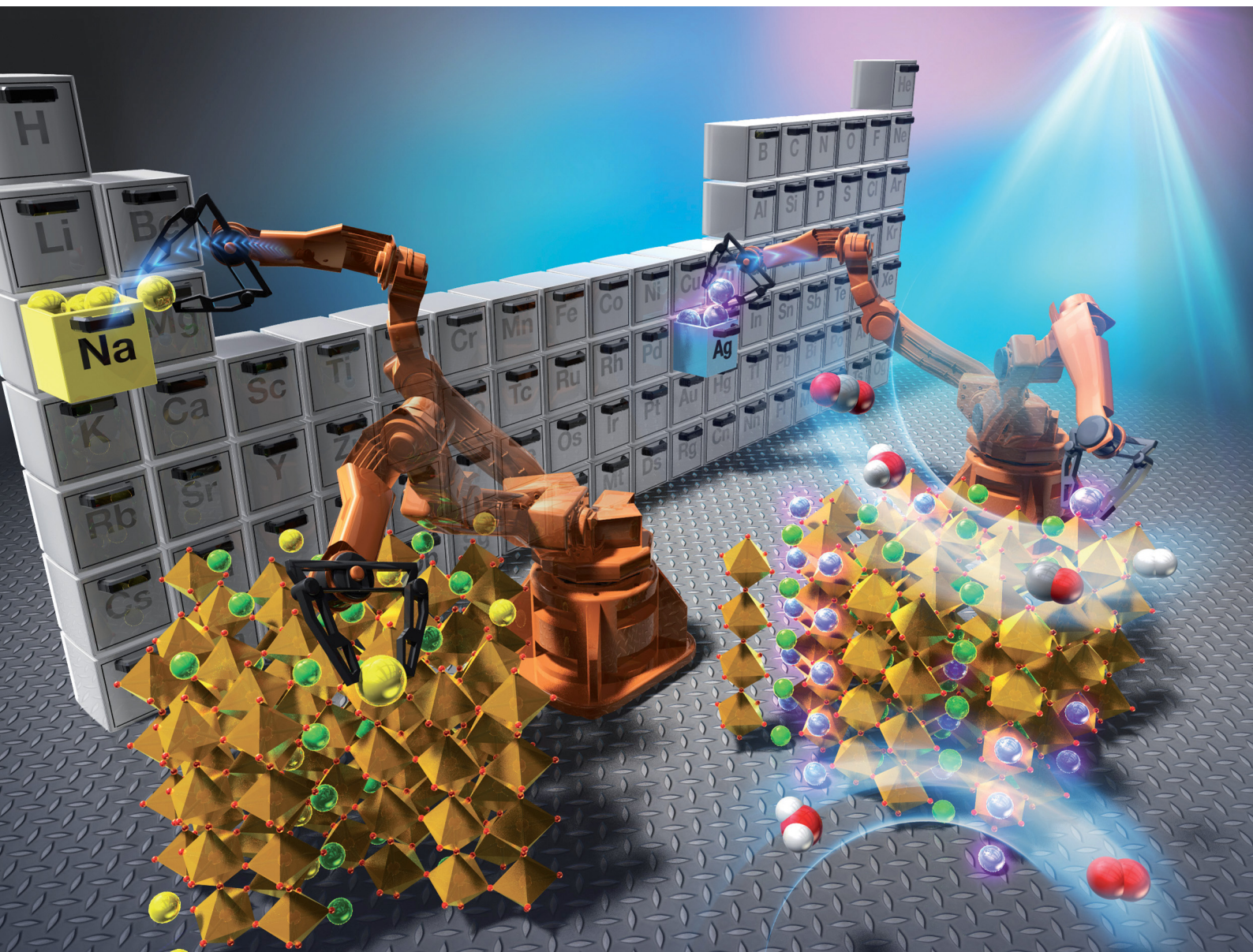


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Ag⁺ substitution was applied to a tungsten-bronze-type metal oxide. An AgSr₂Ta₅O₁₅ photocatalyst has emerged for water splitting and CO₂ reduction. DFT calculation and diffuse reflection spectra revealed that the Ag d-orbital formed a new valence band, leading to a narrow band gap (3.91 eV) compared to that of NaSr₂Ta₅O₁₅ (4.11 eV).

Photocatalytic water splitting and CO₂ reduction using water as an electron donor are attractive from the viewpoint of artificial photosynthesis.^{1,2} Metal oxides have been widely studied as photocatalysts.¹ This is because most metal oxides are stable under photocatalytic reaction conditions. However, these metal oxide photocatalysts generally possess wide band gaps, resulting in limitation of their responses to irradiation lights with shorter wavelengths. In this context, many efforts have been made to narrow their band gaps.

Band engineering,³ including valence band control, doping, and solid solution formation, is an effective strategy for narrowing the band gap. Among them, the valence band control technique has indeed developed metal oxide photocatalysts with narrower band gaps. In this strategy, Cu⁺(3d¹⁰),^{4–9} Ag⁺(4d¹⁰),^{10–16} Sn²⁺(5s²),^{17–20} Pb²⁺(6s²),^{13,21} and Bi³⁺(6s²)^{13,22–25} make new valence bands at shallower levels than O2p-based valence bands. Among the photocatalysts developed by this strategy, AgTaO₃¹⁰ and Na_{0.5}Bi_{0.5}TiO₃²⁴ photocatalysts with perovskite structures efficiently split water to H₂ and O₂ in stoichiometric amounts. However, the numbers of

Water splitting and CO₂ reduction over an AgSr₂Ta₅O₁₅ photocatalyst developed by a valence band control strategy†

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valence-band-controlled metal oxide photocatalysts for water splitting in a one-photon excitation mechanism are still limited to mainly the typical perovskites, resulting in a few crystal structures being useful for the valence band control strategy.

A tungsten-bronze-type crystal structure is one of the families of perovskite materials which are generally denoted as the chemical formula ABO₃. A notable feature in the crystal structure of tungsten bronze is that it is easy to replace A and A' site cations of its chemical formula (AA'₂M₅O₁₅) with various cations. For example, the A site can contain Na⁺ and K⁺ cations, and the A' sites can contain Ca²⁺, Sr²⁺, and Ba²⁺ cations, whereas the M sites can contain Nb⁵⁺ and Ta⁵⁺ cations. To date, it has been reported that KCaSrTa₅O₁₅^{26,27} and KSr₂Ta₅O₁₅²⁸ show photocatalytic activities for water splitting and CO₂ reduction using water as an electron donor. A series of AA'₂Ta₅O₁₅ (A = K, Na; A' = Sr, Ba)^{29,30} and K₂RETa₅O₁₅ (RE = rare earth metal)³¹ are also tungsten-bronze-type photocatalysts. Therefore, these materials are expected to contribute to expanding the crystal structures for a valence band controlled photocatalyst.

In this study, we successfully prepared AgSr₂Ta₅O₁₅ with a tungsten-bronze-type structure and compared its band structure to that of NaSr₂Ta₅O₁₅ based on diffuse reflectance spectra and density functional theory (DFT) calculation. Moreover, the photocatalytic property of AgSr₂Ta₅O₁₅ for water splitting and CO₂ reduction was evaluated.

NaSr₂Ta₅O₁₅ was prepared by a polymerized complex method (PC method) that usually gives high photocatalytic performances compared with a conventional solid-state reaction.²⁷ AgSr₂Ta₅O₁₅ was prepared by a solid-state reaction because it would not be easy to prepare it by the PC method due to the isolation of metallic Ag. The obtained AgSr₂Ta₅O₁₅ was treated with an aqueous HNO₃ solution, if necessary. Their crystal phases were identified by X-ray diffraction. Their diffuse reflectance spectra were obtained using the Kubelka–Munk method. Particle shapes of AgSr₂Ta₅O₁₅ and NaSr₂Ta₅O₁₅ were observed using a scanning electron microscope. Photocatalytic CO₂ reduction and water splitting were conducted

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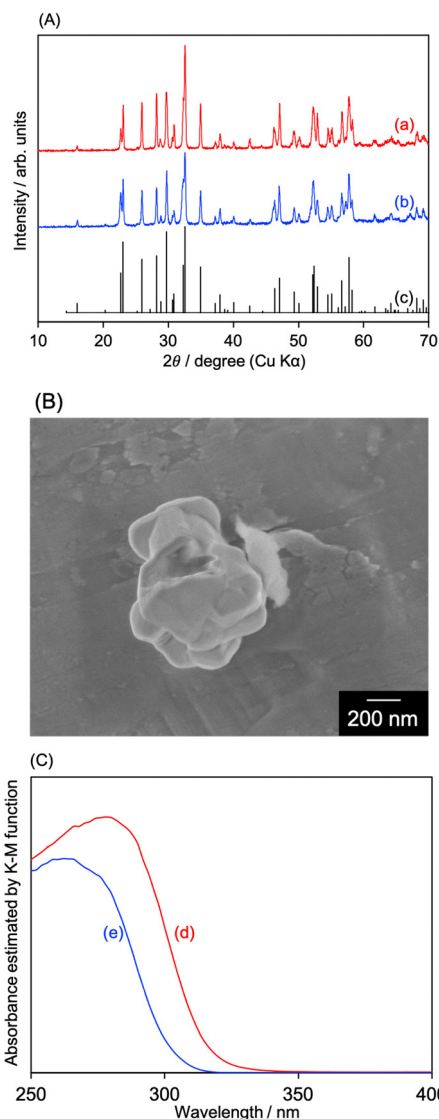


Fig. 1 (A) XRD patterns of (a) AgSr₂Ta₅O₁₅ (w/o HNO₃) and (b) NaSr₂Ta₅O₁₅, and PDF of (c) NaSr₂Ta₅O₁₅ (PDF No.: 39-1439). (B) SEM image of AgSr₂Ta₅O₁₅ (w/o HNO₃). (C) DRS of (d) AgSr₂Ta₅O₁₅ (w/o HNO₃) and (e) NaSr₂Ta₅O₁₅.

using a gas-flow system equipped with inner irradiation cells made of quartz and Pyrex, and a 400 W high-pressure mercury lamp. Density functional theory (DFT) calculations were performed using the CASTEP code to obtain band structures of AgSr₂Ta₅O₁₅ and NaSr₂Ta₅O₁₅. The detailed information of these experiments is summarized in the supporting information (including Fig. S1–S3 and Table S1, ESI[†]).

Fig. 1(A) shows X-ray diffraction patterns (XRDs) of AgSr₂Ta₅O₁₅ (not treated with an aqueous HNO₃ solution; denoted with “w/o HNO₃”) and NaSr₂Ta₅O₁₅. The diffraction peaks of both samples were well consistent with those of a powder diffraction file (PDF) of NaSr₂Ta₅O₁₅. This is because of the resembled ionic radii of Ag⁺ (115 pm) and Na⁺ (102 pm) in the 6 coordination number. For AgSr₂Ta₅O₁₅ (w/o HNO₃), AgTaO₃ and metallic Ag were not observed in the XRD pattern

(Fig. S4, ESI[†]). Scanning electron microscopy (SEM) was performed to observe AgSr₂Ta₅O₁₅ and NaSr₂Ta₅O₁₅ particles (Fig. 1(B) and Fig. S5, ESI[†]). Sintered particles with a size of several hundred nm were observed. Diffuse reflectance spectra (DRS) of AgSr₂Ta₅O₁₅ and NaSr₂Ta₅O₁₅ are shown in Fig. 1(C). The absorption spectrum red-shifted by replacing Na⁺ with Ag⁺, resulting in their band gaps of 3.91 eV for AgSr₂Ta₅O₁₅ and 4.11 eV for NaSr₂Ta₅O₁₅. The reason why the band gap was narrowed by containing Ag⁺ is due to a new valence band formed by the hybridization of O2p and Ag4d orbitals. These physico-chemical analyses indicate that AgSr₂Ta₅O₁₅ of a tungsten-bronze-type crystal structure was successfully formed, and that its band gap was narrowed by Ag⁺ substitution as seen for NaTaO₃ and AgTaO₃.¹⁰ Density functional theory (DFT) calculation was performed to discuss the band structures of AgSr₂Ta₅O₁₅ and NaSr₂Ta₅O₁₅, as shown in Fig. 2. Conduction band minima of both samples were mainly formed by Ta d-orbital and O p-orbital, whereas both valence band maxima contained O p-orbital. Most importantly, the Ag d-orbital took part in making the valence band of AgSr₂Ta₅O₁₅, whereas the Na s-orbital did not make such a valence band. This is well consistent with the band structure of the AgTaO₃ photocatalyst.¹⁰ Thus, Ag⁺ substitution is effective to narrow the band gap of the tungsten-bronze-type metal oxide by forming the new valence band. The calculated band gaps of AgSr₂Ta₅O₁₅ and NaSr₂Ta₅O₁₅ were 3.25 and 3.28 eV, respectively. These values are

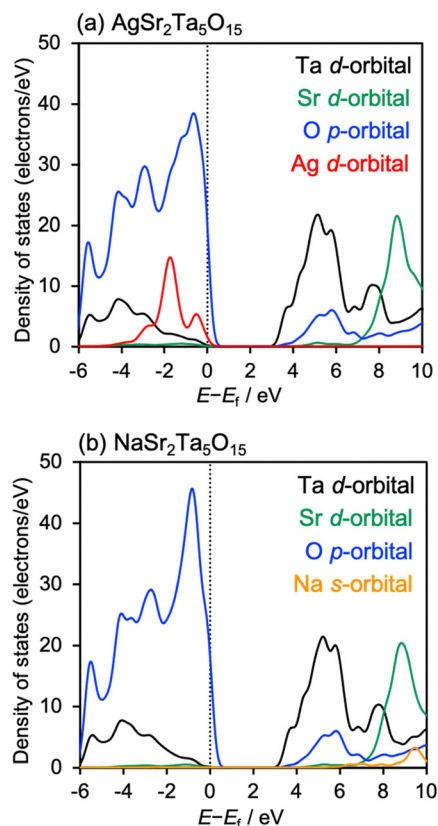


Fig. 2 DOS of (a) AgSr₂Ta₅O₁₅ and (b) NaSr₂Ta₅O₁₅. The dotted lines indicate their Fermi levels.



small as compared to those experimentally obtained from DRS, even though HSE06 was used. This might be due to deviation of the optimized structures in the DFT calculation from the experimentally obtained samples; *e.g.*, structural isomerism (Fig. S1 and S2, ESI†).^{32–34}

Photocatalytic performances of $\text{AgSr}_2\text{Ta}_5\text{O}_{15}$ and $\text{NaSr}_2\text{Ta}_5\text{O}_{15}$ were evaluated, as shown in Table 1. $\text{NaSr}_2\text{Ta}_5\text{O}_{15}$ with NiO and Ag cocatalysts showed higher photocatalytic activities for water splitting and CO_2 reduction than $\text{AgSr}_2\text{Ta}_5\text{O}_{15}$ (entries 1, 2, 5, 7). This is probably due to the enhancement of recombination between photogenerated e^- and h^+ at a silver site, more or less. Next, let us see $\text{AgSr}_2\text{Ta}_5\text{O}_{15}$ newly obtained in the present study.

Bare $\text{AgSr}_2\text{Ta}_5\text{O}_{15}$ split water into H_2 and O_2 (entry 3). Its performance was improved by loading NiO, which is a typical cocatalyst for water splitting (entry 4).³ Considering the literature about AgTaO_3 ,¹⁰ there is a possibility that Ag nanoparticles are segregated on the surface. Therefore, $\text{AgSr}_2\text{Ta}_5\text{O}_{15}$ was treated with an aqueous HNO_3 solution to remove the Ag nanoparticles, resulting in an improvement in the water splitting performance (entry 5). The treated $\text{AgSr}_2\text{Ta}_5\text{O}_{15}$ photocatalyst was applied to CO_2 reduction using water as an electron donor (entries 6–9). We have reported that an Ag cocatalyst loaded by impregnation works as an active site for CO_2 reduction to form CO.^{2,35–37} The Ag-impregnated $\text{AgSr}_2\text{Ta}_5\text{O}_{15}$ produced not only H_2 and O_2 but also CO under CO_2 gas conditions. Because bare $\text{AgSr}_2\text{Ta}_5\text{O}_{15}$ did not give CO under Ar (entry 3), we can conclude that the evolved CO was generated from not contamination of carbonous species over the photocatalyst but CO_2 . When the amount of Ag cocatalyst was increased, the CO formation rate and its selectivity were improved. The addition of NaHCO_3 was effective for CO_2 reduction.

Fig. 3 shows photocatalytic CO_2 reduction over Ag(3 wt%)-loaded $\text{AgSr}_2\text{Ta}_5\text{O}_{15}$ (Table 1 entries 8, 9). H_2 , CO, and O_2 were formed from water dissolved with CO_2 gas (1 atm). The activity was improved by adding NaHCO_3 . It is reported that the hydrogen carbonate enhances O_2 production in water splitting over a Pt/TiO₂ photocatalyst.³⁸ The selectivity for CO formation (Sel_{CO}) was also drastically improved up to 77%. This is because

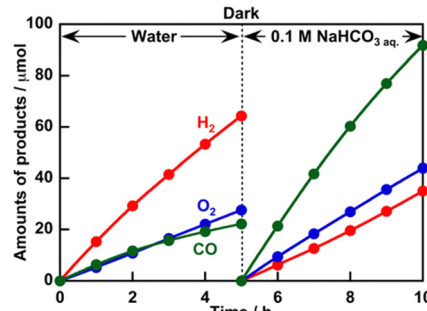


Fig. 3 CO_2 reduction using water as an electron donor over the Ag (3 wt%)-loaded $\text{AgSr}_2\text{Ta}_5\text{O}_{15}$ photocatalyst. Photocatalyst: 0.5 g, Reactant solution: water (350 mL), Reactor: a gas-flow system with an inner irradiation cell made of quartz, Light source: a 400 W high-pressure mercury lamp, Concentration of the aqueous NaHCO_3 solution: 0.1 mol L^{-1} .

of the smooth supply of CO_2 molecules onto the active site due to a chemical equilibrium of the hydrogen carbonate.^{2,36} The ratios of H_2/O_2 and $(\text{H}_2 + \text{CO})/\text{O}_2$ were slightly beyond stoichiometry (*i.e.*, beyond two). According to the literature about AgTaO_3 ,¹⁰ a part of the evolved O_2 might be adsorbed on the AgTaO_3 photocatalyst, resulting in the O_2 evolution being slightly less than the stoichiometry in an early period for water splitting. For the present CO_2 reduction over Ag/ $\text{AgSr}_2\text{Ta}_5\text{O}_{15}$, the rates of gas evolution became gradually close to stoichiometry with the reaction time (Fig. S6, ESI†). Therefore, there is a possibility that the evolved O_2 was partly adsorbed on $\text{AgSr}_2\text{Ta}_5\text{O}_{15}$.

Fig. 4 shows the effect of the wavelength of the irradiation light on photocatalytic CO_2 reduction over $\text{AgSr}_2\text{Ta}_5\text{O}_{15}$ without HNO_3 treatment (w/o HNO_3). $\text{AgSr}_2\text{Ta}_5\text{O}_{15}$ (w/o HNO_3) was active for CO_2 reduction even without additional Ag cocatalyst loading (1st run). The CO formation rate and its selectivity were improved by adding NaHCO_3 (2nd run). This result implies that a small amount of Ag nanoparticles would be segregated on the surface of $\text{AgSr}_2\text{Ta}_5\text{O}_{15}$ prepared by a solid-state reaction as seen in AgTaO_3 , though it was not detected by XRD and DRS. The segregated Ag worked as the active site for CO_2 reduction. Additionally, it is noteworthy that the $\text{AgSr}_2\text{Ta}_5\text{O}_{15}$ (w/o HNO_3)

Table 1 Photocatalytic water splitting and CO_2 reduction over $\text{AgSr}_2\text{Ta}_5\text{O}_{15}$

Entry	Photocatalyst	HNO_3 treatment	Cocatalyst (wt%)	Gas	NaHCO_3 addition	Activity/ $\mu\text{mol h}^{-1}$			
						H_2	O_2	CO	Sel_{CO} %
1	$\text{NaSr}_2\text{Ta}_5\text{O}_{15}$	No	NiO(0.2)	Ar	No	1365	714	—	—
2	$\text{NaSr}_2\text{Ta}_5\text{O}_{15}$	No	Ag(0.5)	CO_2	Yes	25	29	29	54
3	$\text{AgSr}_2\text{Ta}_5\text{O}_{15}$	No	—	Ar	No	80	34	0	0
4	$\text{AgSr}_2\text{Ta}_5\text{O}_{15}$	No	NiO(0.2)	Ar	No	197	76	—	—
5	$\text{AgSr}_2\text{Ta}_5\text{O}_{15}$	Yes	NiO(0.2)	Ar	No	457	204	—	—
6	$\text{AgSr}_2\text{Ta}_5\text{O}_{15}$	Yes	Ag(0.5)	CO_2	No	25	11	2.5	9.1
7	$\text{AgSr}_2\text{Ta}_5\text{O}_{15}$	Yes	Ag(0.5)	CO_2	Yes	17	12	13	43
8	$\text{AgSr}_2\text{Ta}_5\text{O}_{15}$	Yes	Ag(3)	CO_2	No	15	5.2	6.2	29
9	$\text{AgSr}_2\text{Ta}_5\text{O}_{15}$	Yes	Ag(3)	CO_2	Yes	6.2	9.3	21	77

Photocatalyst: 0.5 g, Reactant solution: water (350 mL), Reactor: a gas-flow system with an inner irradiation cell made of quartz, Light source: a 400 W high-pressure mercury lamp, Concentration of the aqueous NaHCO_3 solution: 0.1 mol L^{-1} . Selectivity of CO formation (Sel_{CO}) was estimated as follows; Sel_{CO} (%) = (the CO formation rate)/[(the H_2 formation rate) + (the CO formation rate)] \times 100.



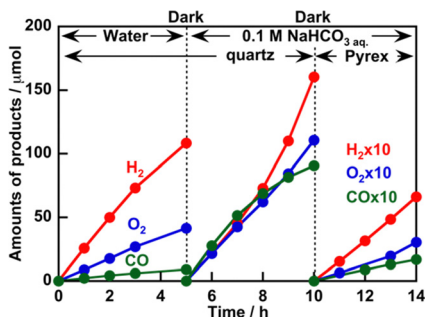


Fig. 4 CO₂ reduction using water as an electron donor over the AgSr₂Ta₅O₁₅ (w/o HNO₃) photocatalyst without any additional cocatalyst loading. Photocatalyst: 0.5 g. Reactant solution: water (350 mL). Reactor: a gas-flow system with an inner irradiation cell made from quartz ($\lambda > 250$ nm) or Pyrex ($\lambda > 300$ nm). Light source: a 400 W high-pressure mercury lamp. Concentration of an aqueous NaHCO₃ solution: 0.1 mol L⁻¹.

produced H₂, CO, and O₂ under irradiation of light with wavelength longer than 300 nm. This is a feature of the AgSr₂Ta₅O₁₅ possessing a red-shifted absorption edge as shown in Fig. 1(C) being different from NaSr₂Ta₅O₁₅. AgSr₂Ta₅O₁₅ is superior to NaSr₂Ta₅O₁₅ in this photoresponse. Thus, AgSr₂Ta₅O₁₅ (w/o HNO₃) is a photocatalyst that is active not only for water splitting but also for CO₂ reduction using water as an electron donor.

In conclusion, AgSr₂Ta₅O₁₅ was prepared by a conventional solid-state reaction based on a valence band control strategy using Ag⁺ substitution. Its crystal structure was almost the same as that of NaSr₂Ta₅O₁₅ due to the resembled ionic radii of Ag⁺ and Na⁺. This Ag⁺ substitution resulted in red-shift of the absorption spectrum from that of NaSr₂Ta₅O₁₅. The band gap of AgSr₂Ta₅O₁₅ was 3.91 eV, while that of NaSr₂Ta₅O₁₅ was 4.11 eV. DOS estimated by DFT calculations revealed that the Ag d-orbital took part in making the new valence band. Furthermore, AgSr₂Ta₅O₁₅ was a new photocatalyst for water splitting and CO₂ reduction. This study demonstrated the usefulness of the valence band control strategy for the development of new metal oxide photocatalysts, resulting in the AgSr₂Ta₅O₁₅ photocatalyst with a tungsten-bronze type crystal structure. This finding will contribute to liberating the valence band control strategy from the material design space mainly limited in typical perovskite-type metal oxides for the development of active photocatalysts for water splitting and CO₂ reduction.

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Conflicts of interest

There are no conflicts to declare.

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