Band gap and Morphology Engineering of Hematite Nanoflakes from an Ex Situ Sn Doping for Enhanced Photoelectrochemical Water Splitting

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ABSTRACT: In this article, we report a simple ex situ Sn-doping method on hematite nanoflakes (coded as MSnO₂-H) that can protect the nanoflake (NF) morphology against the 800 ºC high-temperature annealing process and activate the photoresponse of hematite until 800 nm wavelength excitation. MSnO₂-H has been fabricated by dropping SnCl₄ ethanol solution on hematite nanoflakes homogeneously grown over the conductive FTO glass substrate and annealed at 500 ºC to synthesize the SnO₂ nanoparticles on hematite NFs. The Sn-treated samples were then placed in a furnace again, and the sintering process was conducted at 800 ºC for 15 min. During this step, structure deformation of hematite occurs normally due to the grain boundary motion and oriented attachment. However, in the case of MSnO₂-H, the outer SnO₂ nanoparticles efficiently prevented a shape deformation and maintained the nanoflake shape owing to the encapsulation of hematite NFs. Furthermore, the interface of hematite/SnO₂ nanoparticles became the spots for a heavy Sn ion doping. We demonstrated the generation of the newly localized states, resulting in an extension of the photoresponse of hematite until 800 nm wavelength light irradiation. Furthermore, we demonstrated that SnO₂ nanoparticles can effectively act as a passivation layer, which can reduce the onset potential of hematite for water splitting redox reactions. The optimized MSnO₂-H nanostructures showed a 2.84 times higher photocurrent density and 300 mV reduced onset potential compared with a pristine hematite nanoflake photoanode.

INTRODUCTION

Hematite iron oxide (α-Fe₂O₃) is one of the promising candidates for the production of hydrogen via photoelectrochemical water splitting (PEC-WS) owing to its suitable band gap (2.1 eV) providing a high theoretical solar-to-hydrogen efficiency (15.3%), high chemical and photocorrosion stability, as well as earth abundance.¹−³ It is an n-type semiconductor and hence is utilized as the photoanode material in the PEC-WS cells. However, the performance of the hematite photoanodes is still limited due to several drawbacks such as a high electrical resistivity, short hole-diffusion length (Lₜh ≈ 2−4 nm), high charge recombination rate, and poor oxygen evolution reaction kinetics taking place on its surface.⁴−⁶ A number of approaches have been introduced to address these problems including, particularly, various nanostructuring and morphology controls (e.g., thin film,⁷ nanoflake,⁸ nanorod,⁹ and nanoporous structure¹⁰), doping by foreign elements (Sn⁴⁺,¹¹ Ti⁴⁺,¹² Pt⁴⁺,¹³ B³⁺,¹⁴ etc.), deposition of cocatalysts on the hematite surface (e.g., Zn-Co LDH,¹⁵ Co-Pi,¹⁶ and FeOOH¹⁷), and/or deposition of isocrystalline ultrathin passivation layers.¹⁸,¹⁹

Morphologically controlled hematite nanostructures are highly desired in terms of increasing light absorption because of their high specific area and addressing problems associated with a short diffusion length of photoholes, which both lead to
Elemental doping is the efficient way to increase a donor density in hematite and thus the electrical conductivity. \(^{23}\) Tin (Sn) is the most typical example of metal impurity used for the hematite doping. The substitution of iron by Sn\(^{4+}\) ions in the hematite lattice has led to an increase in the donor density \(N_D\) from \(7.86 \times 10^{19}\) to \(1.95 \times 10^{20} \text{ cm}^{-3}.\)\(^{24-26}\) Consequently, the dynamics of photocharges is enhanced because of better electrical conductivity. Both \textit{in situ} and \textit{ex situ} methods have been described to incorporate tin ions into hematite structures. In the case of \textit{in situ} doping, Sn dopants were added to the precursor solution of hematite during hydrothermal growth.\(^{25}\) \textit{In situ} doping is a plain process that provides flexibility in the selection of dopants and uses relatively low sintering temperatures without additional doping steps.\(^{26}\) However, deformation of morphology and changes in crystallinity are observed from \textit{in situ}-doped hematite.\(^{27}\) The most frequent strategy for \textit{ex situ} doping is a thermal diffusion of tin ions coming from the FTO glass substrate (the glass substrate is coated by a conductive film of fluorine-doped SnO\(_2\)) at high temperatures (\(\sim 800 ^\circ\text{C}\)).\(^{15}\) Correspondingly, one can use a tin-containing precursor solution deposited on the hematite or akaganites (\(\beta\)-FeOOH) surface, which is then thermally treated under similar temperatures.\(^{27}\) The key advantage of the \textit{ex situ} processes is that various hematite and/or akaganite nanostructures (nanorods,\(^{28}\) nanotubes,\(^{29}\) nanoflakes,\(^{30}\) etc.) can be utilized as the starting substrates. Furthermore, Sn doping also leads to a slightly reduced optical band gap and enhanced optical adsorption coefficient by structural distortion of the hematite lattice.\(^{31}\) In addition, from computational approaches a band gap reduction of hematite is expected by newly localized energy levels, resulting from orbital hybridization between Fe ions (3d orbital) and Sn ions (5s and 5p orbitals).\(^{32}\) However, there are only a few studies dealing with the relationship between PEC performance and increased optical property of hematite.\(^{31,33}\) Especially, the photoresponse at long wavelength (\(\lambda \geq 650 \text{ nm}\)) of the incident light without plasmon resonances by novel metals and/or light-trapping structures, which is an important issue for improving the PEC performance of hematite, has been rarely reported.\(^{24,35}\)

The passivation overlayers, for example, TiO\(_2\),\(^{18}\) Al\(_2\)O\(_3\),\(^{19}\) or Ga\(_2\)O\(_3\)\(^{36}\) conformally and homogeneously covering the hematite surface generally provide two beneficial effects; namely, they improve stability of photoanodes by preventing a direct contact between electrolyte and hematite, as well as they passivate the detrimental surface states that work as recombination centers. As a consequence of the surface state inactivation and thus of reduced recombination of the charge carriers, the photocurrent density increases, and simultaneously, the onset potential is shifted to a more cathodic region, which results in significantly higher PEC-WS activity.\(^{37}\)

In this work, we report morphology-controlled hematite nanoflakes that were treated with a SnO\(_2\) coating, which acts as a passivation layer (MSnO\(_2\)-H) and provides photoresponses at long wavelength (\(\sim 800 \text{ nm}\)) using \textit{ex situ} surface treatments and a high-temperature annealing process. The photocurrent density of the MSnO\(_2\)-H obtained is 0.847 mA/cm\(^2\) at 1.23 V\(_{RHE}\) which is about 16-fold enhanced PEC activity over pristine hematite nanoflakes (P-H). We attribute the significant enhancement not only to a reduced recombination by surface passivation effects that can be defined using an intensity-modulated photocurrent spectroscopy (IMPS) analysis but also to an enhanced conductivity and extended photoresponses (650 \(\leq\) \(\lambda\) \(\leq\) 800 nm) by newly localized energy levels resulting from a high concentration of Sn\(^{4+}\) doping.

**RESULTS AND DISCUSSION**

The fabrication of hematite nanoflake-based photoanodes follows several steps, as depicted in Figure 1. First, a 600 nm thick film of pure iron was deposited onto a FTO substrate by using magnetron sputtering. It is worth noting that it is a novel strategy for preparing fully transparent hematite photoanodes with a nanoflake coverage, that is, we use a total thermal oxidation of the iron thin film to obtain this morphology.\(^{38}\) In the second step, the FTO/iron film substrates were annealed at 400 \(^\circ\text{C}\) for 2 h to grow pristine hematite nanoflakes (hereafter, the samples denoted as P-H). In the third step, a precursor solution of SnCl\(_2\) diluted in ethanol was drop-casted over the P-H samples and then annealed at 800 \(^\circ\text{C}\) for 15 min (hereafter, the samples are denoted as SnO\(_2\)-H). Alternatively, prior to the high-temperature treatment, the samples were
annealed first at 500 °C for 1 h in order to preserve the nanoflake morphology (hereafter, the samples are denoted as MSnO\(_2\)-H). In other words, during the 500 °C annealing process, the thin and small SnO\(_2\) NPs are uniformly formed on the surface of hematite nanoflakes, which can prevent a morphology deformation resulting from the restricted grain boundary motion and oriented attachment.\(^{33}\) It is a strategy similar to the SiO\(_2\) encapsulation described by Srivula et al.\(^{34}\)

The top-view scanning electron microscopy (SEM) images of the hematite photoanodes treated under different conditions are displayed in Figure 2. The as-grown hematite samples (Figure 2a, S1b) show a dense array of well-developed nanoflakes, having a length varying between 0.3 and 2 μm and thickness between ~150 and ~20 nm at the bottom and their terminating tips, respectively. During the single annealing process at 800 °C of bare hematite nanoflakes (i.e., those without applied SnCl\(_2\) solution), an undesirable sintering process of the nanoflakes clearly occurred. It means that the nanoflake morphology transformed to a much sharper nanowire-like shape due to grain boundary diffusion, as demonstrated by SEM and transmission electron microscopy (TEM) images (Figures 2b and S2). In this procedure, the tin doping in the hematite lattice took place via the mechanism of the thermal diffusion of Sn\(^{3+}\) ions realized from the bottom FTO substrate (the sample is hereafter coded as Sn-H).\(^{35,36}\) A semi-preserved nanoflake structure was achieved despite the same high-temperature annealing in the case of SnCl\(_2\)-treated hematite nanoflakes (Figure 2c). Finally, it can be observed in Figure 2d that the samples treated with the SnCl\(_2\) solution and then annealed in two sequential steps, first at 500 °C for 1 h and then at 800 °C for 15 min (see Figure 1), well-maintained the desired nanoflake morphology (MSnO\(_2\)-H, Figure S3). During the first annealing step, the dried drops of SnCl\(_2\) precursor oxidized to SnO\(_2\) NPs, which uniformly covered the hematite nanoflake surface. These nanoparticles then provide two functions during the following second annealing step; namely, they form an encapsulation scaffold to prevent morphology change (a simpler approach than previously reported silica encapsulation) and are a simultaneous source of the \textit{ex situ} Sn\(^{4+}\) doping of hematite.

The TEM images of P-H, SnO\(_2\)-H, and MSnO\(_2\)-H are well consistent with corresponding SEM images, as shown in Figure 2. The energy-dispersive spectroscopy (EDS) mapping (Figure 3e–g) visualizes the distribution of Sn, Fe, and O ions in MSnO\(_2\)-H. In particular, the quantitative analysis of a single SnO\(_2\) nanoparticle on Fe\(_2\)O\(_3\) NF, which is calculated from EDS mapping (Figure S4), demonstrates that Sn ions from SnO\(_2\) and Fe ions from Fe\(_2\)O\(_3\) NF can be interchangeably diffused into each other during high-temperature annealing, leading to the formation of Fe-doped SnO\(_2\) (F/SnO\(_2\)) and Sn-doped Fe\(_2\)O\(_3\) in MSnO\(_2\)-H. As shown in Figure 3h, the particle size distribution of Fe/SnO\(_2\) is from 1.0 to 8.1 nm with a lattice spacing of 0.33 nm, which corresponds to the (110) plane of tetragonal SnO\(_2\) (inset of Figure 3h).\(^{40}\)

The crystalline structure of the photoanodes was determined by X-ray diffraction. All the samples tested showed a well-crystalline hematite structure with the preferential orientation of the crystallites along the (110) crystalline plane, which provides the highest electrical conductivity. One of the important features is that only the P-H sample contained a contribution of the magnetite iron oxide (Fe\(_3\)O\(_4\)) phase, which commonly accompanies iron oxide nanoflakes prepared by thermal oxidation of iron substrates. The presence of magnetite, however, decreases the overall efficiency of the hematite photoanodes. Thanks to the second annealing step at 800 °C, the magnetite phase was fully transformed into the pure hematite phase.

To study the chemical compositions of the P-H and MSnO\(_2\)-H samples, X-ray photoelectron spectroscopy (XPS) was performed (Figures 3i and S4). Figure 3i presents the Fe 2p scans showing the Fe 2P\(_{3/2}\) (711 eV) and the Fe 2P\(_{1/2}\) (724.5 eV) peaks that are well consistent with those reported for hematite. Furthermore, the coexistence of Fe 2P peaks and an additional peak at 715.8 eV, which is indicative of the Sn 3P\(_{3/2}\) in SnO\(_2\)–H, demonstrates the decoration of SnO\(_2\) particles on hematite nanoflakes. In addition, the Fe ion diffusion from hematite NFs into SnO\(_2\) (Fe/SnO\(_2\)) because of the ion diffusion due to the high-temperature sintering process can be observed by EDX mapping (Figure S4d).\(^{13,41}\) The XPS analysis of the MSnO\(_2\)-H shows two major peaks at 487.3 eV (Sn 3d\(_{5/2}\)) and 495.7 eV (Sn 3d\(_{3/2}\)) which are matched with the reported XPS data for Sn-treated hematite, indicating substitutational doping of Sn\(^{3+}\) ions in the hematite lattice (Figure S5).\(^{23}\) Figure S6 shows the valence band maximum (VBM) of P-H (1.20 eV) and MSnO\(_2\)-H (1.55 eV) assessed by linearly fitting the leading edge of the valence band retrieved from the XPS measurements. The analysis indicates that the Fermi level of MSnO\(_2\)-H is shifted toward the conduction band (CB) compared with pristine P-H. This Fermi-level shifting demonstrates that hematite nanoflakes are doped by Sn\(^{3+}\) ions. A concentration of 12.08% of Sn on MSnO\(_2\)-H was estimated from the XPS analysis. This value includes the Sn-ion doping in Fe/SnO\(_2\) NPs. To calculate the Sn concentration of MSnO\(_2\)-H more precisely, we can assume that the spots of the highest Sn concentration in EDS (red spots in Figure S7) correspond to a Sn concentration of pristine SnO\(_2\) (33.73 at. %). This leads to a Sn concentration at the interface of Fe/SnO\(_2)/hematite NFs of approximately 10–12.5% and the average Sn concentration of hematite NFs in MSnO\(_2\)-H of 7.5%, respectively. The band gap for the samples can be determined from the plot (\(I_0^p/hv\)^{1/2} versus photo energy (hv), where \(I_0^p\) is photocurrent density, as shown in Figure 3k). In particular, the band gap of P-H and MSnO\(_2\)-H can be read as approximately 2.0 and 1.87 eV, respectively, which are the values well corresponding to those reported for hematite oxide. Interestingly, from the plot corresponding to the MSnO\(_2\) sample, potentially, one more value of a band gap
of 1.53 eV can be observed caused by newly localized energy levels resulting from the high concentration of Sn-ion doping (ca. 10–12.5%). This result is well consistent with the computational simulation, which shows the reduced band gap (1.57 eV) of hematite with 12.5 atom % of Sn.32

The linear sweep voltammetry of P-H, Sn-H, SnO₂-H, and MSnO₂-H in a 1 M KOH solution with the Ag/AgCl reference electrode under an AM 1.5 solar simulator is shown in Figure 4a. The PEC performance of the bilayer structure of hematite nanoflakes and thin film using an optimized process for its preparation has been already reported by our group elsewhere.38 The charge compensations between the photoexcited electrons from hematite nanoflakes and photoexcited holes from the bottom hematite film layer can effectively reduce the probability of a recombination rate of photoanode. The P-H had a photocurrent density of 0.38 mA/cm² at 1.50 V_RHE and an onset potential of 1.21 V_RHE and the photocurrent density of Sn-H increased by 0.63 mA/cm² at 1.50 V_RHE with an onset potential of 1.13 V_RHE. The increased PEC performance of the Sn-H compared with P-H is caused by not only the reduced magnetite layer located between hematite nanoflakes and FTO glass that hinders the electron transfer, as shown in X-ray diffraction (XRD) data (see Figure 3i), but also the enhanced conductivity by Sn-ion doping from bottom FTO glass due to the 800 °C annealing process. When the SnCl₄ was treated on Fe₂O₃ NF, as shown in Figure 1, the photocurrent density of SnO₂-H reached 0.92 mA/cm² at 1.50 V_RHE with the onset potential of 0.93V_RHE due to surface passivation and Sn⁴⁺ ion...
doping. In addition, the photocurrent density of MSnO$_2$-H is further enhanced to 1.08 mA/cm$^2$ at 1.50 V$_{RHE}$ with an onset potential of 0.93 V$_{RHE}$. This can be ascribed to the larger surface area of MSnO$_2$-H than that of SnO$_2$-H obtained by a simple morphology engineering, which helps to preserve the shape of nanoflakes similar to P-H compared with SnO$_2$-H (nanowire-like shape, Figure 3b). As a consequence, more light, including long wavelength, can be absorbed by the nanoflakes, and thus a higher photocurrent density can be reached. The IPCE data in Figure 4b shows a higher photoresponse of SnCl$_2$-H, Sn-H, and P-H measured at 1.50 V$_{RHE}$ and MSnO$_2$-H at 1.50 V$_{RHE}$ under illumination ($\lambda$ = 800 nm). (d) Charge transfer efficiency of P-H and MSnO$_2$-H calculated from the IMPS measurement.

Figure 4. (a) Linear sweep voltammetry for P-H, Sn-H, SnO$_2$-H, and MSnO$_2$-H with chopped light under 1 sun condition. (b) IPCE of P-H, Sn-H, SnO$_2$-H, and MSnO$_2$-H measured at 1.50 V$_{RHE}$. (c) Chronoamperometry measurements of P-H, Sn-H, SnO$_2$-H, and MSnO$_2$-H at 1.50 V$_{RHE}$ under illumination ($\lambda$ = 800 nm). (d) Charge transfer efficiency of P-H and MSnO$_2$-H calculated from the IMPS measurement.
recombination resulting from passivated surface states of the hematite. This indicates that tiny Fe-doped SnO$_2$ NPs (1.0–8.1 nm) can be a superior passivation layer on hematite. Last but not the least, to elucidate the charge transfer mechanism between the surface of the hematite and electrolyte, electrochemical impedance spectroscopy (EIS) was carried out in the frequency range of 100 kHz to 0.1 Hz at 1.50 V$_{RHE}$ applied bias and with 369 nm light source. Nyquist plots for the P-H, Sn-H, SnO$_2$-H, and MSnO$_2$-H were fitted by using the equivalent circuit model shown in the inset image of Figure 5. The equivalent circuit consisted of the series resistance of the electrochemical cell, namely $R_0$, the trapping/detrapping resistance of electrons, $R_1$, the space charge capacitance of the bulk hematite, $C_1$, the charge transfer resistance between the electrolyte and the surface of the hematite, $R_2$, and the space charge capacitance at the interface between the electrolyte and the surface of the hematite, $C_2$. The $R_0$ values for every sample show similar values, indicating the same experimental condition in the electrochemical measurement.\textsuperscript{17} Since the Sn$^{4+}$ ions by diffusion from bottom FTO glass can effectively increase the conductivity of hematite, the $R_1$ and $R_2$ value of Sn-H (3,550 and 9,449 $\Omega$) is lower than that of the P-H (4,608 and 12,380 $\Omega$), as shown in Figure 5 and Table S2.\textsuperscript{60} After the decoration of the SnO$_2$ NPs on Fe$_2$O$_3$ NF by an \textit{ex situ} SnCl$_4$ solution treatment, the $R_1$ and $R_2$ value of MSnO$_2$-H is decreased to 649.3 and 3,510 $\Omega$, respectively. This indicates that the SnO$_2$ NPs on hematite NF act as a passivation layer, which strongly suppresses the surface recombination owing to the reduced surface defect states, causing the high charge recombination and inefficient water oxidation by photogenerated holes.

Taking into consideration XPS, band gap calculation, photoresponse, and IMPs measurement, the band diagram of P-H and MSnO$_2$-H can be described, as illustrated in Figure 6a,b, respectively. When P-H absorbs the light, the electron–hole pairs (EHPs) are generated. Although the EHPs, which are generated in the depletion region, can be flowed to the electrolyte to participate in the water splitting reaction, the photoexcited holes in P-H are captured by surface states, resulting in recombination at the surface of P-H, as aforementioned. Meanwhile, the EHPs in the MSnO$_2$-H can be easily extracted from the electrolyte without recombination due to the passivation layer consisting of Fe/SnO$_2$ NPs. Furthermore, a high concentration of Sn doping can generate a localized Fe$^{3+}$ 3d state above the VB, which can reduce the band gap, as described in Figures 3k and 6b. The Sn doping level at the interface of Fe/SnO$_2$ and hematite is higher than that of the plain surface of MSnO$_2$-H, as shown in EDS analysis (Figure S4b,c). Since the energy level of the localized Fe$^{3+}$ 3d state is variable by the Sn doping amount, the interface between Fe/SnO$_2$ and hematite could be the site for absorbing the long wavelength (800 nm).\textsuperscript{45} This demonstrates that \textit{ex situ} doping by a high concentration of Sn$^{4+}$ ions on hematite not only creates the passivation layer consisting of Fe/SnO$_2$ NPs but also reduces the band gap, which can generate additional EHPs at a long wavelength.

In conclusion, we explored shape-preserved hematite nanoflakes with Fe-doped SnO$_2$ NPs fabricated by a simple \textit{ex situ} decoration method to produce an enhanced PEC performance. The SnO$_2$ NPs on hematite nanoflakes not only sustain the original shape of pristine hematite nanoflakes but also act as a passivation layer. Furthermore, MSnO$_2$-H showed greatly reduced recombination and presented a photocurrent density of 1.08 mA/cm$^2$ at 1.50 V$_{RHE}$ with a photoresponse even at a long wavelength (800 nm). Our strategy demonstrates the simple way to reduce the EHP recombination of hematite NF and extend the capability of light absorption of hematite for the PEC reaction to the near-infrared region.

**EXPERIMENTAL SECTION**

**Preparation of HNF and Sn-HB Samples.** The iron films with a thickness of 600 nm were deposited on FTO glass by using the magnetron sputtering technique, as reported in our previous paper.\textsuperscript{30} To grow the hematite NFs on the iron film, the prepared iron film/FTO samples were heated at 400 °C for 2 h and then cooled down to room temperature. The sample was annealed once again at 800 °C for 15 min to prepare MSnO$_2$-H. For SnO$_2$-H (without the morphology control), the annealing procedure at 500 °C was skipped. In the case of Sn-H, the
hematite NF was placed in the furnace for 15 min at 800 °C without SnCl₄ treatment.

**Characterization of the Samples.** The morphology of the samples was investigated using SEM (Hitachi, S-4800). The EDS analysis was carried on by using a TEM machine (HRTEM, Titan G2). XRD was performed with an X’pert Philips MPD (equipped with a Panalytical X’celerator detector) with graphite monochromatic Cu Kα radiation (λ = 1.54056 Å). The chemical composition and the VBM were characterized by XPS (PHI S600), and the peak positions were calibrated according to the C 1s peak at 284.8 eV.

**Photoelectrochemical Measurements.** The three-electrode system, which consists of a Pt mesh and an Ag/AgCl (3 M KCl) electrode as the counter electrode and Ag/AgCl reference electrode, respectively, was used to measure the photoelectrochemical performances of the samples under AM 1.5 illumination in 1 M KOH electrolyte. Photocurrent density was measured based on the linear sweep voltammetry method by using a potential range from −0.5 to 0.7 V at a scan rate of 2 mV s⁻¹. All potentials were converted to the reversible hydrogen electrode (RHE) using the following equation: $E_{\text{RHE}} = 0.210 + E_{\text{Ag/AgCl}} + 0.059 \, \text{pH}$, where $E_{\text{Ag/AgCl}}$ is the experimentally measured potential. The incident photocurrent conversion efficiency measurements were carried out in the wavelength range from 300 to 700 nm at the fixed potential of 1.23 V_RHE and in the 1 M KOH electrolyte. The EIS data were obtained at 1.23 V_RHE in the frequency range from 100 kHz to 0.1 Hz with a 369 nm L.E.D light source. The IMPS analysis was conducted in the range from 1.0 to 1.7 V_RHE under 452 nm light illumination at an intensity of 10 mW/cm².

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c04028.

Cross-sectional SEM image of 600 nm of iron film and Fe₂O₃ NF on FTO glass; TEM image of Sn/H; high-resolution SEM image of MSnO₂-H; high-magnification TEM image of MSnO₂-H and the corresponding EDS mapping of Sn/Fe, Sn, and Fe; XPS spectra of Sn 3d scans, O 1s scans for the P-H and MSnO₂-H; surface atomic composition obtained from XPS analysis for MSnO₂-H and P-H; VBM of P-H (1.20 eV) and MSnO₂-H (1.55 eV); calculated Sn ion concentration of MSnO₂-H from the EDS measurement; chronoamperometry measurements of P-H and MSnO₂-H at 1.50 V_RHE under different wavelengths; typical IMPS response for P-H and MSnO₂-H respectively, as a function of applied potential and the rate constants of electron−hole recombination ($K_e$) and hole transfer ($K_h$) for P-H and MSnO₂-H respectively, as a function of applied potential; IMPS response for SnO₂-H, as a function of applied potential, charge transfer efficiency of SnO₂-H calculated from IMPS measurement, rate constants of electron−hole recombination ($K_e$), and hole transfer ($K_h$) for P-H and MSnO₂-H, respectively, as a function of applied potential; EIS fitting results of P-H, Sn-H, SnO₂-H, and MSnO₂-H (PDF)

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**Notes**

The authors declare no competing financial interest.

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