $2\theta = 68^\circ$ in Figure 4(A-2) is assigned to the (220) phase. This peak shifted to a lower angle with increasing calcination temperature, which indicates that Ti$^{4+}$ in the bulk structure of SrTiO$_3$ was steadily replaced with Mg$^{2+}$. Therefore, Mg doping into SrTiO$_3$ can be enhanced by increasing the calcination temperature in the flux treatment. As shown in Figure 5(A), Ag–Co/Mg–SrTiO$_3$–1118 K generated a small amount of CO during the photocatalytic reaction. Mg–SrTiO$_3$–1118 K can be considered as “un-doped” SrTiO$_3$ because 1118 K is lower than the melting point of the SrCl$_2$ flux (1147 K). This is confirmed by the fact that the edge-shaved cubic structure was not observed in the SEM image of Mg–SrTiO$_3$–1118 K (Figure S8). Moreover, the CO formation rate drastically improved at the calcination temperature of 1268 K, which is higher than the melting point of the SrCl$_2$ flux. As shown in Figure 5(B), a clear correlation was observed between the CO formation rate and the XRD peak positions, suggesting that greater doping amounts result in greater photocatalytic activity for the conversion of CO$_2$.
Figure 5. (A) Formation rates of CO (red), H₂ (blue), and O₂ (green) and the selectivity toward CO evolution (black diamond) in the photocatalytic conversion of CO₂ in H₂O over Ag–Co/Mg–SrTiO₃ₓ K photocatalysts (𝐧 = 1118, 1268, 1318, 1368, and 1418).

Reaction conditions: Amount of photocatalyst: 0.2 g; Ag loading: 1 wt%; Co loading: 0.3 wt%; volume of reaction solution (H₂O): 0.2 L; additive: 0.1 M NaHCO₃; CO₂ flow rate: 30 mL min⁻¹; light source: monochromatic LED lamp at 365 nm; photoirradiation time: 1 h. (B) Dependence of peak position on CO formation rate.
Figure S9(A) shows the XRD patterns of Mg–SrTiO$_3$$_y$ h, where $y$ is the calcination time ($y = 1$, 10, 15, and 20 h) for the doping process at 1418 K. The peak top position of the (220) phase shifted with increasing doping time, as shown in Figure S9(A-2), indicating that Mg doping into SrTiO$_3$ is enhanced by prolonging the doping time. Moreover, as shown in Figure S10(B), a positive correlation is observed between the photocatalytic activity for the conversion of CO$_2$ to CO and the peak top position of the (220) phase diffraction. These results confirm that the extent of Mg doping via the replacement of Ti$^{4+}$ sites in SrTiO$_3$ with Mg$^{2+}$ is a significant parameter for CO evolution.

Figure S11 shows the XRD pattern of Mg($z$)–SrTiO$_3$, where $z$ is the molar ratio (mol%) of the Mg dopant to SrTiO$_3$ ($z = 0$, 2, 4, 8, 24, and 100). Clear diffraction patterns corresponding to the perovskite structure of SrTiO$_3$ were observed in all cases. However, the diffraction patterns of Mg(0)–SrTiO$_3$ and Mg(2)–SrTiO$_3$ indicate a small impurity phase, which is attributed to Y$_2$O$_3$. This suggests that the Mg–SrTiO$_3$ samples were contaminated with the yttria crucible during their preparation. In contrast, a small diffraction peak corresponding to MgO was observed for Mg(24)–SrTiO$_3$ and Mg(100)–SrTiO$_3$, which is ascribed to excess amounts of the corresponding Mg dopants. The diffraction peak corresponding to the (220) facets of Mg(4)–SrTiO$_3$ appeared at lower angle than that of the pristine sample, while the peak top position of Mg(8)–SrTiO$_3$
slightly shifted to a higher angle than that of Mg(4)−SrTiO$_3$. We attribute the former case to the replacement of Ti$^{4+}$ sites of SrTiO$_3$ with Mg$^{2+}$ species and the latter case to the replacement of some Sr$^{2+}$ sites with Mg$^{2+}$ species.

Figure 6 shows the photocatalytic activity of Ag−Co/Mg(z)−SrTiO$_3$ in the conversion of CO$_2$ in water. Ag−Co/Mg(0)−SrTiO$_3$ exhibited negligible activity and the products hardly evolved. However, the CO formation rate increased with increasing amounts of Mg dopants. The highest CO formation rates were observed for Ag−Co/Mg(4)−SrTiO$_3$ and Ag−Co/Mg(8)−SrTiO$_3$. These rates decreased slightly upon addition of excess Mg dopants, suggesting that the use of 4 mol% of Mg dopants in the Mg-doping process is optimal for CO evolution. Furthermore, our results suggest that the replacement of the Sr$^{2+}$ sites with Mg$^{2+}$ species and the presence of precipitated MgO do not influence the photocatalytic activity for the conversion of CO$_2$. 
Figure 6. Formation rates of CO (red), H$_2$ (blue), and O$_2$ (green) and selectivity toward CO evolution (black diamond) in the photocatalytic conversion of CO$_2$ in H$_2$O over the Ag–Co/Mg(z)–SrTiO$_3$ photocatalysts (z = 0, 2, 4, 8, 24, and 100). Reaction conditions: Amount of photocatalyst: 0.2 g; Ag loading: 1 wt%; Co loading: 0.3 wt%; volume of reaction solution (H$_2$O): 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 S12 shows the results of the control experiments for the photocatalytic conversion of CO$_2$ in water using optimised Ag–Co/Mg–SrTiO$_3$. The reduction of CO$_2$ to CO did not proceed well in the absence of the photocatalyst, photoirradiation, or the NaHCO$_3$ additive. These results clearly indicate that the presence of Ag–Co/Mg–SrTiO$_3$ photocatalyst and NaHCO$_3$ additive under UV-LED photoirradiation significantly enhanced the conversion of CO$_2$ to CO.$^{46}$ To confirm the origin of the evolved CO in the photocatalytic conversion of CO$_2$ in the presence of Ag–Co/Mg–SrTiO$_3$, we conducted isotope-labelling experiments using $^{13}$CO$_2$ gas as the substrate. Figure 7 shows the chromatogram of TCD-GC and quadrupole mass spectrometer (Q-MS) profiles of $m/z =$ 28 and 29 in the online GC-MS analysis for the photocatalytic conversion of $^{13}$CO$_2$. In the TCD-GC chromatogram, H$_2$ and O$_2$ were observed at 2 and 4 min, respectively, in addition to N$_2$ from air. Q-MS analysis of the outlet gas revealed no quantifiable peak at $m/z =$ 28 except for N$_2$ contamination. In contrast, a clear peak appeared at approximately 19 min in the Q-MS profile of $m/z =$ 29, indicating that $^{13}$CO was produced from the introduced $^{13}$CO$_2$. This isotopic experiment confirmed that $^{13}$C-labeled CO ($m/z =$ 29) evolved preferentially over $^{12}$CO ($m/z =$ 28). This suggests that the CO gas evolved in our system originated from the CO$_2$ gas bubbled into the suspension. Furthermore, the apparent quantum efficiency (AQE) of optimal Mg–SrTiO$_3$ in the photocatalytic
conversion of CO$_2$ using Ag–Co/Mg–SrTiO$_3$ photocatalyst under monochromatic UV-light irradiation (365 nm) was determined to be 0.05% (See ESI for the details).

**Figure 7.** TCD-GC chromatogram and Q-MS profiles at $m/z = 28$ and 29 for the photocatalytic conversion of $^{13}$CO$_2$ in H$_2$O over Ag–Co/Mg–SrTiO$_3$. Reaction conditions: Amount of photocatalyst: 0.2 g; Ag loading: 1 wt%; Co loading: 0.3 wt%; volume of reaction solution (H$_2$O): 0.2 L; additive: 0.1 M NaHCO$_3$; $^{13}$CO$_2$ flow rate: 30mL min$^{-1}$; light source: monochromatic LED lamp at 365 nm; photoirradiation time: 1.5 h.
Scheme 1 shows the proposed mechanism for the photocatalytic conversion of CO\textsubscript{2} over Ag–Co/Mg–SrTiO\textsubscript{3} with H\textsubscript{2}O as the electron donor. As mentioned previously, a Mg–SrTiO\textsubscript{3} particle has an edge-shaved cube with exposed \{100\} and \{110\} facets. We inferred that the photocatalytic conversion of CO\textsubscript{2} to CO occurs at the Ag cocatalyst on the \{100\} facets of Mg–SrTiO\textsubscript{3}, whereas oxidation of H\textsubscript{2}O to O\textsubscript{2} proceeds at the Co cocatalyst on the \{110\} facets.\textsuperscript{13,47} As shown in Figure S13, a highly stable and selective CO formation was observed continuously for 15 h.

**Scheme 1.** Proposed mechanism of the photocatalytic conversion of CO\textsubscript{2} in H\textsubscript{2}O over Ag–Co/Mg–SrTiO\textsubscript{3}
Conclusions

An Mg-doped SrTiO\(_3\) photocatalyst (Mg–SrTiO\(_3\)) was successfully synthesised using a previously reported flux method. Mg–SrTiO\(_3\) exhibited excellent photocatalytic activity under monochromatic UV-light irradiation at 365 nm, resulting in selective conversion of CO\(_2\) to CO in the presence of Ag–Co cocatalyst. The AQE of this reaction was determined to be 0.05%. Moreover, isotope experiments revealed that the evolved CO originated from gaseous CO\(_2\). The CO formation rate drastically improved by doping Mg into SrTiO\(_3\). SEM images of Mg–SrTiO\(_3\) revealed the presence of edge-shaved cubic particles with \{110\} facets in addition to \{100\} facets. This was correlated to the separation of photogenerated carriers and consequent suppression of charge recombination, which dramatically improved the photocatalytic activity for the conversion of CO\(_2\) to CO.

Associated content

Supporting Information

The Supporting Information is available free of charge at ***

XRD patterns and UV-Vis spectra of M–SrTiO\(_3\), Reaction results for photocatalytic conversion of CO\(_2\) over Ag–Co/Mg–ATiO\(_3\) (A = Ba, Ca, and Sr), Ag K-
edge XANES spectra of Ag–Co/Mg–SrTiO$_3$, TEM image of Mg–SrTiO$_3$ whose cocatalysts were loaded by PD method, Reaction results for photocatalytic conversion of CO$_2$ over Mg–SrTiO$_3$ in the presence of Ag–Co cocatalysts loaded by PD, IMP, and CR method, Particle diameter distributions of Ag loaded by PD, IMP, and CR method, Reaction results for photocatalytic conversion of CO$_2$ over Ag–Co/MgO/SrTiO$_3$, Ag–Co/MgO/Al–SrTiO$_3$, Ag–Co/Al–SrTiO$_3$ and Ag–Co/Mg–SrTiO$_3$, A SEM image of Mg–SrTiO$_3$ 1118 K, XRD patterns of Mg–SrTiO$_3$ _y h, Reaction results for photocatalytic conversion of CO$_2$ over Ag–Co/Mg–SrTiO$_3$ _y h, XRD patterns of Mg(z)–SrTiO$_3$, Blank tests for Ag–Co/Mg–SrTiO$_3$, A time-course reaction result for photocatalytic conversion of CO$_2$ over the Ag–Co/Mg–SrTiO$_3$ for 15 h, The scheme of the reaction vessel and the light source, The calculation of AQE.
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