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Journal:	*Catalysis Science & Technology*
Manuscript ID	CY-ART-06-2022-001089.R1
Article Type:	Paper
Date Submitted by the Author:	18-Aug-2022
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A biomimetic all-inorganic photocatalyst for the artificial photosynthesis of hydrogen peroxide

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The artificial photosynthesis of H_2O_2 from water and O_2 presents a sustainable route for the production. Remarkable progress in the rate of reaction has recently been achieved mainly by using semiconducting organic polymer photocatalysts. In view of the use under harsh oxidative conditions, the development of robust inorganic photocatalysts is highly desired. Here we present a photocatalyst with the unit consisting of a single Au particle and an interconnected cluster of SnO_2 nanocrystals with the surface modified by $SbCl_3$ (Au@SnO_2-Sb(III)). Under visible-light irradiation (λ_{ex} = 420 nm), Au@SnO_2-Sb(III) stably produces H_2O_2 with a rate of 6.1 mM g^{-1} h^{-1} and an external quantum yield of 1.1%. This striking photocatalytic activity of Au@SnO_2-Sb(III) originates from the action of SnO_2-Sb(III) as a "light antenna" and "electron transporter", the electrocatalytic activity of Au NPs for two electron–oxygen reduction reaction, the visible-light induced activity of SnO_2-Sb(III) for oxygen evolution reaction, the weak adsorptivity for H_2O_2, and the robustness.

Introduction

Hydrogen peroxide (H_2O_2) is not only a very useful clean oxidant for organic synthesis[1] and water purification[2] but also a hopeful fuel for fuel cells.[3-6] Presently, most H_2O_2 is industrially produced by the energy-consuming anthraquinone autoxidation *via* the multi-steps. As the alternatives, various chemical and physical methods for H_2O_2 production have recently been intensively studied.[7] Among them, the solar-to-H_2O_2 conversion from earth-abundant water and O_2 can be a promising artificial photosynthesis to be challenged in chemistry (Eq. 1).[8,9]

$$H_2O + 1/O_2 \rightarrow H_2O_2 \quad \Delta_r G^0 = +115.8 \text{ kJ mol}^{-1} \quad (1)$$

where $\Delta_r G^0$ is the standard Gibbs energy of reaction.

The photocatalyst for efficient H_2O_2 synthesis should possess the following features: (1) visible-light responsiveness, (2) efficient charge separation, catalytic activities for (3) oxygen evolution reaction (OER) and (4) two electron-oxygen reduction reaction (2e$^-$-ORR), (5) weak adsorptivity for H_2O_2, and (6) high stability. Recently, various semiconducting polymer photocatalysts with high conversion efficiency have been developed.[10,11] However, these materials can undergo degradation because the photocatalytic synthesis of H_2O_2 is accompanied by the

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generation of activated oxygen species damaging the organic structures.[12] For the use under the harsh oxidative conditions, robust inorganic metal oxide-based photocatalysts are more favourable.[13] The metal oxide-based visible-light photocatalysts for the H_2O_2 production from water and O_2 reported so far are only limited to the systems including Au/TiO_2[14], Au/WO_3[15,16], Au/$BiVO_4$[17], graphene oxide[17], N-doped Cu_2O@Cu[18], Pt-PtO_x/WO_3[19], and Pd/Mo:$BiVO_4$/CoO_x.[20] However, no photocatalyst satisfying all the requirements has been developed to date, and in most of the systems, the rate of H_2O_2 production remains lower than ~2 mM g^{-1} h^{-1} (Table S1†).

In this study, an all-inorganic hybrid photocatalyst mimicking the natural photosynthesis[21] has been designed to enhance the photocatalytic activity. The photocatalyst with the unit structure consisting of a single Au NP (~50 nm) and an interconnected cluster (> ~100 nm) of many antimony chloride-surface modified SnO_2 nanocrystals (NCs, ~30 nm) (Au@SnO_2-Sb(III)). Au@SnO_2-Sb(III) has been shown to fulfil the requirements (1)-(6), stably producing H_2O_2 from water and O_2 with a rate of 6.1 mM g^{-1} h^{-1} and an external quantum efficiency over 1% at λ_{ex} = 420 nm. To our knowledge, this is the first report on the H_2O_2 production from water and O_2 by SnO_2-based photocatalysts.

Results and discussion

H$^+$-coupled 2e$^-$-ORR directly yields H_2O_2 in the reduction process of the photocatalytic H_2O_2 synthesis (Eq. 2), where E^0 denotes the standard redox potential with respect to the standard hydrogen electrode (SHE).[22] Also, H_2O_2 can be produced via one electron-ORR (Eqs. 3-5), but the resulting $O_2^{-\bullet}$ undergoes oxidation by the holes to generate singlet oxygen ($^1O_2$, Eq. 6).[23]

Reduction processes

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad E^0 = +0.695 \text{ V} \qquad (2)$$

$$O_2 + e^- \rightarrow O_2^{-\bullet} \qquad E^0 = -0.330 \text{ V} \qquad (3)$$

$$O_2^{-\bullet} + H^+ \rightarrow HO_2^\bullet \qquad (4)$$

$$HO_2^\bullet + H^+ + e^- \rightarrow H_2O_2 \qquad (5)$$

Oxidation process

$$O_2^{-\bullet} + h^+ \rightarrow {}^1O_2 \qquad (6)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^0 = +1.229 \text{ V} \qquad (7)$$

Thus, the conduction band (CB) edge potential of the metal oxide (MO) photocatalyst should be situated between -0.330 V and +0.695
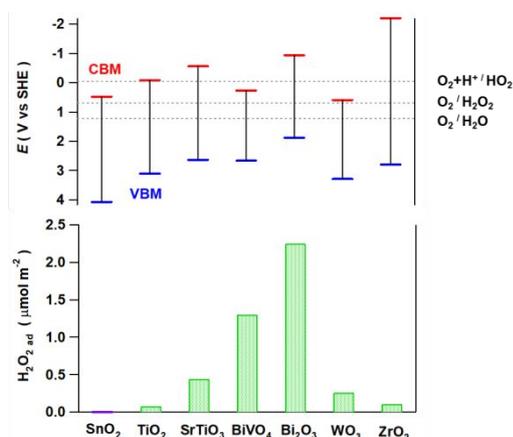
Fig. 1. Band edge potentials of various metal oxides with respect to the redox potentials of water and O_2 (upper). Saturated adsorption amount of H_2O_2 on various metal oxides at 298 K (lower).

V to increase the selectivity for $2e^-$-ORR by inhibiting one electron-ORR. Simultaneously, the VB edge potential of the MO semiconductor should be more positive than the potential for OER of +1.229 V (Eq. 7). Among various MOs, SnO_2, WO_3, and $BiVO_4$ satisfy these conditions (Fig. 1, upper). On the other hand, the oxidation of H_2O_2 ($E^0(O_2/H_2O_2)$ = +0.695 V) more easily occur than OER ($E^0(O_2/H_2O)$ = +1.229 V), while H_2O_2 adsorbed on MOs is apt to reductive decomposition during the photocatalytic process.[24] To break through this thermodynamically unsolvable problem, the adsorption of H_2O_2 on the photocatalyst must be suppressed. Then, the adsorption amount of H_2O_2 on various MOs were measured (Table S2†). The adsorption amount of H_2O_2 varies greatly depending on the type of MOs, and the adsorption capacity of SnO_2 to H_2O_2 is particularly low (Fig. 1, lower). Additionally, SnO_2 has an extraordinary physicochemical stability, and then, it was selected as the base MO semiconductor for the photocatalyst in this study. On the other hand, Au NP[14,25,26] and Au-Ag alloy NPs[27] are promising electrocatalysts for $2e^-$-ORR because of its excellent activity. However, Au NP is catalytically active also for the decomposition of H_2O_2. In the design for the photocatalyst with Au NPs for H_2O_2 production, the use of large Au NPs with small surface area is crucial to minimize the loss of H_2O_2.[25]

SbCl₃ was adsorbed on SnO_2 NCs with particle size ~30 nm and specific surface area = 100 m² g⁻¹ (FUJIFILM Wako Pure Chemical Co.) from the methanol solutions with various concentrations (SnO_2-Sb(III)), and the amount of the adsorbed Sb ions were quantified by inductively coupled plasma (ICP) spectroscopy. The adsorption of SbCl₃ on SnO_2 NCs at 293 K apparently follows the Langmuir-type behavior with the adsorption amount (Γ_{ad}) increasing in the equilibrium concentration (C_{eq}) (Fig. S1a†). From the slope and intercept of the Langmuir plot, the saturated adsorption amount and adsorption equilibrium constant were calculated to be 6.96×10^{-1} mmol g⁻¹ and 1.14×10^3 M⁻¹, respectively. The large adsorption equilibrium constant suggests strong chemisorption of SbCl₃ on SnO_2.

The adsorption amount (Γ_{ad}) can be precisely controlled by the initial concentration of SbCl₃ (C_0) (Fig. S1b†).

In the high resolution-transmission electron microscopic (HR-TEM) image of unmodified SnO_2 (Fig. 2a), regularly aligned O-atom rows are observed. The d-spacing in the lattice fringe (3.35 Å) is in agreement with the value for the SnO_2(110) crystal planes (3.35 Å) (ICDD No. 01-075-2893). Elemental mapping of SnO_2-Sb(III) by the TEM-energy dispersive spectroscopic (EDS) (Fig. S2†) shows that Sb is uniformly distributed on the whole surface of SnO_2 NCs. In the HR-TEM image (Fig. 2b), many molecular scale dark spots are present on the O-atom rows, whereas the O-atom sequences are connected in the HR-TEM image for the unmodified SnO_2 (Fig. 2a). Further to study the state of the adsorbed Sb ions, Sb3d- and Cl2p-X-ray photoelectron (XP) spectra were measured. In the Sb3d-XP spectra of the samples with varying Γ_{ad} (Fig. 2c), two signals are observed at the binding energy (E_B) = 540.1 eV and 530.7 eV assignable to the emission from the Sb3d$_{3/2}$ and Sb3d$_{5/2}$ orbitals of Sb(III) ions (Fig. S3†).[28] Both the signals intensify as a result of the increase in Γ_{ad} with the E_B values hardly changed. As shown by the Cl2p-XP spectra in (Fig. 2d), the samples have the Cl2p signals at E_B = 200.0 eV and 198.7 eV due to the emission from the Cl2p$_{1/2}$ and Cl2p$_{3/2}$ orbitals.[28] Clearly, SbCl₃ is adsorbed on SnO_2 while retaining some of the Cl⁻ ligands. The Cl in the solution after the adsorption of SbCl₃ on SnO_2 NCs can exist as SbCl₃ 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 ($n_{ad,Sb}$) (Fig. S4†). Diffuse reflectance infrared (DRIFT) spectra for SnO_2–Sb(III) with varying Γ_{ad} were measured (Fig. S5†). In the spectrum of unmodified SnO_2, a signal due to the stretching vibration of Sn_s-OH groups is observed at 3700 cm⁻¹, where Sn_s denotes the surface Sn atom. The absorption intensity decreases
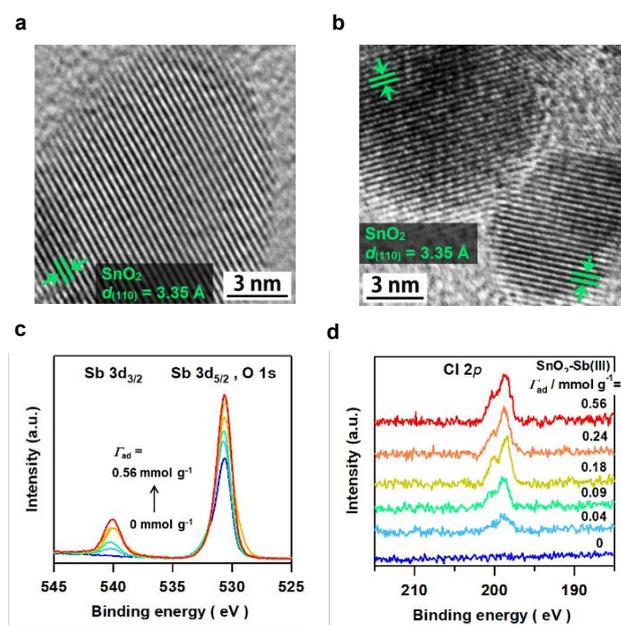
Fig. 2. (a) HR-TEM image of unmodified SnO_2. (b) HR-TEM image of SnO_2-Sb(III) prepared at C_0 = 50 mM. (c) Sb3d (c) and Cl2p (d)-XP spectra of SnO_2-Sb(III) with varying Γ_{ad}.

with the Sb(III)-surface modification, almost disappearing at $\Gamma_{ad} = 0.56$ mmol g^{-1}. These results indicate that a mixed ligand surface complex is formed by the adsorption of SbCl$_3$ on SnO$_2$ via the ligand exchange between Cl$^-$ ions and Sn$_s$-OH groups (Eq. 8).

$$SbCl_3 + 2HO\text{-}Sn_s \rightarrow SbCl\text{-}O_b\text{-}Sn_s + 2HCl \qquad (8)$$

where O$_b$ denotes the oxide ion bridging Sb and surface Sn ion.
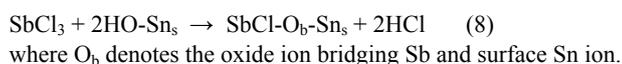
This scheme is consistent with the presence of the dark spots on the O-atom rows in the SnO$_2$ plane (Fig. 2b), and the density of the dark spots ($> \sim2$ nm^{-2}) comparable with the value calculated from the adsorption amount of SbCl$_3$ (2.6 nm^{-2}). Thus, the dark spots with highly dispersed at a molecular level in the HR-TEM image can be assigned to the SbCl species chemisorbed on SnO$_2$.

Diffuse reflectance spectra of SnO$_2$-Sb(III) with varying Γ_{ad} were measured. In the Kubelka-Munk transformed absorption spectra (Fig. 3a), unmodified SnO$_2$ has absorption edge of ~400 nm (or ~3.1 eV), and the Tauc plots provides a direct forbidden band gap of 3.58 eV (Fig. S6†) close to the reported value of 3.59 eV.[29] The Sb(III)-surface modification causes redshift in the absorption edge of which amount increases with an increase in Γ_{ad} from ~400 nm at $\Gamma_{ad} = 0$ to ~500 nm at $\Gamma_{ad} = 0.56$ mmol g^{-1}. To clarify the origin for the Sb(III)-surface modification-induced absorption, density functional theory (DFT) calculations were carried out for [Sn$_{12}$O$_{25}$]-(SbCl)$_2$ used as a model of
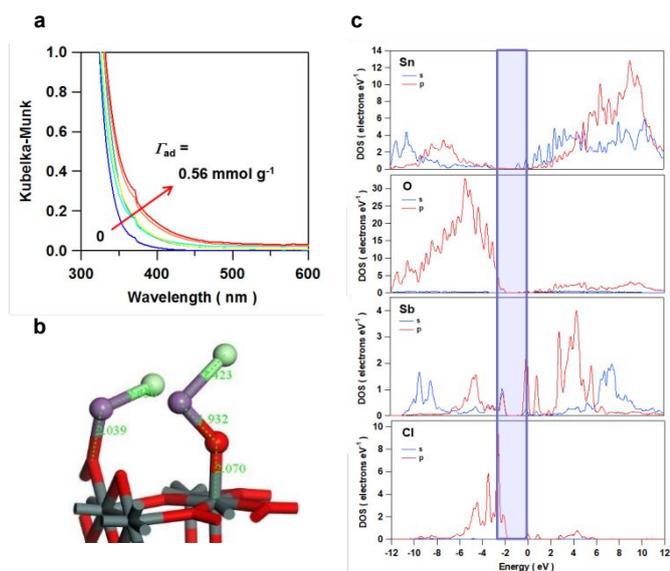
Fig. 3. (a) Absorption spectra of SnO$_2$-Sb(III) NCs with varying Γ_{ad}. (b) Optimized structure of [Sn$_{12}$O$_{25}$]-(SbCl)$_2$. (c) PEDOS of Sn$_{12}$O$_{25}$]-(SbCl)$_2$. Pale perpule region expresses the band gap of unmodified SnO$_2$.

SnO$_2$-Sb(III). In this model, SbCl was bonded to the O atom on the most stable SnO$_2$(110) plane.[30] The DFT-optimized structure of [Sn$_{12}$O$_{25}$]-(SbCl)$_2$ and the projected electronic density of states (PEDOS) are shown, where the pale purple region expresses the band gap of unmodified SnO$_2$ (Fig. 3b,c). The CB minimum and VB maximum of unmodified SnO$_2$ consist of Sn5s-5p and O2p orbitals, respectively. The band gap of ~3 eV is close to the absorption edge energy (~3.1 eV) rather than the direct forbidden band gap (3.58 eV). These results indicate that the Sb(III)-surface modification of SnO$_2$ generates the surface levels consisting of Sb5s-5p and Cl3p orbitals

above the VB maximum of SnO$_2$ to induce the band gap narrowing and the visible-light absorption.

SnO$_2$ NC films without and with the Sb(III)-surface modification were formed on fluorine-doped tin oxide electrodes (SnO$_2$/FTO, SnO$_2$-Sb(III)/FTO). Electrochemical properties of the SnO$_2$/FTO and SnO$_2$-Sb(III)/FTO electrodes for OER were studied by measuring the current (J)-potential (E) curves in deaerated 0.1 M NaClO$_4$ electrolyte solutions (pH 5.7) in the dark (dotted curves) and under visible-light irradiation ($\lambda_{ex} = 420$ nm, solid curves) (Fig. 4a). In the dark, anodic current due to OER rises at $E \approx 1.5$ V in each electrode. Visible-light irradiation of the SnO$_2$/FTO electrode hardly affects the current. On the contrary, in the SnO$_2$-Sb(III)/FTO electrode, significant photocurrent is induced with the onset potential shift to $0 \sim +0.1$ V. The value reduced at pH 0 ($+0.34 \sim +0.44$ V) is close to the CB-edge potential of SnO$_2$ ($+0.48$ V at pH 0).[31] This is consistent with the DFT-simulation results that the CB minimum of SnO$_2$ is hardly affected by the Sb(III)-surface modification (Fig. 3c). Photochronoamperometry curves were measured for the SnO$_2$-Sb(III)/FTO electrodes at the rest potential in the dark (Fig. 4b). In the J vs. Γ_{ad} plots (Fig. 4c), the photocurrent initially rises with increasing Γ_{ad} to slowly decrease through a maximum at $\Gamma_{ad} = 0.18$ mmol g^{-1}. Further, in the action spectrum of the photocurrent for OER over the SnO$_2$-Sb(III)/FTO electrode (Fig. 4d), the photocurrent rises at $\lambda_{ex} \sim 470$ nm to increase as the λ_{ex} becomes shorter, and the profile of the action spectrum well traces the absorption spectrum of SnO$_2$-Sb(III) NCs. Evidently, the Sb(III)-surface modification endows SnO$_2$ with the visible-induced OER ability.
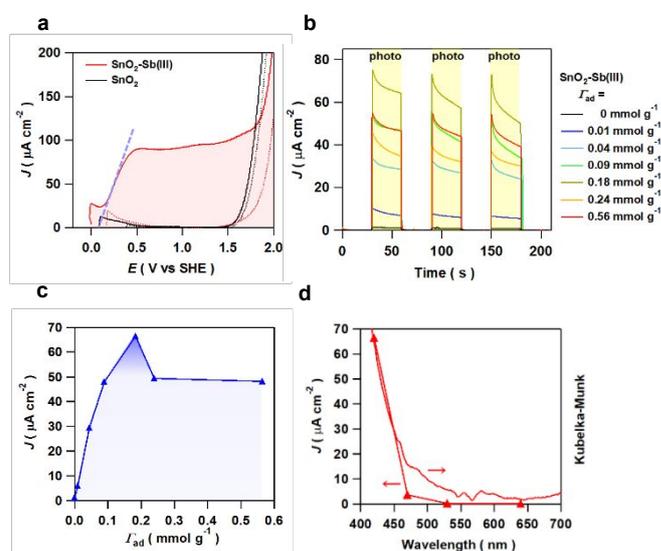
Fig. 4. (a) Current (J)-potential (E) curves for SnO$_2$/FTO and SnO$_2$-Sb(III)/FTO electrodes in deaerated 0.1 M NaClO$_4$ electrolyte solution (pH 5.7) in the dark and under visible-light irradiation ($\lambda_{ex} = 420$ nm, 8.1 mW cm^{-2}). (b) Photochronoamperometry curves of SnO$_2$-Sb(III)/FTO electrodes with varying Γ_{ad} at the rest potential in the dark. (c) Plots of J vs. Γ_{ad}. (d) Action spectrum for the photocurrent of the SnO$_2$-Sb(III)/FTO electrode. The absorption spectrum is also shown for comparison.

Au NPs (loading amount x_{Au} = 2.66 mass%) were deposited on SnO_2 NCs by the deposition precipitation (DP) method,[32] and then, $SbCl_3$ was chemisorbed on the sample. The d-spacing of the lattice fringe in the deposit (2.36 Å) in the HR-TEM image (Fig. 5a) is in agreement with the value of Au(111) (2.355 Å) (ICDD No. 00-004-0784). In the absorption spectra of Au@SnO_2-Sb(III) (Fig. 5b), new absorption due to the localized surface plasmon resonance (LSPR) appears around 550 nm with Au NP-loading on SnO_2-Sb(III). As shown in the TEM-EDS elemental mapping (Fig. 5c), a single Au NP (~50 nm) is present on a cluster (~500 nm) of many SnO_2-Sb(III) NCs with a primary particle size of ~30 nm (Au@SnO_2-Sb(III)). Intriguingly, every SnO_2 cluster contains ~one Au NP (Fig. S7†). The HR-TEM image for the SnO_2 cluster shows that SnO_2 NCs are interconnected through an epitaxial junction with the $(101)_{SnO2}//(101)_{SnO2}$ orientation (Fig. S8†). Downsizing Au particle below 5 nm causes a steep decrease in its melting point (T_m) from $T_m \approx$ 1100 K at Au particle size (d_{Au}) = 5 nm to $T_m \approx$ 700 K at d_{Au} = 2 nm.[33] In the DP method, small Au NPs are initially generated during the heating process at temperature (T_c) = 773 K, and the surface diffusion on the cluster of SnO_2 NCs would be greatly enhanced finally to be fused into a single Au NP (~50 nm). For comparison, Au NPs were loaded on SnO_2 NPs consisting of isolated particles (~100 nm) by the DP method, and $SbCl_3$ were adsorbed on the samples (Au/SnO_2-Sb(III)). Au NPs are dispersed on the surface of SnO_2 NPs in Au/SnO_2-Sb(III) (Fig. S9†) as observed for the usual Au/MOs.[34]

Au/SnO_2 NCs are inactive, SnO_2-Sb(III) NC yields H_2O_2 with an initial rate (v_0-H_2O_2) of 0.9 mM h^{-1} g^{-1}. Strikingly, loading Au NPs on SnO_2-Sb(III) NCs enhances the v_0 value to 6.1 mM h^{-1} g^{-1}, while no H_2O_2 is formed without O_2. O_2 gas bubbling of the reaction solution was confirmed to hardly affect the rate of H_2O_2 generation probably because it is limited by OER. The time courses for H_2O_2 generation in the Au/SnO_2-Sb(III) and Au@SnO_2-Sb(III) systems (Fig. 6b) show the comparable initial rates. In the Au/SnO_2-Sb(III) system, the photocatalytic activity decreases with the passage of reaction time. In contrast, in the Au@SnO_2-Sb(III) system, the concentration of H_2O_2 increases in proportion to irradiation time. This marked difference partly stems from the catalytic activity of Au@SnO_2-Sb(III) much lower than Au/SnO_2-Sb(III) for H_2O_2 decomposition (Fig. 6c). The rate of H_2O_2 generation is further boosted from 6.1 mM g^{-1} to 20 mM g^{-1} under illumination of simulated sunlight (AM-1.5, one sun) (Fig. S10†). The photocatalytic activity of Au@SnO_2-Sb(III) exceeds the values for most of the state-of-the-art inorganic photocatalysts for H_2O_2 synthesis from water and O_2 (Table S1†). Very recently, an exceptionally high photocatalytic activity of ~59.4 mM g^{-1} h^{-1} has been reported for H_2O_2 photosynthesis using a faceted $BiVO_4$-based photocatalyst.[20] However, the H_2O_2-generating rate decreases with reaction time because of the high affinity of $BiVO_4$ for H_2O_2 (Fig. 1 lower, Table S2†). The plot of the photocatalytic activity of Au@SnO_2-Sb(III) and the photocurrent of the SnO_2-Sb(III)/FTO

Fig. 5. (a) HR-TEM image of Au@SnO_2-Sb(III) prepared at C_0 = 50 mM. (b) Absorption spectra of Au@SnO_2-Sb(III) (solid lines) and SnO_2-Sb(III) (dotted lines) with varying Γ_{ad}. (c) TEM-EDS mapping of Au@SnO_2-Sb(III) prepared at C_0 = 50 mM.

The visible-light activities of various samples for H_2O_2 generation from air-sated water were evaluated (Fig. 6a). While SnO_2 and
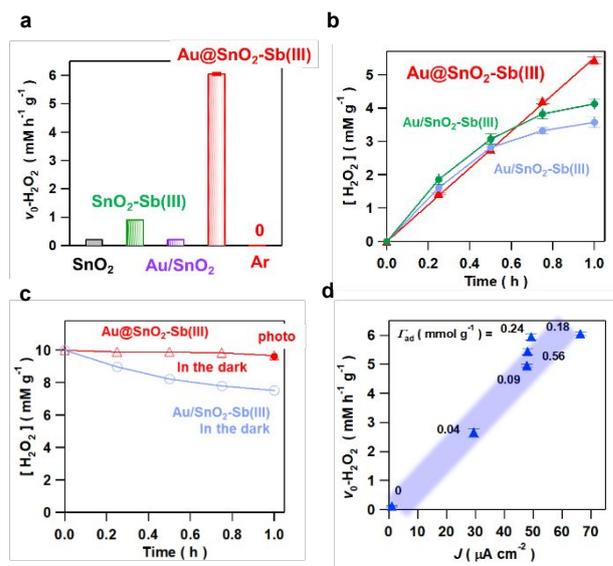
Fig. 6. (a) Comparison of the photocatalytic activity of SnO_2, SnO_2-Sb(III) (Γ_{ad} = 0.18 mmol g^{-1}), Au/SnO_2, and Au@SnO_2-Sb(III) (Γ_{ad} = 0.18 mmol g^{-1}) for H_2O_2 generation from air-saturated water under visible-light irradiation (λ_{ex} = 420 nm) at 298 K. (b) Time courses for the photocatalytic H_2O_2 generation from air-saturated water in the Au@SnO_2-Sb(III) and Au/SnO_2-Sb(III) with d_{Au} = 6.4 nm, x_{Au} = 2.59 mass% (green) and d_{Au} = 3.1 nm, x_{Au} = 2.66 mass% (blue) systems under irradiation (λ_{ex} = 420 nm) at 298 K. (c) Time courses for H_2O_2 decomposition by Au@SnO_2-Sb(III) (Γ_{ad} = 0.18 mmol g-1) in the dark or under visible-light irradiation (λ_{ex} = 420 nm) or by Au/SnO_2-Sb(III) (Γ_{ad} = 0.18 mmol g^{-1}) in the dark at 298 K. (d) The relation between the photocatalytic activity of Au@SnO_2-Sb(III) with varying Γ_{ad} for H_2O_2 generation and the photocurrent of the SnO_2-Sb(III) electrodes at the rest potential in the dark.

electrode provides a positive correlation between them (Fig. 6d), indicating that the OER is the key step in this reaction. To check the stability of Au@SnO$_2$-Sb(III), the photocatalytic reaction was repeated under the same conditions. The photocatalytic activity is maintained even after the reaction was repeated 5 times (Fig. S11a†). Further, the absorption spectra (Fig. S11b†) and XP spectra (Fig. S12†) of Au@SnO$_2$-Sb(III) show that not only the amounts of Sb and Au but also the states hardly change before and after the repeated reaction. The external quantum yield (ϕ_{ex}) for the reaction in the Au@SnO$_2$-Sb(III) system reaches 1.1% at λ_{ex} = 420 nm (Fig. S13†), and the action spectrum is similar to that of the photocurrent (Fig. 4d), strongly suggesting that this reaction is induced by the excitation of not the LSPR of Au NPs but SnO$_2$-Sb(III) NCs. Also, SnO$_2$ has broad emission around 440 nm due to the surface vacancy in the photoluminescence (PL) spectrum (Fig. S14†),[35] and the spectrum hardly changes with the Sb(III)-surface modification. A significant decrease in the signal intensity is observed with the loading of Au NPs in spite that the unit structure of Au@SnO$_2$-Sb(III) has only ~one Au NP. In this system, the excited electrons can be transported and collected to a single Au NP from the surrounding SnO$_2$ NCs interconnected each other.

On the basis of the energy diagram (Scheme 1a), the action mechanism of Au@SnO$_2$-Sb(III) for the photocatalytic H$_2$O$_2$ synthesis from water and O$_2$ is discussed in terms of the analogy with the natural photosynthesis (Scheme 1b). Excitation of Au@SnO$_2$-Sb(III) by photons with λ_{ex} = 420 nm promotes the electrons in the Sb(III)-induced levels above the VB of SnO$_2$ to the CB of SnO$_2$. The holes generated in the Sb(III)-surface levels oxidize water to yield O$_2$ and H$^+$ without the diffusion to the surface and with the assistance by the photoelectrocatalytic activity. On the other hand, a recent electrochemical study using Au/fluorine-doped SnO$_2$ rotating electrode have shown that Au NPs loaded on SnO$_2$ possess electrocatalytic activity for 2e$^-$-ORR.[36] Thus, H$^+$-coupled 2e$^-$-ORR effectively proceeds on the surface of Au NP with the aid of the electrocatalytic activity,[25,37] generating the concentration gradient of the excited electrons in the SnO$_2$ NCs towards the radial direction of Au NP to be the driving force for the one-directional electron transport in the functional unit of Au@SnO$_2$-Sb(III). Consequently, the excited electrons in the cluster of SnO$_2$-Sb(III) NCs are transported and collected to a single Au NP via the interparticle electron transport through the high-quality interface, and effective charge separation is achieved. The electron transport between SnO$_2$ NPs was previously utilized for the photoanode of quantum dot-sensitized solar cells.[38] Although the Sb(III)-surface modification somewhat increases the adsorptivity of SnO$_2$ for H$_2$O$_2$, it is still much weaker than the other MOs (Table S2†), and the decomposition of H$_2$O$_2$ once generated can be suppressed over SnO$_2$-Sb(III). In this case, the importance of the large Au particle size (d_{Au} = ~50 nm) in Au@SnO$_2$-Sb NCs should be emphasized. In the Au/semiconductor photocatalysts, the charge separation through the interfacial electron transfer from the semiconductor to Au NP is enhanced with increasing Au particle size.[39] Although Au NP shows the catalytic activity for H$_2$O$_2$ decomposition, the activity decreases with increasing Au particle size and negligibly small at d_{Au} > 12 nm.[25] In addition, the robustness of each component in the photocatalyst and the strong chemical bond between the SbCl species and SnO$_2$ would lead to the stable production of H$_2$O$_2$. In this manner, Au@SnO$_2$-Sb(III) fulfils the requirements (1)-(6) to exhibit the remarkable photocatalytic activity and stability for the production of H$_2$O$_2$ from water and O$_2$ under
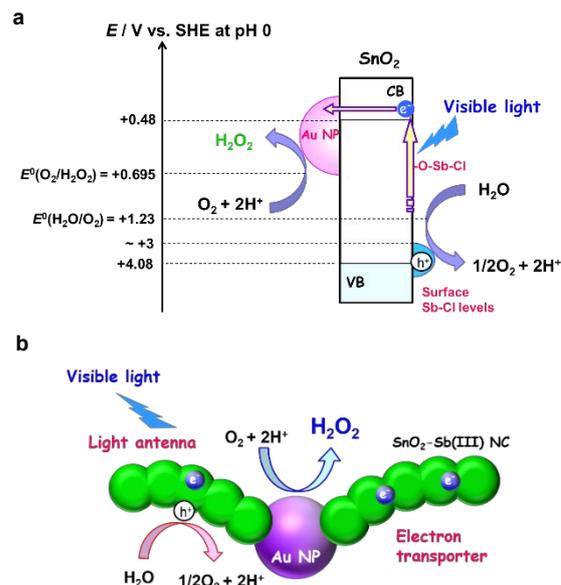
Scheme 1. (a) The energy diagram of Au@SnO$_2$-Sb(III) was constructed by assuming that the CB edge potential of SnO$_2$ is approximated by the flat band potential of +0.48 V (SHE at pH 0).[31] The VB maximum potential and the top of the surface levels due to the SbCl species were estimated from the band gap of SnO$_2$ and the absorption edge of SnO$_2$-Sb(III) to be 4.08 V and ~+3 V, respectively. (b) Analogy with the natural photosynthetic system.

visible-light irradiation. Compared this system to the natural photosynthetic system, the cluster of SnO$_2$-Sb(III) NCs acts as "light harvester (antenna chlorophylls)", "electron transporter and collector (light energy transporter and collector in antenna chlorophylls)" and "oxidation reaction end (P680)", while Au NP operates as "reduction reaction end (P700)".

Conclusions

This study has shown that visible-light irradiation (λ_{ex} = 420 nm) of Au@SnO$_2$-Sb(III) stably yields H$_2$O$_2$ from water and O$_2$ with a rate of 6.1 mM g^{-1} h^{-1} and an external quantum yield of 1.10%. Au@SnO$_2$-Sb(III) has a unique unit structure consisting of a single Au NP (~50 nm) and a cluster (> 150 nm) of SnO$_2$-Sb(III) NCs (~30 nm). The remarkable activity stems from the efficient charge separation through the interparticle electron transfer from SnO$_2$-Sb(III) NCs to a single Au NP, the electrocatalytic activity of Au NPs for 2e$^-$-ORR, the visible light-induced activity of SnO$_2$-Sb(III) for OER, the weak adsorptivity of SnO$_2$-Sb(III) for H$_2$O$_2$, and the low catalytic activity of large Au NP for H$_2$O$_2$ decomposition. We believe that this study would pave the way of a new biomimetic design of highly active robust inorganic nanohybrid photocatalysts for the solar-to-chemical conversion.

Data availability

The data supporting the findings can be found in the article and ESI, and are available from the authors upon reasonable request.

Author Contributions

M. T., S. N., and Y. Y. conducted catalysts synthesis, characterization, and photocatalytic reaction experiments, T. S. performed TEM observation and analysis, H. K. performed DFT simulations, and H. T. supervised the work and data analysis.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1   R. Noyori, M. Aoki and K. Sato, *Chem. Commun.,* 2003, **39**, 1977-1986.
2   D. B. Miklos, C. Remy, M. Jekel, K. G. Linden, J. E. Drewes and U. Hübner, *Water Res.,* 2018. **139**, 118-131.
3   S.-i. Yamazaki, Z. Siroma, H. Senoh, T. Iori, N. Fujiwara and K. A. Yasuda, *J. Power Sources,* 2008, **178**, 20-25.
4   Y. Yamada, S. Yoshida, T. Honda and S. Fukuzumi, *Energy Environ. Sci.,* 2011, **4**, 2822-2825.
5   A. M. Shaegh, N.-T. Nguyen, S. M. M. Ehteshami and S. H. Chan, *Energy Environ. Sci.,* 2012, **5**, 8225-8228.
6   K. Mase, M. Yoneda, Y. Yamada and S. Fukuzumi, *Nat. Commun.,* 2016, **7,** 11470.
7   J. M. Campos-Martin, G. Blanco-Brieva and J. L. G. Fierro, *Angew. Chem. Int. Ed.*, 2006, **45**, 6962-6984.
8   H. Hou, X. Zeng and X. Zhang, *Angew. Chem. Int. Ed.,* 2020, **59**, 17356-17376.
9   H. Tada, *Nanoscale Adv.,* 2019, **1**, 4238-4245.
10 S. Wu and X. Quan, *ACS EST Eng.,* **2022** DOI: 10.1021/acsestengg.1c00546, and the references therein.
11 Q. Tian, L. Jing, S. Ye, J. Liu, R. Chen, C. A. H. Price, F. Fan and J. Liu, *Small,* 2012, **17**, 2103224, and the references therein.
12 J. Xiao, Q. Han, Y. Xie, J. Yang, Q. Su, Y. Chen and H. Cao, *Environ. Sci. Technol.*, 2017, **51**, 13380-13387.
13 L. Wang, J. Zhang, Y. Zhang, H. Yu, Y. Qu and J. Yu, *Small,* 2022, **18**, 2104561, and the references therein.
14 N. Kaynan, B. A. Berke, O. Hazut and R. Yerushalmi, *J. Mater. Chem. A.,* 2014, **2**, 13822-13826.
15 H. Hirakawa, S. Shiota, Y. Shiraishi, H. Sakamoto, S. Ichikawa and T. Hirai, *ACS Catal.,* 2016, **6**, 4976-4982.
16 Y. Wang, Y. Wang, J. Zhao, M. Chen, X. Huang and Y. Xu, *Appl. Catal. B,* 2021, **284**, 119691/1-11.
17 W.-C. Hou and Y.-S. Wang, *ACS Sustain. Chem. Eng.,* 2017, **5**, 2994-3001.
18 W. Zhang, X. Chen, X. Zhao, M. Yin, L. Feng and H. Wang, *Appl. Surf. Sci.,* 2020, **527**, 146908/1-9.
19 W. Xie, Z. Huang, R. Wang, C. Wen and Y. Zhou, *J. Mater. Sci.,* 2020, **55**, 11829-11840.
20 T. Liu, Z. Pan, J. J. M. Vequizo, K. Kato, B. Wu, A. Yamakata, K. Katayama, B. Chen, C. Chu and K. Domen, *Nat. Commun.,* 2022, **13**, 1034/1-8.
21 L. Yang, D. Fan, Z. Li, Y. Cheng, X. Yang and T. Zhang, *Adv. Sustain. Syst.*, 2022, **6**, 2100477.
22 Electrochem. Soc. Jpn. Ed., *Denkikagaku Binran* (*Handbook of Electrochemistry*), Maruzen, Tokyo, **2000**.
23 S. Zhao, X. Zhao, *Appl. Catal. B*, 2019, **250**, 408-418.
24 X. Li, C. Chen, J. Zhao, *Langmuir*, 2001, **17**, 4118-4122.
25 M. Teranishi, S. Naya and H. Tada, *J. Am. Chem. Soc.,* 2010, **132**, 7850-7851.
26 K. Kim, J. Park, H. Kim, G. Y. Jung, M.-G. Kim, *ACS Catal.*, 2019, **9**, 9206-9211.
27 D. Tsukamoto, A. Shiro, Y. Shiraishi, Y. Sugano, S. Ichikawa, S. Tanaka, T. Hirai, *ACS Catal.*, 2012, **2**, 599-603.
28 XPS database, http://techdb.podzone.net/
29 M. Voinov and J. Augustynski, *Heterogeneous Photocatalysis,* Edited by Schiavello, M. John Wiley & Sons, New York **1997**.
30 J. Oviedo and M. J. Gillan, *Surf. Sci.,* 2000, **463**, 93-101.
31 H. Tada, A. Hattori, Y. Tokihisa, K. Imai, N. Tohge and S. Ito, *J. Phys. Chem. B,* 2000, **104**, 4585-4587.
32 S. Tsubota, M. Haruta, T. Kobayashi, A. Ueda and Y. Nakahara, *Preparation of catalysts V*, Elsevier, Amsterdam, **1991**.
33 P. Buffat and J.-P. Borel, *Phys. Rev. A,* 1976, **13**, 2287-2298.
34 T. Ishida, T. Maruyama, A. Taketoshi and M. Haruta, *Chem. Rev.*, 2020, **120**, 464–525.
35 X. Zhang, F. Guo, L. Zhuang, Q. Jin and X. Zhang, *Opt. Quantum Electronics,* 2022, **54**, 82/1-12.
36 T. Kunimoto, S. Naya and H. Tada, *Chem. Lett.*, 2021, **50**, 1589-1591.
37 C. M. Sánchez-Sánchez and A. J. Bard, *Anal. Chem.,* 2009, **81**, 8094-8100.
38 K. Tvrdy, P. A. Frantsuzov and P. V. Kamat, *Proc. Natl. Acad. Sci.,* 2011, **108**, 29-34.
39 H. Tada, T. Kiyonaga and S. Naya, *Chem. Soc. Rev.,* 2009, **38**, 1849-1858.