Supplementary information

Theoretical Prediction for Visible-light Sensitive Photocatalysts toward Water Oxidation

Authors:
Peng Li, a Naoto Umezawa, abc* Hideki Abe abc* and Jinhua Ye abd

a Catalytic Materials Group, Environmental Remediation Materials Unit, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

b PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

c TU-NIMS Joint Research Center, School of Materials Science and Engineering, Tianjin University, 92 Weijin Road, Nankai District, Tianjin, P. R. China

d International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

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**SI-1 Experimental Section**

**Calculation details**

To understand the origin of the different photocatalytic properties of $\text{Ag}_2\text{Sr(VO}_3)_4$ and $\text{Sr(VO}_3)_2$, we have investigated their electronic structures in comparison with that of $\text{Ag}_3\text{PO}_4$. Our calculations are based on the density-functional theory using a hybrid exchange-correlation energy functional proposed by Heyd, Scuseria, and Ernzerhof (HSE).\(^1\) The Hartree-Fock missing parameter was set at 25% following the original work. It is known that the HSE functional with the mixing constant gives reasonable lattice parameters and electronic structures for semiconductor materials.\(^2\) Projector-augmented wave pseudopotentials were employed as implemented in the VASP code.\(^3\),\(^4\) The valence configurations of the pseudo-potentials were $5d^{10}6s^1$ for Ag, $5s^25p^66s^2$ for Sr, $3s^23p^44s^1$ for V, and $2s^22p^4$ for O. The energy cutoff for the plane-wave basis set expansion was set at 400 eV. The Monkhorst-Pack k-point sets of $4\times4\times4$, $3\times3\times3$ and $1\times3\times1$ were used for a 16-atom $\text{Ag}_3\text{PO}_4$ (space group $P-43n$), 38-atom $\text{Ag}_2\text{Sr(VO}_3)_4$ (space group $P4/nbm$) and 36-atom $\text{Sr(VO}_3)_2$ (space group $Pnma$), respectively. These unit cells were fully relaxed for atomic positions and cell volume until the total energy converges within 0.001 eV. The spin polarity was also taken into account. The optimized lattice parameters are listed in Table 1.

**Material preparation**

The $\text{Sr(VO}_3)_2$ and $\text{Ag}_2\text{Sr(VO}_3)_4$ samples were synthesized via a solid state reaction.\(^5\) $\text{AgNO}_3$, $\text{SrCO}_3$, and $\text{V}_2\text{O}_5$ were used as the starting reagents. The stoichiometrically mixed powder reagents ($\text{SrCO}_3$ and $\text{V}_2\text{O}_5$ for $\text{Sr(VO}_3)_2$; $\text{SrCO}_3$, $\text{AgNO}_3$ and $\text{V}_2\text{O}_5$ for $\text{Ag}_2\text{Sr(VO}_3)_4$; $\text{AgNO}_3$ and $\text{V}_2\text{O}_5$ for $\text{Sr(VO}_3)_2$) were grinded in the present of 95% ethanol solution. Next, the mixture was calcined at 350°C for 2 h and then 480°C for 24 h. After that, the obtained powder was grinded in
dry state and pressed into a pellet. Finally, the sample was calcined at 500°C for 48 h to obtain the final products.

**Sample characterization**

The crystal structures were determined with an X-ray diffractometer (X'Pert Powder, PANalytical B.V., Netherlands) with Cu-Kα radiation. The diffuse reflection spectra were measured with an integrating sphere equipped UV–visible recording spectrophotometer (UV-2600, Shimadzu Co., Japan) using BaSO4 as reference and the optical absorptions were converted from the reflection spectra according to Kubelka-Munk equation. The specific surface areas were determined with a surface-area analyzer (BEL Sorp-II mini, BEL Japan Co., Japan) by the Brunauer–Emmett–Teller (BET) method. Photoelectron Spectroscopy (XPS) experiments were performed in type Theta probe (Thermo Fisher Co., USA) using monochromatized Al Kα at hν = 1486.6 eV and the peak positions were internally referenced to the C 1s peak at 284.6 eV. Raman spectra were measured by a laser Raman spectrophotometer (NRS-1000, JASCO Corp., Japan) equipped with a 532 nm laser source.

**Photocatalytic O₂ evolution**

The O₂ evolution experiments were carried out in a gas-closed circulation system. The catalyst powder (0.3 g) was dispersed by using a magnetic stirrer in Ce(SO₄)₂ aqueous solution (270 mL of distilled water + 3 mmol of Ce(SO₄)₂) in Pyrex cell with a side window. The light source was a 300 W of Xe arc lamp with an L42 cut-off filter (λ > 400 nm). The O₂ evolution was measured with an on-line gas chromatograph (GC-8A, Shimadzu) with a thermal conductivity detector (TCD) according to the standard curve.
SI-2 Rietveld refinement of the as-prepared $\text{Ag}_2\text{Sr(VO}_3\text{)}_4$ and $\text{Sr(VO}_3\text{)}_2$

**Fig. S1** Refined XRD pattern of $\text{Ag}_2\text{Sr(VO}_3\text{)}_4$ by GSAS.

**Fig. S2** Refined XRD pattern of $\text{Sr(VO}_3\text{)}_2$ by GSAS.
SI-3 O$_2$ evolution over Ag$_2$Sr(VO$_3$)$_4$ with different sacrificial reagents

![Graph showing photocatalytic O$_2$ evolution over Ag$_2$Sr(VO$_3$)$_4$ samples with different sacrificial reagents.

**Fig. S3** Photocatalytic O$_2$ evolution from the aqueous solution (270 mL of distilled water + 3 mmol of sacrificial reagent over the as-prepared Ag$_2$Sr(VO$_3$)$_4$ samples (0.3 g) under the irradiation of visible light ($\lambda > 400$ nm, 300 W Xe arc lamp with L42 cut-off filter).
SI-4 $p$-XRD patterns of $\text{Ag}_2\text{Sr(VO}_3\text{)}_4$ before and after $\text{O}_2$ evolution with different sacrificial reagents

**Fig. S4** (a) $p$-XRD patterns of $\text{Ag}_2\text{Sr(VO}_3\text{)}_4$ before and after $\text{O}_2$ evolution with $\text{AgNO}_3$ or $\text{Ce(SO}_4\text{)}_2$ as sacrificial reagent. (b) $p$-XRD patterns of $\text{Sr(VO}_3\text{)}_2$ before and after $\text{O}_2$ evolution with $\text{Ce(SO}_4\text{)}_2$ as sacrificial reagent.
SI-5 O₂ evolution rates over Sr(VO₃)₂ with/without co-catalysts

![Graph showing O₂ evolution rates over Sr(VO₃)₂ samples with/without co-catalyst](image)

**Fig. S5** Photocatalytic O₂ evolution from the aqueous solution (270 mL of distilled water + 3 mmol of Ce(SO₄)₂ over Sr(VO₃)₂ samples (0.3 g) with/without co-catalyst under the irradiation of visible light (λ > 400 nm, 300 W Xe arc lamp with L42 cut-off filter).
SI-6 XPS Analysis of Ag₂Sr(VO₃)₄ before and after O₂ evolution experiment.

Fig. S6 XPS spectra of Ag₂Sr(VO₃)₄ before and after O₂ evolution experiment.
Long time $O_2$ evolution over $\text{Sr(VO}_3\text{)}_2$

**Fig. S7** Photocatalytic $O_2$ evolution from the aqueous solution (270 mL of distilled water + 5 mmol of $\text{Ce(SO}_4\text{)}_2$ over the as-prepared $\text{Sr(VO}_3\text{)}_2$ samples (0.3 g) under the irradiation of visible light ($\lambda > 400$ nm, 300 W Xe arc lamp with L42 cut-off filter).
SI-8 Raman spectra of Sr(VO$_3$)$_2$ and Ag$_2$Sr(VO$_3$)$_4$ before and after O$_2$ evolution experiments.

Fig. S8 Raman spectra of (a) Ag$_2$Sr(VO$_3$)$_4$ and (b) Sr(VO$_3$)$_2$ before and after O$_2$ evolution experiment.
Partial charge density of valence band bottoms (VBM) of Ag₃PO₄, Sr(VO₃)₂, and Ag₂Sr(VO₃)₄

**Fig. S9** Partial charge density of valence band bottoms (VBM) of Ag₃PO₄, Sr(VO₃)₂, and Ag₂Sr(VO₃)₄.