High-Throughput Screening and Surface Interrogation Studies of Au-Modified Hematite Photoanodes by Scanning Electrochemical Microscopy for Solar Water Splitting

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ABSTRACT: Au-modified hematite photoanode was screened for photoelectrochemical (PEC) water oxidation by the scanning electrochemical microscopy (SECM) technique with a scanning probe of the optical fiber for visible light irradiation of the photoanode substrate. The Au-modified hematite exhibited an enhancement in the photocurrent up to 3% (at. %), and the performance drop was observed with 4–10% (at. %) of Au modification. Subsequently, pristine and Au-modified hematite thin-film photoanodes were fabricated by the spin-coating method to confirm the results of SECM. The PEC response confirms that 3% (at. %) of Au is the optimum concentration to provide the best enhancement of PEC water oxidation with a ~6-fold increase compared to the pristine hematite sample. Direct Au oxidation, charge recombination, and strong light absorption by Au are responsible for the decrease in PEC performance when the Au percentage is above 3%. The pristine and Au-modified hematite materials were also characterized by scanning electron microscopy and X-ray photoelectron spectroscopy. Au was found to exist in the form of embedded metallic nanoparticles in the modified hematite. Mott–Schottky analysis of the bulk samples confirms an improvement in charge carrier density for the Au-modified hematite. Additionally, there was little plasmonic enhancement as evidenced by UV–vis spectroscopy, with a minimal contribution toward photoactivity. Surface interrogation SECM quantitatively probed the reactive surface states (RSSs) such as OH* formed on hematite and Au-modified hematite surfaces during water oxidation. The coverage of RSSs was found to increase with the substrate potential. The interrogated charge under the dark condition for the 3% Au-modified hematite sample is higher than the pristine hematite sample because of the enhanced electronic conductivity of the hematite film.

1. INTRODUCTION

Solar cells are the best example for the direct production of electricity by harvesting and converting solar energy to electric energy.1–3 Solar fuel generation through a photoelectrochemical (PEC) system provides promising applications in solar energy storage by harvesting and storing solar energy into chemical bonds.4–6 PEC water splitting has been studied intensively for sustainable solar hydrogen since the first demonstration of unassisted water splitting for hydrogen at a semiconductor electrode of TiO2.7–11 Many visible light-sensitive photocatalysts of metal oxides (e.g., BaLa4Ti4O15,12 and Co–BiVO4,13) have been investigated for solar energy-driven water splitting reactions because of their tunable band gap and visible light absorptivity and reasonable stability under harsh conditions in a PEC cell.14–17 n-Type hematite (α-Fe2O3) is considered as an ideal photocatalytic material of choice for PEC water oxidation because of its good chemical stability, strong visible light absorption, and low cost.18–22 However, its poor conductivity and short hole-diffusion length are the major limiting factors that dictate the photoactivity of hematite. Several efforts of surface passivation,23–26 nanostructuring,27–30 heterojunction,31,32 and doping with higher conductive materials have been made to overcome these issues.31–37 Different doping materials have been utilized to enhance the photocatalytic efficiency of hematite. For example, Pt, Pd, Ta, Au, and Ag have been incorporated into the powdered and thin-film hematite to suppress the charge recombination and to promote the charge-transfer processes of photogenerated electrons and holes at the photocatalyst/electrolyte interfaces.38–40 In our previous studies,41,42 the Au nanoparticles (NPs) and Au nanorods (NRs) have been successfully incorporated in hematite thin films to improve the photoactivity for solar water splitting. It was discovered that Au NPs deposited underneath the hematite film increased the light absorption cross-section in the visible region, because of their localized surface plasmon resonance (LSPR), and charge collection from hematite thereby leading to maximizing the photogenerated charge carriers in the film for the enhanced water-splitting reaction. Recent literature studies on Au-decorated hematite photoanode for solar water splitting are summarized in Table 1. Among these representative works, the major contributions

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Table 1. Recent Literature on Au Decorated Hematite Photoanode for Solar Water Splitting

| #  | Au preparation method                                      | PEC performance              | the major contribution of Au                                           | reference                        |
|----|-----------------------------------------------------------|------------------------------|------------------------------------------------------------------------|----------------------------------|
| 1  | nanosphere lithography (Au nanohole array pattern)        | \( I_{\text{photo}} = 0.92 \text{ mA cm}^{-2} \) at 1.23 V vs RHE in 1 M NaOH | absorption enhancement through LSPR                                    | Nat. Commun.\(^{50}\)          |
| 2  | sputtered (10% Au–90% Ag) as a reflector                  | \( I_{\text{photo}} = 1.44 \text{ mA cm}^{-2} \) at 1.23 V vs RHE in 1 M NaOH (pH = 13.6) | absorption enhancement through LSPR                                    | Adv. Mater.\(^{50}\)          |
| 3  | spin-coated (Au–Pt core–shell NPs)                        | \( I_{\text{photo}} = 0.83 \text{ mA cm}^{-2} \) at 1.23 V vs RHE in 0.5 M NaSO_4 (pH = 7) | efficient electron and hole pair separation                            | Dalton Trans.\(^{51}\)        |
| 4  | immersed in 5 mM HAuCl_4 solution by "top-down" method    | \( I_{\text{photo}} = 3.2 \text{ mA cm}^{-2} \) at 1.23 V vs RHE in 1 M KOH (pH = 13.6) | efficient electron and hole pair separation                            | Nano Energy\(^{52}\)          |
| 5  | embedded Au in porous hematite by pulse reverse electrodeposition | \( I_{\text{photo}} = 1.025 \text{ mA cm}^{-2} \) at 1.23 V vs RHE in 1 M NaOH | enhanced charge transport and absorption enhancement through LSPR     | Chem. Commun.\(^{39}\)        |
| 6  | annealing and evaporation of thin Au films                 | \( I_{\text{photo}} = 0.5 \text{ mA cm}^{-2} \) at 1.23 V vs RHE in 1 M NaOH | absorption enhancement through LSPR                                    | J. Mater. Chem. C\(^{53}\)    |
| 7  | Au NPs on hematite by a co-precipitation technique         | \( I_{\text{photo}} = 0.21 \text{ mA cm}^{-2} \) at 1.23 V vs RHE in 1 M NaOH | Fermi level equilibration and surface catalysis                        | J. Mater. Res.\(^{54}\)       |
| 8  | solution chemistry decoration of Au NPs onto hematite nanoflake | \( I_{\text{photo}} = 1.0 \text{ mA cm}^{-2} \) at 1.23 V vs RHE in 1 M NaOH | absorption enhancement through LSPR                                    | ChemSusChem\(^{55}\)          |
| 9  | dropwise deposition of Au NPs on hematite NRs array        | \( I_{\text{photo}} = 0.13 \text{ mA cm}^{-2} \) at 1.23 V vs RHE in 0.5 M NaSO_4 | absorption enhancement through LSPR                                    | Nanoscale\(^{56}\)           |
| 10 | sandwiched Au/Zr–Fe/Au structure by electrodeposition on ITO | \( I_{\text{photo}} = 0.3 \text{ mA cm}^{-2} \) at 1.23 V vs RHE in 1 M NaOH (pH = 14) | improved film conductivity                                           | J. Power Sources\(^{57}\)     |
| 11 | drop-casting of presynthesized Au NPs on Ti–Fe_2O_3 NRs    | \( I_{\text{photo}} = 1.5 \text{ mA cm}^{-2} \) at 1.23 V vs RHE in 1 M NaOH (pH = 13.6) | enhancing energy transfer and relaxed Fermi-level pinning by surface passivation | ChemSusChem\(^{58}\)         |
| 12 | spin-coating of HAuCl_4 on electron beam evaporated hematite | \( I_{\text{photo}} = 1.75 \text{ mA cm}^{-2} \) at 1.23 V vs RHE in 1 M NaOH (pH = 13.6) | plasmonic and facilitating surface charge transfer                     | ChemCatChem\(^{59}\)         |
| 13 | chemical spray pyrolysis (α-Fe_2O_3/Au/ZnO)               | \( I_{\text{photo}} = 0.05 \text{ mA cm}^{-2} \) at 1.23 V vs RHE in 1 M NaOH | improved film conductivity, fast charge transfer kinetics, and absorption enhancement through LSPR | Sol. Energy Mater. Sol. Cells\(^{60}\) |

\( I_{\text{photo}} \) is the photocurrent density in mA cm\(^{-2}\); RHE represents reversible hydrogen electrode; LSPR is localized surface plasmon resonance.

Figure 1. (A) Schematic showing the design of a photoactive hematite array incorporated with Au; SECM photocurrent image of the Au-modified hematite array on the Ti substrate obtained at substrate potentials of 0.3 (B) and 0.5 V (C) vs Ag/AgCl. The SECM image was obtained by scanning the array with a 200 μm (in diam.) optical fiber illuminated with a xenon lamp; and (D) statistical averaging analysis of the PEC current dependence on Au percentage, revealing the PEC performance increment for 1–3% of Au modification followed by gradual decrease for 4–10% of Au modification.

from Au nanostructures to the enhancement of photoactivity of hematite include (1) efficient charge separation, (2) improved bulk charge transport, (3) plasmonic light absorption enhancement, and (4) surface catalytic activity of Au. Although few studies have revealed the optimum percentage for Au in hematite photocatalysts, it is not clear what forms of Au (e.g., NP or atomic doping) and percentage of Au are optimum for enhancing hematite PEC activities. It is also not yet clear how the optical configuration (e.g., surface vs bottom modification configurations) of Au modification affects the PEC activities of a photoelectrode. One of the best approaches to identify the concentration effects of such metallic nanostructures on a catalyst is to utilize a rapid screening and optimizing technique called scanning electrochemical microscopy (SECM) with a
scanning optical fiber. In this operation mode of SECM technique, an optical fiber is used to illuminate a photocatalytic array, while photocurrent response of the array is recorded to provide the spatial distribution of its PEC activity.\textsuperscript{13,14,44} Jang et al.\textsuperscript{45} studied the photocatalytic activity of the Ag–hematite nanocomposite by SECM for water oxidation with different compositions of Ag and Fe. Such composite hematite was further doped with Sn and found the optimum condition for water oxidation with 50–50% Ag–Fe and 2% Sn. In the follow-up study,\textsuperscript{40} Ta-doped hematite was investigated by SECM, yielding ~32 times increment in photocurrent by 2% of Ta doping against the pristine sample. The preferential growth of Ta along the (001) facet of hematite greatly improved the conductivity of the film thereby enhancing the photocactivity. Recently, Conzuelo and co-workers\textsuperscript{46} utilized the SECM technique to provide information about the local photocurrent generated at photocatalytic surfaces of TiO$_2$ and BiVO$_4$ photoanodes with X, Y grid increment of 20 $\mu$m. SECM has also been used to investigate the plasmonic enhancement for PEC reactions. For example, the enhancement mechanism of photo-induced hot carriers and thermal effect by light illumination can be isolated and studied independently by the SECM technique.\textsuperscript{7} Zhou et al.\textsuperscript{36} studied TiO$_2$ photoanodes with subsurface Al nanodimers under different excitation directions and light polarization angles to investigate the impact on photoanode reactions.

Herein, we present the screening of the photocatalytic Au-modified hematite for solar water oxidation by SECM with a scanning optical fiber. The SECM performance of photocatalytic spots prepared with PL dispenser method is compared with that of thin-film electrodes to reveal the effects of Au on PEC performance of hematite. The surface interrogation mode of scanning electrochemical spectroscopy (SI-SECM) is used to quantitatively measure the reactive surface states (RSSs) such as OH$^-$ formed on hematite surfaces. This study suggested that Au exists in the form of well-distributed and embedded NPs into the hematite film. Au modification significantly contributed to the electronic conductivity of the hematite film with PEC enhancement obtained at <3.0 at. % of Au. These findings are well supported by surface characterization techniques and the capacitance measurements.

### 2. RESULTS AND DISCUSSION

2.1. SECM for Searching Optimal Au Concentration of the Hematite Photoanode. The SECM screening technique with a 200 $\mu$m (in diam.) optical fiber is used to study the localized PEC activity of the photocatalyst array. This screening technique is briefly described in the experimental section. More details of this screening technique are described in recent publications.\textsuperscript{13,14,44} Figure 1A shows the array design for studying Au effects on PEC of hematite spots produced by the PL dispensing technique as described in the experimental section. The top three rows and the bottom three rows of the array were control spots containing only hematite in the absence of Au. This allows one to level the substrate and minimize the random errors caused by the PL dispensing technique from droplet to droplet. The middle four rows are four replicates of the Au-modified spots with Au concentration varying from 1 to 10% from left to right in order to have an average PEC response without reproducibility concerns of the dispensing technique. Figure 1B shows the two-dimensional SECM photocurrent images of Au-modified hematite arrays prepared on the Ti substrate with varying Au percentages at the substrate potential equal to 0.3 V versus Ag/AgCl. The top and bottom three row control spots show identical photocurrent responses as reference, while the middle four rows show the variance of photocurrent with 1–10% of Au modification. The raster scan of the array with the optical fiber under white light illumination from a xenon lamp produces photocurrent response at each location at a substrate potential of 0.3 V (Figure 1C) and 0.5 V (Figure 1D) versus Ag/AgCl. These SECM photocurrent images were obtained at a step size of 100 $\mu$m in XY directions and a parking distance of 100 $\mu$m from the fiber to the sample surface. These SECM results clearly indicate that an improved photocurrent can be obtained with 1–3% of Au modification. The modification has a negative effect on the photocurrent for 4–10% of Au. It should be noted that background current in the SECM images is greatly eliminated at a higher potential applied (0.5 V vs Ag/AgCl) as shown in Figure 1C because of a higher PEC current than that at 0.3 V. We also obtained more pronounced Au effects at the large substrate potential because of high PEC current response in the more positive potential bias. As shown in Figure 1D, the average current from pristine and Au-modified hematite spots in their respective columns are plotted against Au percentage. It clearly shows that the average photocurrent response of hematite is enhanced by the Au percentage until 3% Au. This result obtained on the Ti substrate is consistent with the ones obtained on fluorine-doped tin oxide (FTO) substrates, agreeing that 3% of Au modification provides the best PEC enhancement for the hematite photoanode. In order to validate the results obtained from arrays produced by the droplet dispensing technique, thin-film samples containing 1, 3, 5, and 10% of Au are also prepared to compare with the SECM study.

2.2. Absorption Spectra and Morphology of Au-Modified Hematite Thin Films. Thin-film hematite samples were prepared directly from ethylene glycol (EG) solution containing Fe(NO$_3$)$_3$ and HAuCl$_4$. The spin-coated film of Fe(NO$_3$)$_3$ decomposed to hematite and NO$_2$ and oxygen in the air at elevated temperature. UV–vis absorption spectroscopy was performed for the spin-coated samples as shown in Figure 2. The absorption of Au-modified samples decreases in the wavelength region of 300–550 nm, where the major contribution for absorption in this wavelength range is hematite. The relative hematite ratio decreases as Au percentage rises. From 550 to 800 nm, the absorption slightly increases with the amount of Au because of the increase in the absorption of Au NPs, but this plasmon absorption above 3%
provides only a small light absorption increase, that cannot support the pronounced PEC enhancement obtained from our SECM study. Thus, plasmonic enhancement by Au has a minimal contribution to the photoactivity of hematite for water oxidation. Accurate thickness control of the sample fabrication would bring more precise absorption comparison.

To understand how Au modification on the hematite film affects the PEC performance and its spatial distribution in the hematite film, topside and cross-sectional scanning electron microscopy (SEM) analysis was performed. Figure 3 shows the SEM images obtained for the Au-incorporated hematite array for 1, 3, 5, and 10% of Au concentration. These SEM images suggest that Au exists as NPs and are evenly distributed in hematite film with an average particle size of ∼20 nm. EG serves as a reducing agent of HAuCl4 to produce Au NPs during the thermal annealing process of the hematite film. The Au particles number increases with the increase of Au percentage and reaches a maximum at 10% Au concentration. As stated earlier, the light absorption increase shown in Figure 2 from Au NPs near the wavelength region of 500−800 nm cannot help justify the pronounced PEC performance enhancement by 3% Au, yet increase in light absorption and scattering in this region by densely packed Au NPs can decrease the light absorption of hematite to decrease its PEC activity. Figure 4 shows the cross-sectional SEM image of spin-coated Au-incorporated hematite thin film. The average Au−hematite film thickness is about 100 nm on a ∼270 nm thickness FTO substrate, as shown in the figure.

2.3. X-ray Photoelectron Spectroscopy Characterization of Au-Modified Hematite Thin Film. To understand the chemical identity of Au in the hematite sample, an X-ray photoelectron spectroscopy (XPS) analysis was performed for pristine and optimized 3% Au-modified Fe2O3 thin-film samples prepared on FTO by the spin coating method. Figure 5 shows the survey spectra of pristine and 3% Au-incorporated Fe2O3 samples. Survey spectra of both the samples reveal XPS lines of Sn, which has been reported previously by several researchers for the Fe2O3 films prepared on FTO (F:SnO2). Sn diffuses from FTO substrate upon annealing the samples at temperatures ≥500 °C. The elemental compositions obtained for Fe 2p, O 1s, Sn 3d, and Au 4f lines are listed in Table 2. The relative concentration of Au on the surface of hematite is only 1.3% compare to Fe, which is due to the presence of scattered Au 20−30 nm size NPs as observed from SEM study previously (Figure 3). Figure 6 shows the high-resolution XPS spectra of the Fe 2p, O 1s, Sn 3d, and Au 4f lines for the 3% Au-modified hematite film. As shown in Figure 6A, the Fe 2p1/2 binding energy (BE) peak at 709.91 ± 0.1 eV confirms the +3-oxidation state of Fe and the formation of hematite (α-Fe2O3) phase. The deconvoluted O 1s peak demonstrates four types of oxygen species (Figure 6B). The O 1s (Fe−O) peak at ∼529.81 ± 0.1 eV originates from the Fe2O3 moiety. The peaks O 1s (O−Sn) at 531.01 eV is ascribed to Sn-oxide, which is formed due to the diffusion of Sn4+ ions to the hematite surface from FTO. The O 1s (O−C/ O−H) peak at 531.93 eV and minor O 1s (O−Si) peak at 533.04 eV are due to adsorbed carbonyl/hydroxyl groups and
surface impurity, respectively. The Sn 3d_{5/2} peak at 486.98 ± 0.1 eV and a spin–orbit splitting (Δ = 8.4 eV) of doublet lines for Sn 3d spectrum confirm the presence of Sn^{4+} state (Figure 6C). The BE of Au 4f_{7/2} peak at 83.97 ± 0.1 eV and spin–orbit splitting (Δ = 3.7 eV) of doublet lines for Au 4f confirms that gold exists in metallic NPs form on the surface of the hematite film (Figure 6D). The absence of any peak at 86 eV excludes the possibility of gold oxidation. As seen from Table 2, the Sn content in pristine and Au-incorporated hematite films is almost identical (~0.2 at. %). Hence, the PEC performances of both pristine and Au-incorporated hematite should not be affected by Sn.

2.4. PEC Characterization of Au-Modified Hematite Thin Film Photoanode Electrodes. Based on the above SECM study, it is conclusive to say that PEC performance enhancement is observed at low Au percentage while decrement in PEC performance is noticed when Au percentage exceeds 3% Au modification. To further understand the Au modification effects, a bulk thin film with the large area was prepared using the spin-coating method to obtain an improved understanding of the Au effect mechanism. Figure 7 shows the photocurrent–voltage (J−V) curves of pristine and Au-modified hematite thin-film photoanodes fabricated by the spin-coating method, under standard 1 sun illumination measured in 0.1 M NaOH. The 3% Au-modified hematite thin film exhibits remarkable net PEC response with ~6 folds increase in photocurrent density at 0 V versus Ag/AgCl (~1.0 V vs RHE) with respect to the pristine hematite electrode. Such improved performance can further be improved by controlling the film thickness. Furthermore, there is an oxidation peak at around 0 V versus Ag/AgCl under the dark condition for 5% and 10% Au, which is attributed to the oxidation of Au in direct contact with electrolyte. The high percentage of Au above 3% will form conductive channels through the hematite film to allow charge recombination, decreasing the photocurrent. Au NPs are separated from each other below 3% Au modification to provide direct electrochemical oxidation. Action spectra were recorded for both pristine and 3% Au-modified hematite films from 400 to 750 nm irradiation. No peak shift in the action spectra upon Au NP modification at 3% indicates no prominent plasmonic contribution through water oxidation, although the photocurrent suffers from stability issue particularly for Au modified film because of the corrosion effect of Au. Figure 8 presents the bar graph plotted at different applied potentials showing the comparison of dark and light currents for pristine and Au-modified hematite. At ~0.2 V versus Ag/AgCl, the net photocurrent density of 3% Au–hematite is 0.046 mA cm\(^{-2}\), which is about four times higher than that of pristine hematite. The net photocurrent density of 3% Au–hematite further increases to 0.075 mA cm\(^{-2}\) at 0 V versus Ag/AgCl, about 7-fold enhancement compared to the pristine hematite at the same potential. Moreover, the dark current of 5 and 10% Au–hematite samples increase dramatically at 0 V versus Ag/AgCl, which corresponds to the Au-oxidation peak as shown in Figure 8. It is apparent that the dark current increases significantly with higher Au percentage at 0, 0.2, and 0.5 V versus Ag/AgCl, which indicates the possible oxidation of Au NPs. Such photocurrent responses further confirm the optimum 3% of Au modification for enhancing the PEC activity of hematite. The discrepancy in the enhancement factors from SECM study and that of thin-film samples is attributed to how these samples are dried from droplets versus quick-drying through the spin coating and differences in the film thicknesses produced from these two methods. Overall we can conclude that the decrease of PEC performance above 3% Au is because of the increase in background current of direct Au-oxidation which also serves as a charge recombination center for photogenerated charges from hematite. Strong light absorption by Au can also contribute to the decrease in PEC performance when the hematite film is heavily loaded with Au.

2.5. Understanding the Carrier Density, Flat Band Potential, and Impedance of Au-Modified Hematite Photoanode. Capacitance measurements of pristine and Au-modified hematite thin-film samples were performed and presented as Mott–Schottky (M–S) plot (Figure 9). The flat
The flat band potential $E_{fb}$ of hematite photoanode in an electrochemical cell can be estimated by the intercept of the $\Gamma - S$ plot according to the following $\Gamma - S$ equation:

$$\frac{1}{C_{sc}^2} = \frac{2}{\epsilon_0 \epsilon A^2 N_D} \left( E - E_{fb} - \frac{k_b T}{\epsilon} \right)$$

(1)

where $C_{sc}$ is the space charge capacitance; $\epsilon$ is $1.602 \times 10^{-19}$ C; $\epsilon_0$ is the permittivity of free space; $N_D$ is the carrier density; $E$ is the applied potential in V; $k_b$ is the Boltzmann constant, and $T$ represents the temperature in K. The slope of the $\Gamma - S$ plot can be used to calculate $N_D$.

Table 3 summarizes the $E_{fb}$ and $N_D$ for pristine and Au-modified hematite under different percentage. The flat band potential of the Au-modified hematite in 0.1 M NaOH solution at an ac frequency of 1 kHz increases with Au percentage and reaches $-0.751$ V versus Ag/AgCl at 10% of Au, which is about 0.2 V negative compared to that of pristine hematite. The donor density estimated from the slope of the $\Gamma - S$ plot is increased significantly after Au modification and reaches about 3-fold at 10% Au ($1.64 \times 10^{21}$ cm$^{-3}$) as compared to the pristine hematite ($0.56 \times 10^{21}$ cm$^{-3}$). This suggests that the additional conductivity arises from the Au-modified hematite.

Electrochemical impedance spectroscopy (EIS) measurements were performed for pristine and Au-modified hematite samples under dark and standard 1 sun illumination conditions to obtain charge-transfer information, as shown by the Nyquist plots in Figure 10. An equivalent circuit, which consists of series resistance ($R_s$), charge transfer resistance ($R_{CT}$), and space charge capacitance ($C_{sc}$), was used to fit the experimental EIS data. Table 4 lists the EIS parameters obtained from the fittings. The notations D and L represent the dark and light conditions, respectively. The resistance of the electrolyte from the working electrode to the reference electrode, which reflected as $R_s$, are similar for all the samples ($\sim 370$ $\Omega$). The $R_{CT}$, which dictates the photocurrent response of photocatalysts, is highly dependent on the PEC efficiency of the electrode. As shown in Table 4, the $R_{CT}$ values are lower
under light irradiation conditions compared to the dark due to the photo-induced charge transfer. Furthermore, charge transfer resistance decreases with the increase of Au percentage, which indicates the increase of charge carriers in the film. Such phenomenon facilitates the charge transfer of holes to the donor species in the solution and suppresses the recombination of photogenerated electron−hole pairs, thus enhancing the photoactivity of hematite film for water oxidation.

2.6. Surface Active Species Characterization of Au Modified Hematite Photoanode. SI-SECM has been reported to be a promising tool to investigate RSSs of a variety of electrocatalysts and photocatalysts, such as hematite, W/Mo−BiVO₄, TiO₂, Ni₈, and MoS₂. An ultramicroelectrode with sharp tip, instead of optical fiber, is used as a second working electrode. RSSs produced in the electrocatalytic or photocatalytic processes can be quantified by a tip-generated titrant from a redox mediator in the electrolyte. This technique demonstrates selectivity to surface species, the capability to in-situ quantify for both surface coverage and reactivity of adsorbed RSSs, and usefulness to obtain spatially and temporally-resolved information. Kru-mov et al. adopted SI-SECM to study the RSSs formed on hematite during photocatalytic water oxidation. The surface coverage of RSSs was found to be a function of applied bias. SI-SECM measurements were conducted on the same SECM equipment as SECM study. The schematic of SI-SECM setup is shown in Figure 11. Hematite and the Au-modified hematite

Table 4. Summary of Experimental Fit Parameters Obtained by Fitting Nyquist Plots Using the Equivalent Circuit Shown in the Inset of Figure 10A

| sample  | Rₛ (Ω) | Rₛ (Ω) | Cₛ (μF) |
|---------|--------|--------|---------|
| pristine_D | 370    | 1.0000 × 10⁷ | 10      |
| pristine_L | 377    | 2.4609 × 10⁶  | 6.7     |
| 1% Au_D   | 370    | 2.0934 × 10⁶  | 11      |
| 1% Au_L   | 362    | 6.2022 × 10⁵  | 8.5     |
| 3% Au_D   | 370    | 1.4795 × 10⁶  | 11      |
| 3% Au_L   | 362    | 6.2006 × 10⁵  | 8.5     |
| 5% Au_D   | 373    | 4.4314 × 10⁵  | 12      |
| 5% Au_L   | 365    | 5.7888 × 10⁵  | 9.1     |
| 10% Au_D  | 378    | 8.6734 × 10⁵  | 12      |
| 10% Au_L  | 374    | 4.5776 × 10⁵  | 10      |

Figure 10. Nyquist plots of 1 (A), 3 (B), 5 (C), and 10 (D) Au-modified hematite thin films under dark conditions (black) and standard 1 sun irradiation (red).

Figure 11. (A) Schematic of the SI-SECM setup. Side (B) and top (C) view of the Pt disk microelectrode. (D) Schematic showing the two steps involved in the SI-SECM experiments.
substrate were assembled in a home-made SECM cell with 0.59 cm² of surface area exposed to the electrolyte. Pt wire and Ag/AgCl (sat. KCl) was used as counter and a reference electrode, respectively. A 10 μm (in diameter) Pt disk microelectrode sealed in a glass capillary (Figure 11B,C) was used as the primary working electrode and the photoactive substrates as the second working electrodes. All electrodes were immersed in 0.1 M borate buffer (pH 9.4) containing 2 mM K₃Fe(CN)₆. The photoactive substrate was irradiated by a halogen fiber illuminator at 1 sun irradiation. In the first step of SI-SECM experiment, the substrate was irradiated by the lamp under external bias to generate RSSs during water oxidation. The Pt tip was disconnected in this step. The second step involved bias applied on the Pt tip without bias potential and illumination at the substrate. The Pt tip-generated [Fe(CN)]⁴⁻ in the second step served as a titrant which quantitatively interrogated the RSSs on a substrate (Figure 11D).

After characterizing the photoactivity of pristine and Au-modified hematite samples, we correlated the photoactivity with the surface-active species by the SI-SECM technique. A chronoamperogram is presented in Figure 12 to illustrate the interrogation current under light illumination and the dark condition. During the water oxidation reaction of the substrate, it is believed that adsorbed OH• is generated. The OH• is able to oxidize Fe(CN)⁶³⁻ to Fe(CN)⁶⁴⁻. This surface state generation is highly depended on the external bias applied to the substrate. Thus, an external bias of 0.9, 1.0, 1.1, and 1.2 V versus Ag/AgCl was applied to the substrate with and without light illumination, and the reduction current at the Pt tip was collected as a function of time thereafter. The semilogarithmic plot of net interrogation currents is shown in Figure 12B,E for a series of measurements with an increase in external bias applied for PEC water oxidation. It is apparent to observe that the interrogation current from the Pt tip increases as the substrate is pushing further for water oxidation. In order to compare the surface interrogation from pristine and 3% Au-modified hematite more clearly, bar graphs were obtained showing the light and dark-generated surface coverage of RSSs calculated by integrating the plots of interrogation current versus time. The surface coverage of RSSs on both substrates increases as the higher potential is applied, as well as the surface coverage of net photogenerated RSSs. This trend is consistent with the increase of net substrate current density obtained from CVs. It can be observed that the surface coverage charge of pristine hematite increases from 15 nC (at 0.9 V) to 35 nC (at 1.2 V) under light illumination. For the 3% Au-modified hematite sample, it increases from 20 nC (at 0.9 V) to 47 nC (at 1.2 V) under the same condition. However, the surface coverage of charge under dark conditions increases more rapidly for the Au-modified hematite than that of pristine hematite. The difference of the surface charge under the dark condition is 10 nC from 0.9 to 1.2 V for pristine hematite, whereas it increased to 20 nC for the Au-modified hematite under the same potential window. The rapid increase of interrogation current under dark conditions caused the lower net surface coverage for the Au-modified hematite sample. This also agrees with the rapid increase of dark current under high external potential applied during the PEC measurements.

### 3. CONCLUSIONS

In summary, the SECM technique can be used to efficiently screen Au modification in the hematite photocatalyst for solar water splitting. 3% Au modification provides hematite the best PEC performance, which increases with <3% Au modification but eventually decreases when the Au percentage exceeds 3% due to the charge recombination. SEM images and XPS analysis suggest that Au exists in the form of NPs without changing the electronic structure of the hematite as they are...
well distributed throughout the ~100 nm-thick hematite thin film. A 3% Au-modified hematite photoanode shows ~6-fold increase in its photocurrent density at 0 V versus Ag/AgCl (~1.0 V vs RHE) with a desirable cathodic shift in the flat band potential by 200 mV. With >5% Au modification, Au was oxidized at 0 V versus Ag/AgCl, consequently reducing the photoactivity of the hematite film. The M–S analysis revealed that Au-modification contributes to the electronic conductivity of hematite film. EIS analysis suggests significant improvement in the charge transfer resistance for Au-modified samples. The SI-SECM measurements revealed that RSSs (OH\textsuperscript{−}) generation is correlated to the external bias applied during water oxidation. The dark interrogation current increased more rapidly for Au-modified hematite samples, which agreed with the PEC measurements. Hence, the overall enhancement in water splitting performance is attributed to the electronic conductivity as a significant contributing factor and improved charge separation by embedded Au NPs in the hematite. The enhanced PEC performance cannot be justified by the change of the absorption spectrum of the hematite upon Au modification. Therefore, we conclude that there is no plasmonic effect in the present form of Au modification with 20 nm NPs throughout the film to benefit the light absorption of the hematite electrode by plasmon resonance. Au corrosion and charge recombination may hinder the PEC performance of hematite heavily modified with Au.

4. MATERIALS AND METHODS

4.1. Materials. Iron(III) nitrate nonahydrate (Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O) and EG (HOCH\textsubscript{2}CH\textsubscript{2}OH, 99+%) (Acros Organics), hydrogen tetrachloroaurate(III) hydrate (HAuCl\textsubscript{4}·9H\textsubscript{2}O) and EG (HOCH\textsubscript{2}CH\textsubscript{2}OH, 99.9%-Au, Strem Chemicals), sodium hydroxide (Ward Scientific) were used as received without further purification. Deionized water with resistivity > 18 M\textOmega cm was used for solution preparation. Titanium (0.05 cm thick, Colorado Concept Coatings) and FTO (15–20 Ω cm\textsuperscript{−1}, Pilkington, Toledo, OH) in 1 in x 1 in were used for both SECM studies and preparing thin-film photoanodes for PEC measurements.

4.2. SECM Screening of the 10 × 10 Photocatalyst Array Spots. A 10 × 10 array of Au-modified hematite photocatalytic spots was prepared using a method described in our previous work.\textsuperscript{13} Briefly, 0.1 M Fe(NO\textsubscript{3})\textsubscript{3} and 0.01 M HAuCl\textsubscript{4} solution was prepared in EG and filtered using a 0.450 μm polytetrafluoroethylene syringe filter before dispensing. A pico-liter dispenser (Austin, TX) was used to dispense the 10 × 10 array spots on a pre-cleaned Ti substrate with top and bottom three rows to be pristine Fe(NO\textsubscript{3})\textsubscript{3} and middle four rows to be Au mixed spots. The concentration of Au was varied from 1 to 10 droplets for the four rows in the middle to provide 1–10% of Au (atomic ratio) in hematite. After obtaining the array, the dispersed droplets of individual components (i.e., Fe, Au, and EG) were allowed to mix on a shaker at 500 rpm for 30 min and then dried at 40 °C on a hot plate for 2 h. Then the dried array sample was subsequently annealed in air at 500 °C for 2 h, which was then converted to oxide. A CHI 920D scanning electrochemical microscope (CH Instruments, Inc., Austin, TX) was used for PEC measurements of the array samples.\textsuperscript{13,14,44} A home-made Teflon electrochemical cell was used for SECM measurement. The Ti substrate coated with hematite array was attached to the bottom of the Teflon cell as a working electrode. A Ag/AgCl reference electrode saturated with KCl and a Pt wire counter electrodes were arranged inside the home-made cell to provide sufficient space to accommodate the scanning optical fiber in X–Y directions. The photocatalytic activity of the array of spots was tested under white light illumination via the optical fiber, which moved in X–Y direction with the help of programmed piezo-positioner/controller.

A 0.1 M NaOH solution was used as an electrolyte. As the fiber moves over to a photocatalytic spot, PEC reaction at the hematite spot produces anodic photocurrent to be detected by the substrate electrode. The cumulative current at every position of the array was reconstructed to show as 3D photocurrent map to illustrate PEC activities of the array.

4.3. Fabrication of Au-Modified Hematite Thin-Film Photoelectrode. Pristine and Au-modified hematite thin-film electrodes were prepared using the spin-coating method. The spin coating was conducted on a Laurell 650mz Spinner (Laurell Technologies). The spin speeds were 400 rpm for 5 s followed by 2500 rpm for 30 s for each layer. Each layer was dried at 60 °C on a hot plate before coating the next layer. The 20 layers of pristine and Au-modified hematite films were coated onto pre-cleaned FTO substrates to obtain desired film thickness. The coated samples were then annealed at 500 °C for 2 h at a heating rate of 2 °C/min from room temperature in the air in a tube furnace. Hematite films modified with 0, 1, 3, 5, and 10% (at. %) Au were prepared using the spin coating method and were tested for PEC measurement.

4.4. Characterization of Materials and Electrodes. The hematite electrodes were characterized with a JEOL 700 scanning electron microscope. The accelerating voltage for SEM was set to 20 kV. The UV–vis spectra were obtained using an HP 8452A diode array UV–vis spectrophotometer, recording spectra over the range 300–800 nm with a resolution of 2 nm. The chemical state and surface composition of the freshly-synthesized pristine and Au-modified iron oxide samples were examined by XPS on a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K\textsubscript{α} X-ray source (hv = 1486.6 eV) under ultra-high vacuum conditions (at a base pressure of <8 × 10\textsuperscript{−10} Torr). The survey spectra were obtained in the BE range of 1200–0 eV at room temperature with an analyzer pass energy of 160 eV and an energy step size of 1 eV. High-resolution spectra were obtained with a pass energy of 20 eV and a step size of 0.1 eV. XPS data analysis was performed using the XPS Peak-fit program with Shirley background subtraction and an iterative least-squares optimization algorithm. The adventitious hydrocarbon peak (C 1s line at 284.8 eV) was used as an internal standard to calibrate the binding energies of high-resolution XPS spectra. Deconvolution of the C 1s and O 1s peaks was performed according to their chemical environments. The relative sensitivity factors (RSF) from Kratos library were used to obtain the relative concentration of the following elements: Sn 3d (RSF = 7.875), Au 4f (RSF = 6.25), Fe 3d (RSF = 2.957), O 1s (RSF = 0.78), and C 1s (RSF = 0.278). All PEC measurements were performed by a CHI 760C bipotentiostat (CH Instruments Inc., Austin, TX) in a three-electrode configuration. A three-neck quartz photoreactor with a planar window was used to accommodate the thin-film-coated FTO working electrode, platinum wire counter electrode, and an Ag/AgCl (saturated with KCl) reference electrode. A standard simulated 1 sun (100 mW/cm\textsuperscript{2}) irradiation was provided by a solar simulator using a xenon lamp source (Oriel AM 1.5 filtered, Newport). The M–S measurement was carried out in the dark at an ac frequency.
of 1 kHz by sweeping a dc potential from −0.5 to 0.5 V versus Ag/AgCl.

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**Notes**
The authors declare no competing financial interest.

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