Supporting Information

Water Splitting and CO_2 Reduction over $AgSr_2Ta_5O_{15}$ Photocatalyst Developed by Valence Band Control Strategy

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Experiments

Preparation of $AgSr_2Ta_5O_{15}$ and $NaSr_2Ta_5O_{15}$

$AgSr_2Ta_5O_{15}$ was prepared by a conventional solid-state reaction. The starting materials are summarized as follows; Ag_2O (Kanto Chemical; 99.0%), Ta_2O_5 (Rare Metallic; 99.99%), $SrCO_3$ (Kanto Chemical; 99.9%). For $AgSr_2Ta_5O_{15}$, Ag_2O, Ta_2O_5, and $SrCO_3$ were mixed using an alumina mortar. The amount of Ag_2O was 5% excess as compared to the stoichiometric ratio. The mixture was calcined at 1173 K for 1 h in an alumina crucible, followed by grinding the calcined sample. This calcined sample was further calcined at 1423 K for 10 h to obtain powdered $AgSr_2Ta_5O_{15}$ sample. If necessary, the obtained $AgSr_2Ta_5O_{15}$ was treated using an aqueous HNO_3 solution to remove the excess Ag component. Afterward, the treated $AgSr_2Ta_5O_{15}$ was additionally washed with water until the pH of the supernatant solution reached neutral. $NaSr_2Ta_5O_{15}$ of a reference sample was prepared by a polymerized complex method according to the literature.[1] Cocatalysts of Ag and NiO were loaded by impregnation. $AgNO_3$ (Tanaka Kikinzoku) and $Ni(NO_3)_2$•$6H_2O$ (Wako Pure Chemical; 98.5%) were used as the cocatalyst sources. Water was employed as the solvent of the $AgNO_3$ and $Ni(NO_3)_2$ salts. After the solution contained with either of salts was dropped into the $AgSr_2Ta_5O_{15}$ or $NaSr_2Ta_5O_{15}$ powder, the obtained slurry was placed on a boiling water bath for drying off the water. Afterward, the powder impregnated with either of salts was heated at 723 K for 1 h, and 573 K for 1 h, respectively, in a muffle furnace to load the Ag and NiO cocatalysts.

Characterization

Crystal structures of $AgSr_2Ta_5O_{15}$ and $NaSr_2Ta_5O_{15}$ were identified by X-ray diffraction (XRD: Rigaku; MiniFlex (Cu Kα)). Their diffuse reflectance spectra were obtained using the Kubelka-Munk method (DRS: Jasco; V-570). Particle shapes of $AgSr_2Ta_5O_{15}$ and $NaSr_2Ta_5O_{15}$ were observed using a scanning electron microscope (SEM: JEOL; JSM-7600F).

Computational condition

Density functional theory (DFT) calculations were performed using the CASTEP code[2] to obtain band structures of $AgSr_2Ta_5O_{15}$ and $NaSr_2Ta_5O_{15}$. The Vanderbilt-type ultrasoft pseudopetentials,[3] the generalized gradient approximation (GGA)[4] and the Perdew-Burke-Ernzerh of exchange-correlation functional (PBE)[5] were employed in periodic boundary conditions. Checking the calculation convergence for the geometry optimizations, 500 eV of cut-off energy was employed as optimal parameter The detailed history for the parameter optimization is shown in Figures S2−S4, and Table S1. The reciprocal space was sampled using a *k*-point mesh with a typical spacing of 0.07 $Å^{-1}$, as generated by the Monkhorst-Pack scheme.[6] Geometry optimizations of the supercells were conducted using the limited-memory Broyden-Fletcher-Goldfarb-Shanno (LBFGS) algorithm.[7] Convergence criteria are summarized as follows; (1) self-consistent field tolerance: 2.0×10^{-6} eV per atom; (2) energy tolerance: 2.0×10^{-5} eV per atom; (3) maximum force tolerance: 0.05 eV $Å^{-1}$, and (4) maximum displacement tolerance: 2.0×10^{-3} Å; (5) maximum stress: 0.1 GPa. Projected densities of states (DOS) for various orbitals were calculated using the optimized bulk models and HSE06 that well reproduces experimental band gaps.[8-10] Gaussian broadening of 0.20 eV was applied for plotting the DOS. In DOS calculations, the reciprocal space was sampled using a *k*-point mesh with a typical spacing of 0.04 $Å^{-1}$. Cartesian coordinates of the crystal structure of $NaSr_2Ta_5O_{15}$ provided from the inorganic database[11] was employed as the initial structure for the DFT calculation. The crystal structure of $NaSr_2Ta_5O_{15}$ was altered to satisfy the condition for the DFT calculation (Figure S1). For $AgSr_2Ta_5O_{15}$, its initial structure was generated by replacement of the Na sites of $NaSr_2Ta_5O_{15}$ with Ag. XRD simulations were performed using the optimized structures with X-ray of Cu Kα and plot step of 0.01°.

Photocatalytic Reaction

Photocatalytic CO_2 reduction and water splitting were conducted using a gas-flow system equipped with an inner irradiation cell made of quart or Pyrex, and a 400 W high-pressure mercury lamp. Photocatalysts were dispersed in water. $NaHCO_3$ was added into the aqueous solution, if necessary. CO_2 or Ar gas was continually supplied into the aqueous suspension. The amounts of gaseous products were determined by gas-chromatographs (Shimadzu, GC-8A; TCD, MS-5A, Ar carrier; FID, MS-13X, a methanizer, N_2 carrier).

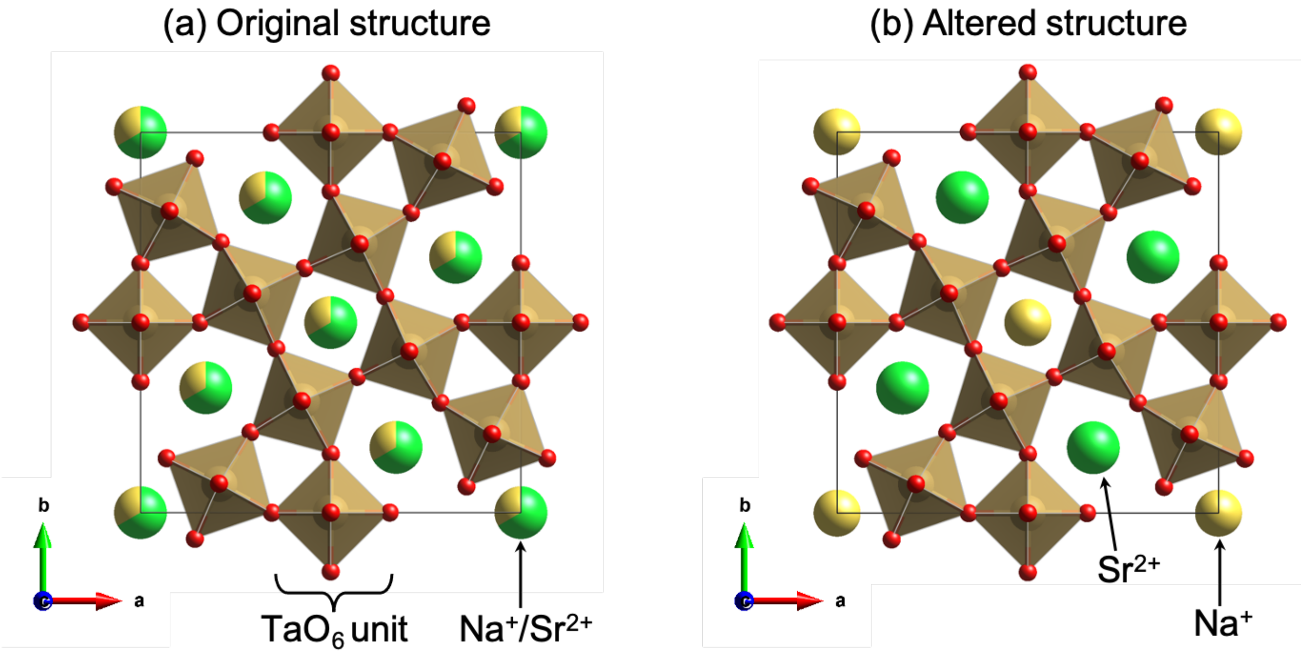

Figure S1. Crystal structures of (a) original $NaSr_2Ta_5O_{15}$ structure obtained from the database,[11] and (b) altered $NaSr_2Ta_5O_{15}$ structure for DFT calculation. These illustrations were drawn by VESTA software.[12]

Table S1. Lattice parameters of $NaSr_2Ta_5O_{15}$ and $AgSr_2Ta_5O_{15}$ before/after geometry optimization using DFT calculations.

Material	Cut-off / eV	Lattice parameters					
		a / Å	b / Å	c / Å	α / °	β / °	γ / °
$NaSr_2Ta_5O_{15}$	initial	12.383	=a	3.861	90.000	=α	=α
	400	12.974	=a	4.101	90.000	=α	=α
	500	12.963	=a	4.099	90.000	=α	=α
	600	12.973	=a	4.101	90.000	=α	=α
$AgSr_2Ta_5O_{15}$	400	12.991	=a	4.098	90.000	=α	=α
	500	12.974	=a	4.095	90.000	=α	=α
	600	12.977	=a	4.094	90.000	=α	=α

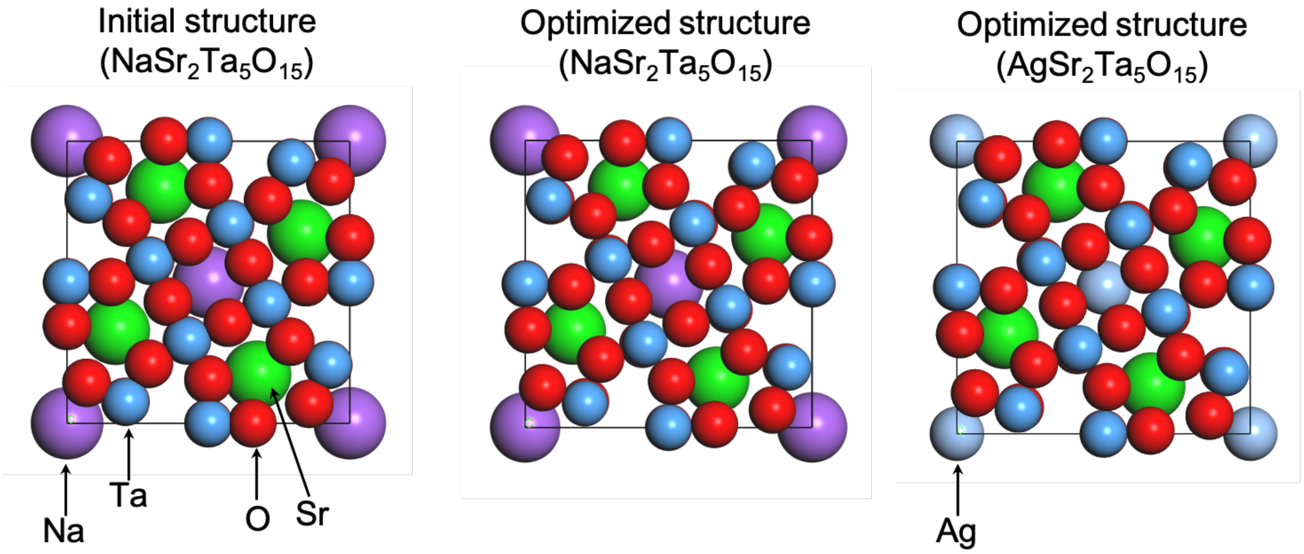

Figure S2. Crystal structures of initial $NaSr_2Ta_5O_{15}$ structure obtained from the database,[11] and optimized $NaSr_2Ta_5O_{15}$ and $AgSr_2Ta_5O_{15}$ structures. Constituent elements are displayed with their element symbols. Black solid lines indicate the periodic boundary.

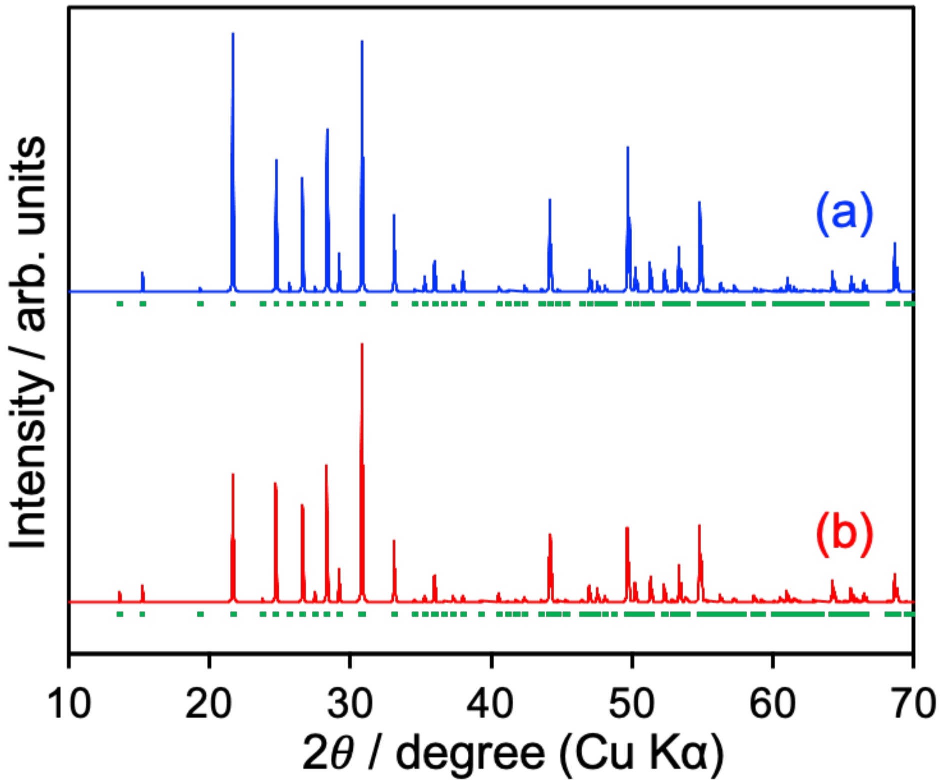

Figure S3. Simulated XRD patterns of (a) $NaSr_2Ta_5O_{15}$ and (b) $AgSr_2Ta_5O_{15}$ after geometry optimization. Green plots indicate their diffraction positions. Steps are 0.01°.

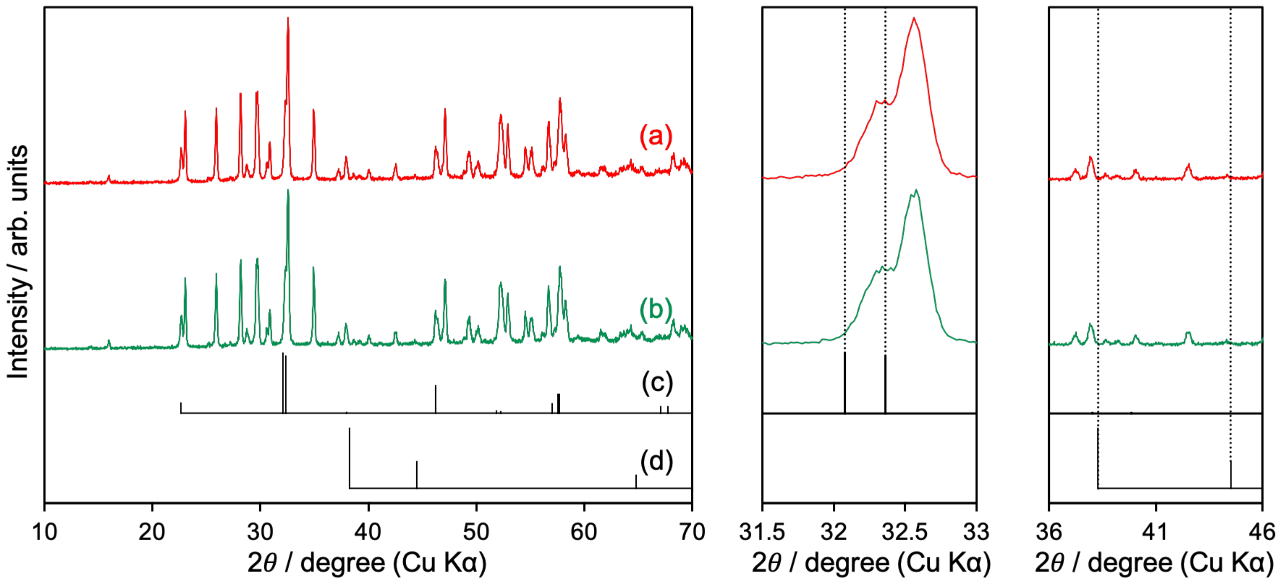

Figure S4. XRD patterns of $AgSr_2Ta_5O_{15}$ (a) without HNO_3 treatment and (b) with HNO_3 treatment, and PDFs of (c) $AgTaO_3$ (PDF No.: 1-72-1383) and (d) Ag (PDF No.: 1-71-4612).

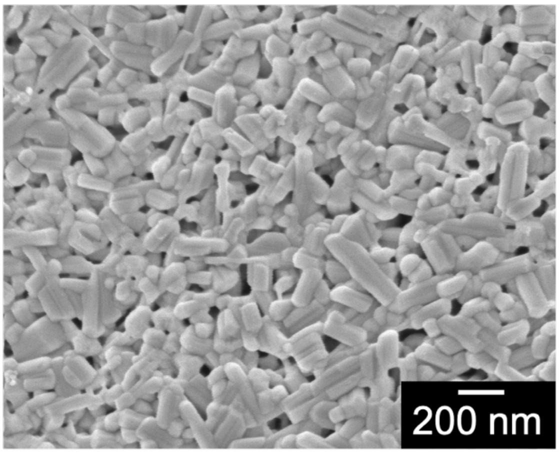

Figure S5 SEM image of $NaSr_2Ta_5O_{15}$ prepared by a polymerized complex method.

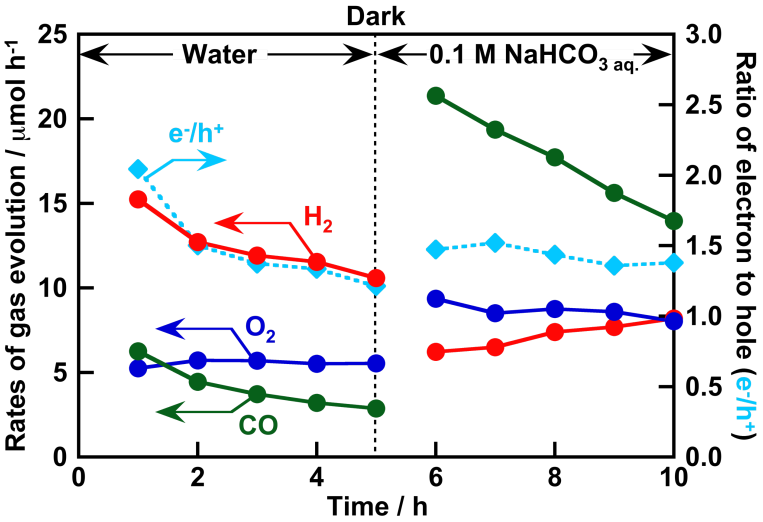

Figure S6. Rates of gas evolutions in CO_2 reduction using water as an electron doner over Ag(3 wt%)-loaded $AgSr_2Ta_5O_{15}$ photocatalyst. Photocatalyst: 0.5 g, Reactant solution: water (350 mL), Reactor: a gas-flow system with an inner irradiation cell made of quartz, Light source: a 400 W high-pressure mercury lamp, Concentration of an aqueous $NaHCO_3$ solution: 0.1 mol L^{-1}. (e^-/h^+) = [(sum of H_2 and CO formation rates)×2]/[(the O_2 formation rate)×4]. This result is the same as Figure 3 on the main text.

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