Electronic supplementary information

A biomimetic all-inorganic photocatalyst for the artificial photosynthesis of hydrogen peroxide

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Experimental Section

Materials

SnO_2 NPs (mean particle size = 22-43 nm, specific surface area = 160 m^2 g^{-1}) were purchased from FUJIFILM Wako Chem. Co. SnO_2 NPs (mean particle size ~100 nm) were purchased from Aldrich. Hydrogen tetrachloroaurate(III) tetrahydrate ($HAuCl_4 \cdot 4H_2O$ > 99%), sodium hydroxide (NaOH > 97.0%), antimony(III) chloride ($SbCl_3$ >98.0%), copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$ > 99.5%), 2,9-dimethyl-1,10-phenanthroline hemihydrate ($C_{14}H_{12}N_2 \cdot 0.5H_2O$), phosphate buffer solution (pH 6.86), sodium perchlorate ($NaClO_4$ >96.0%) were purchased from Kanto Chemical Co. Fluorine-doped tin(IV) oxide film-coated glass (FTO, TEC7) was purchased from Aldrich. All chemicals were used as-received without further purification.

Photocatalyst preparation.

Au NPs were loaded on commercially available SnO_2 NPs (FUJIFILM Wako Chem. Co., mean particle size = 22-43 nm, specific surface area = 160 m^2 g^{-1}) by the deposition-precipitation method.[1] An aqueous solution of $HAuCl_4$ (4.86 mM, 50 mL) was neutralized to pH 6 by 1 M NaOH aq. SnO_2 NPs (5 g) were dispersed into the solution, and the suspension was stirred at 343 K for 1 h. The particles were collected by the centrifugation, and washed with distilled water. After drying, the resulting particles were calcined at 773 K for 4 h in the air to obtain Au/SnO_2. SnO_2 or Au/SnO_2 (1 g) were dispersed into a methanol solution of $SbCl_3$ (0.2-50 mM, 50 mL), and placed in the dark at 293 K for 0.25 h. The resulting sample was washed with methanol, distilled water, and acetone, and dried in vacuo to obtain SnO_2-Sb(III) or Au/SnO_2-Sb(III). For comparison, Au NPs were loaded on SnO_2 NPs consisting of isolated particles (Aldrich, mean particle size ~100 nm) by the deposition-precipitation method using urea as a neutralizer.[2] SnO_2 NPs (0.8 g) and urea (1.17 g) were added into an aqueous solution of $HAuCl_4$ (4.86 mM, 40 mL), and stirred at 353 K for 12 h. The particles were collected by the centrifugation, and washed with distilled water. After drying, the resulting particles were calcined at 673 K for 1 h in the air to obtain Au/SnO_2. Au/SnO_2 (0.2 g) were dispersed into a methanol solution of $SbCl_3$ (50 mM, 10 mL), and placed in the dark at 293 K for 0.25 h. The resulting sample was washed with methanol, distilled water, and acetone, and dried in vacuo to obtain Au/SnO_2-Sb(III).

The Cl in the solution after the adsorption of $SbCl_3$ on SnO_2 NCs can exist as $SbCl_3$ and free Cl^- ions. The mole numbers of Sb ($n_{s,Sb}$) and Cl ($n_{s,Cl}$) in the solutions were determined by ICP spectroscopy and ion chromatography, respectively. The subtraction of $n_{s,Cl}$ - $3n_{s,Sb}$ yields the mole number of free Cl^- ions in the solution (n_{s,Cl^-}). Further, the number of Cl^- ligands liberated by the adsorption (x in $SbCl_{3-x}$) was calculated to be 1.6-2.0 by the ratio of n_{s,Cl^-} to the mole number of the Sb adsorbed on SnO_2 ($n_{ad,Sb}$).

Characterization

Sb loading amounts were quantized by using inductively coupled plasma spectroscopy (ICPE-9820, Shimadzu). Observations of a transmission electron microscopy (TEM) and high- resolution TEM were carried out by means of JEM-2100F (JEOL) operated with an applied voltage of 200 kV. The measurements of X-ray photoelectron spectroscopy (XPS) was carried out by using a Kratos Axis Nova X-ray photoelectron spectrometer with a monochromated Al Kα X-ray source operated at 15 kV and 10 mA using C1s as the energy reference (284.6 eV). Diffuse reflectance UV-Vis-NIR

absorption spectra were collected by a UV-2600 spectrometer (Shimadzu) with integrating sphere unit (Shimadzu, ISR-2600Plus) at room temperature. The reflectance (R_∞) of the samples was recorded by using $BaSO_4$ as the reference. To obtain the relative absorption coefficient, the Kubelka-Munk function [$F(R_\infty) = (1 - R_\infty)^2/2R_\infty$] was used. The photoluminescence (PL) spectra were collected by means of a JASCO FP-6000 spectrofluorometer with an excitation wavelength of 300 nm at 77 K.

Adsorption isotherms of $SbCl_3$ on SnO_2

SnO_2 NPs (50 mg) were dispersed into a methanol solution of $SbCl_3$ (0.2-50 mM, 50 mL), and placed in the dark at 293 K for 3 h. After the centrifugation, the supernatant was filtered by using PTFE membrane filter. The Sb amount of the solution was quantified by using inductively coupled plasma spectroscopy (ICPE-9820, Shimadzu).

Photocatalytic H_2O_2 production

Photocatalyst (10 mg) was dispersed into aerobic distilled water (10 mL) in an open-test tube, and stirred at 25 °C under illumination by LED lamp (λ_{ex} = 420 ± 20 nm, I = 8.1 mW cm^{-2}). After removing the particles, the concentration of H_2O_2 was quantified by the colorimetric method using Cu(II) ion and 2,9-dimethyl-1,10-phenanthroline.[3] The external quantum efficiency (ϕ_{ex}) was calculated with assuming two-electron process as Eq. 1.

$$\phi_{ex}\ (\%) = \{2 \times (\text{number of } H_2O_2 \text{ molecules produced})/\text{number of incident photons}\} \times 100 \quad (1)$$

Photoelectrochemical measurements

SnO_2 nanocrystalline film was formed on fluorine-doped tin oxide (FTO, Aldrich, TEC7). SnO_2 NPs were added to a solution of polyethylene glycol 20,000 (0.2 g), Triton X-100 (0.1 mL), and acetylacetone (1 drop) in distilled water (0.4 mL), and grinded to form the uniform paste. By the doctor blade technique, the paste was coated on FTO with 60 μm thick, and the resulting sample was calcined at 773 K for 1 h to form mp-SnO_2/FTO. The SnO_2/FTO was immersed into a methanol solution of $SbCl_3$ (0.2-50 mM, 10 mL), and placed in the dark at 293 K for 3 h. The resulting electrode was washed with methanol, distilled water, and acetone, and dried in vacuo to obtain SnO_2-Sb(III)/FTO. Photoelectrochemical measurements were performed by the standard three-electrochemical cell with the structure of SnO_2-Sb(III)/FTO (working electrode) │ 0.1 M $NaClO_4$ aqueous solution │ Ag/AgCl (reference electrode) │ glassy carbon (counter electrode). The working electrode was illuminated by monochromatic light using LED lamp.

DFT simulations

DFT calculations with the periodic boundary conditions were carried out using a plane wave based program, CASTEP.[4,5] For the geometry optimization, the Perdew-Burke-Ernzerhof (PBE) functional[6,7] was used together with the ultrasoft-core potentials.[8] The basis set cutoff energy was set to 300 eV. For the present systems, the PBE functional afforded too narrow band gaps, and then the 1-point energy calculation was performed using the hybrid B3LYP functional,[9] the norm conserving core potentials[10] and the cutoff energy of 600 eV with the PBE optimized structures. The electron configurations of the atoms were O: $2s^22p^4$, Cl: $3s^23p^5$, Sn: $5s^25p^2$, and Sb: $5s^25p^3$. The slab mode was prepared by cleaving (110) face of bulk SnO_2. Lattice parameters of the primitive cell were a = 3.186 Å, b = 6.700 Å, α = β = γ = 90°. The c-axis was taken in the direction of surface normal, and set to c = 19.286 Å including the vacuum region. For calculation with adsorbates, the super cell with twice

the primitive cell was adopted (a = 6.373 Å). For the atomic composition of slab models, $(SnO_2)_{12}$ was adopted. Considering the hydrolysis reaction $(SnO_2)_{12} + H_2O \rightarrow HO\text{-}(SnO_2)_{12}\text{-}H$, and a successive reaction with $SbCl_3$, $HO\text{-}(SnO_2)_{12}\text{-}H + SbCl_3 \rightarrow [O\text{-}(SnO_2)_{12}]\text{-}SbCl + 2HCl$, the composition of slab model was set to $[Sn_{12}O_{25}]$-SbCl. For a model of heavier concentration of SbCl, $[Sn_{12}O_{25}]\text{-}(SbCl)_2$ model was also employed, where SbCl unit was bonded to the central and peripheral O atoms.

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Table S1. Comparison of the activity of the metal oxide-based visible light photocatalysts for H_2O_2 production.

Catalyst	Gas	Light wavelength (Intensity)	H_2O_2 generation rate (mM g^{-1} h^{-1})	External quantum yield (Φ_{ex})	Ref.
Au/SnO_2-Sb(III)	Air	420 nm (8.1 mW cm^{-2})	6.1	1.1%	This work
Au/SnO_2-Sb(III)	Air	Solar simulator (AM 1.5)	20.1		This work
Au/TiO_2	Air	> 400 nm (AM 1.5 100 mWcm^{-2})	6.5×10^{-2}		11
Au/WO_3	O_2	420-500 nm (2.69 mW cm^{-2})	2.8×10^{-2}	---	12
Au/$BiVO_4$	O_2	420-500 nm (2.69 mW cm^{-2})	8.0×10^{-2}	0.25%	12
Graphene Oxide	Air	> 400 nm (Xe, 765 W)	0.63	---	13
N:Cu_2O@CuO	Air	> 420 nm (Xe, 300 W)	0.84	---	14
Pt-PtO_x/WO_3	Air	> 420 nm (550 mW cm^{-2})	2.0	---	15
Au/WO_3	Air	> 420 nm (4 mW cm^{-2})	1.6	---	16
Pd/Mo:$BiVO_4$/CoO_x	O_2	Solar simulator (AM 1.5)	59.4	5.8%	17

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Table S2. Comparison for H_2O_2 adsorption amount on metal oxides.

Metal oxides	H_2O_{2ad} (μmol g^{-1})	H_2O_{2ad} (μmol m^{-2})
SnO_2	0.437	0.004
SnO_2-Sb(III) Γ_{ad} = 0.18	2.08	0.021
SnO_2-Sb(III) Γ_{ad} = 0.56	3.88	0.039
Anatase TiO_2	7.01	0.070
Rutile TiO_2	7.70	0.077
$SrTiO_3$	8.60	0.434
$BiVO_4$	1.80	1.295
Bi_2O_3	9.60	2.240
WO_3	2.10	0.251
ZrO_2	9.60	0.096

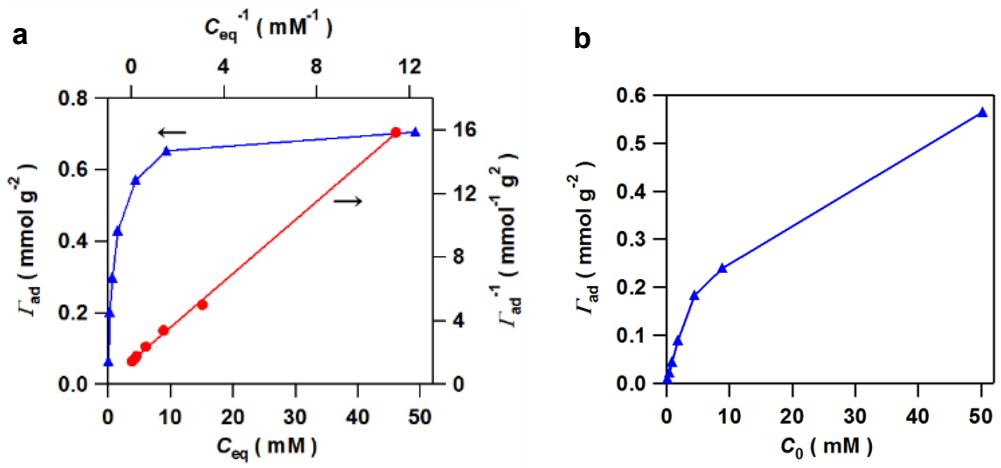

Fig. S1. (a) Adsorption isotherm of $SbCl_3$ on SnO_2 at 293 K (blue curve), and the Langmuir plot (red straight line). $SbCl_3$ was adsorbed on SnO_2 NCs from the methanol solution for 3 h at 293 K to achieve adsorption equilibrium. (b) Adsorption amounts of $SbCl_3$ on SnO_2 NCs from the methanol solution at 293 K vs. initial concentration of $SbCl_3$ (C_0). $SbCl_3$ was adsorbed on SnO_2 NCs from the methanol solution for 15 min at 293 K.

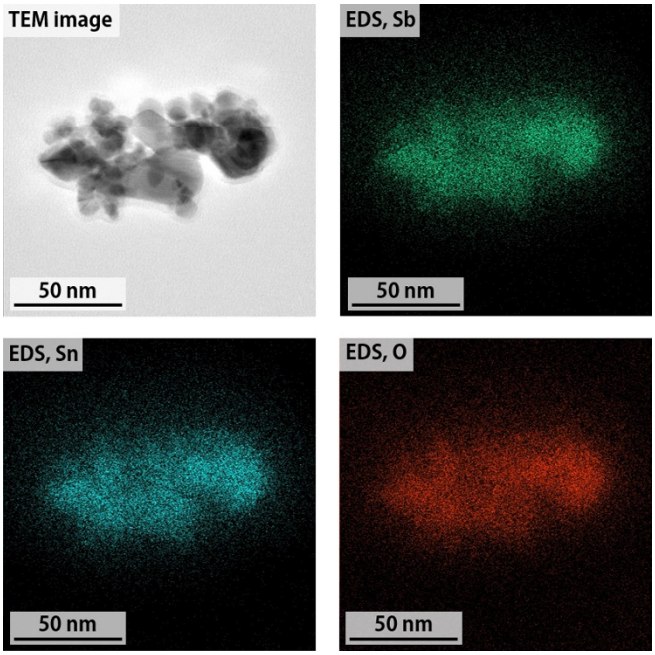

Fig. S2. TEM-EDS mapping of SnO_2-Sb(III) prepared at C_0 = 50 mM.

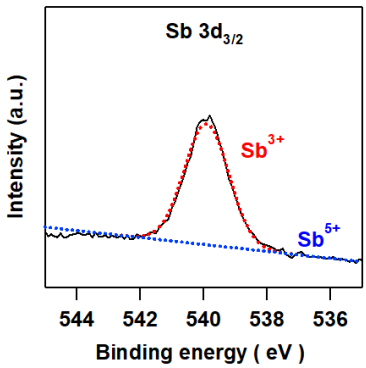

Fig. S3. Deconvoluted Sb 3d3/2-XP spectrum for SnO_2-Sb(III) with Γ_{ad} = 0.56 mmol g^{-1}.

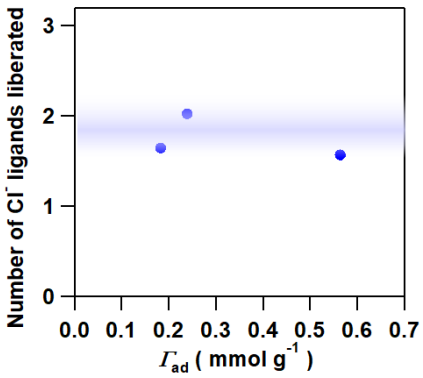

Fig. S4. Number of Cl^- ligands liberated by the adsorption.

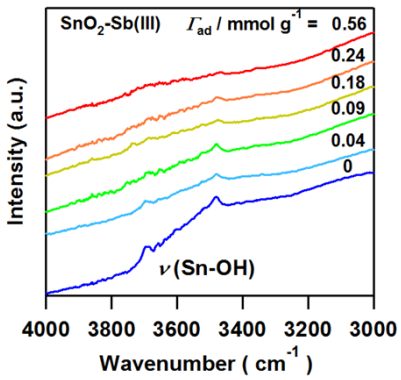

Fig. S5. DRIFT spectra of SnO_2-Sb(III) with varying Γ_{ad}.

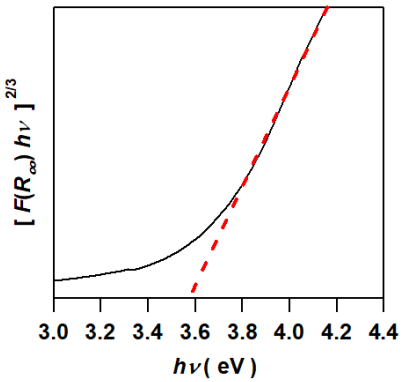

Fig. S6. Tauc plots for the absorption spectrum of ummodified SnO_2.

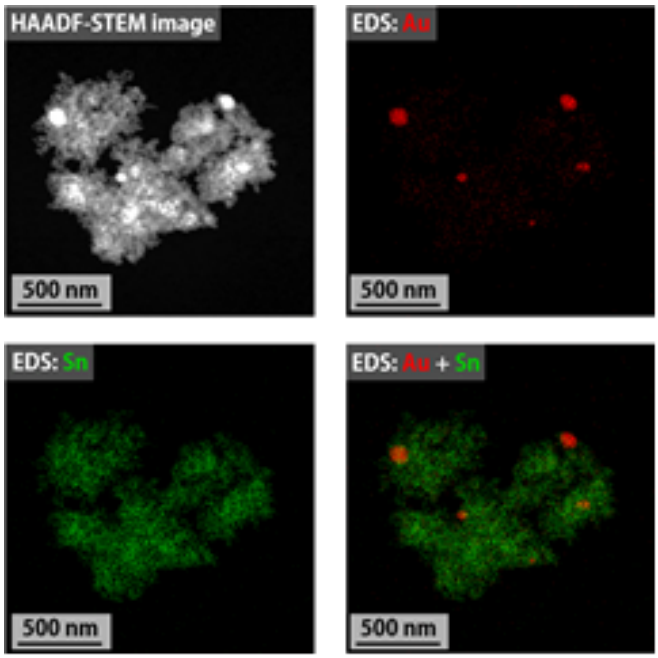

Fig. S7. TEM-EDS mapping of Au@SnO_2.

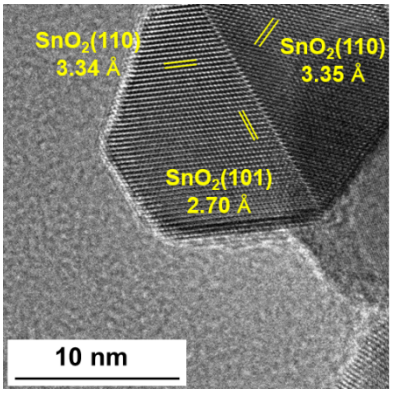

Fig. S8. Homoepitaxial junction between SnO_2 NCs with an orientation of $(101)_{SnO2}//(101)_{SnO2}$.

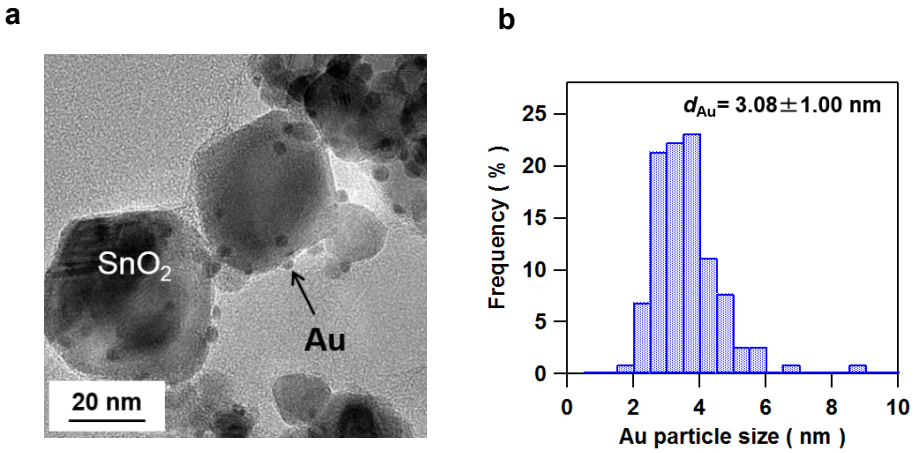

Fig. S9. TEM image (a) and Au particle size distribution (b) of Au/SnO_2-Sb(III) prepared at C_0 = 50 mM.

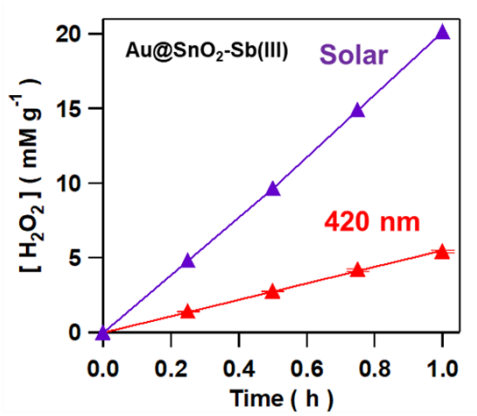

Fig. S10. Comparison of the photocatalytic activity of Au@SnO_2-Sb(III) (Γ_{ad} = 0.18 mmol g^{-1}) for H_2O_2 generation from water and O_2 under visible-light irradiation (λ_{ex} = 420 nm) and simulated sunlight (AM-1.5, one sun) at 298 K.

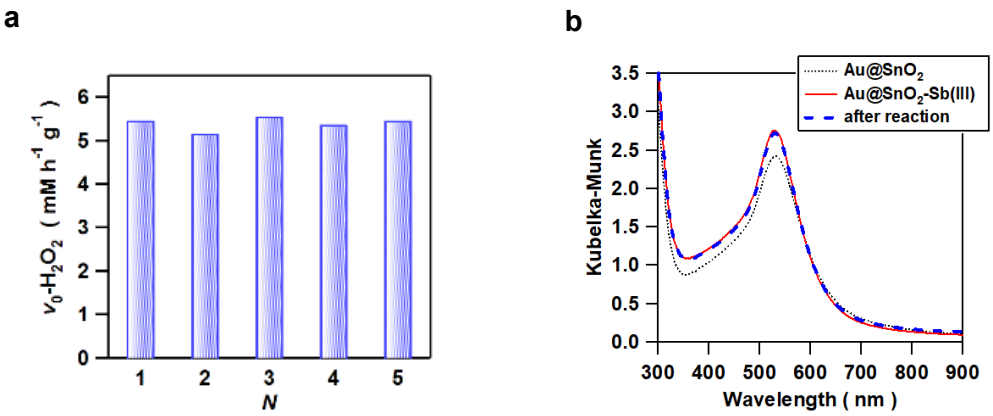

Fig. S11. (a) Stability test of the Au/SnO_2-Sb(III) (Γ_{ad} = 0.56) photocatalyst for H_2O_2 generation. (b) Absorption spectra of Au@SnO_2-Sb(III) before and after 5 times repeated reaction.

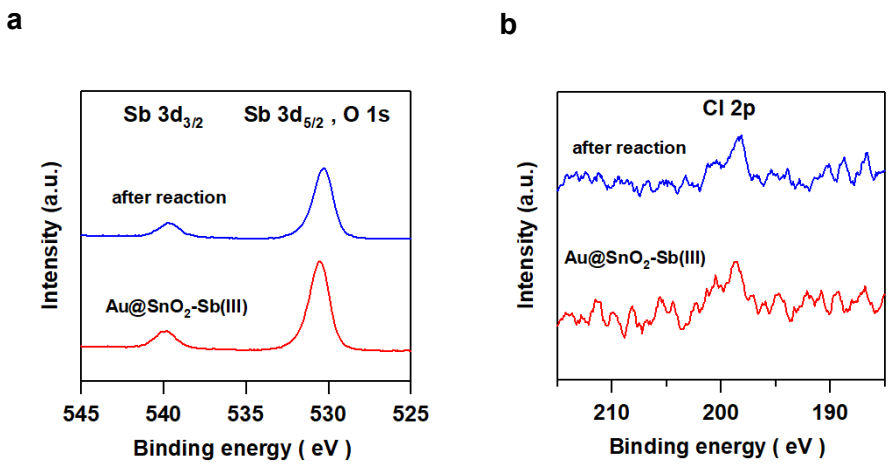

Fig. S12. Sb3d (a) and Cl2p-XP (b) spectra of Au@SnO_2-Sb(III) before and after the repeated reactions.

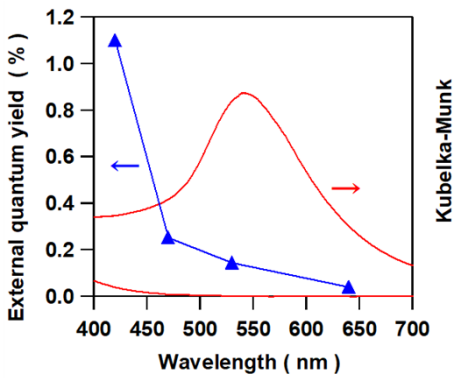

Fig. S13. Action spectrum of the external quantum yield for the reaction in the Au@SnO_2-Sb(III) system.

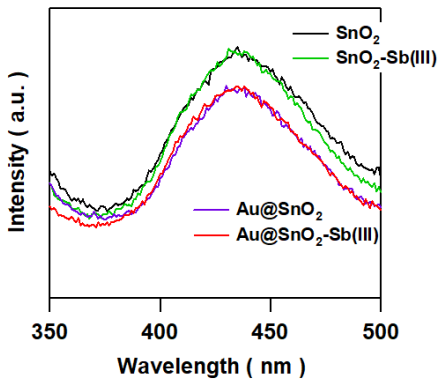

Fig. S14. Photoluminescence spectra of SnO_2, Au@SnO_2, SnO_2-Sb(III), and Au@SnO_2-Sb(III) were measured with excition wavelength of 300 nm at 77 K.