
Moran Gross Koren, Hen Dotan, and Avner Rothschild*

Department of Materials Science and Engineering, Technion – Israel Institute of Technology, Haifa, Israel

ABSTRACT: Hematite (α-Fe₂O₃) photoanodes are widely studied as candidates for solar water splitting. Recent reports suggest that the photocurrent of thin film hematite photoanodes could be enhanced by using gold nanoparticles (Au NPs) that give rise to plasmonic light trapping close to the hematite/electrolyte interface. This work examines the effects of Au NPs on the optical, electrochemical (in the dark) and photoelectrochemical (under illumination) properties of thin film (20 to 150 nm thick) Ti-doped hematite photoanodes. Au NPs were obtained by annealing 2.5 to 15 nm thick Au layers which led to dewetting and formation of 15 to 150 nm Au NPs, respectively. Au NPs on glass substrates displayed broad and shallow plasmonic peaks in the visible range, commensurate with the size distribution of the Au NPs. Two photoanode configurations with Au NPs decorating the surface or embedded under the hematite films were examined. Photoanodes of the first configuration displayed smaller photocurrents compared to counterpart photoanodes without Au NPs, most likely due to wasted absorption by the Au NPs and scattering into inactive parts of the device. The Au NPs underwent a redox reaction (Au + 3OH− ⇌ Au(OH)₃ + 3e⁻) that gave rise to spurious contribution to the current. In addition, they also reduced the onset potential of water oxidation by ~200 mV due to an electrocatalytic effect. Photoanodes of the second configuration displayed considerable enhancement (up to 92%) in absorption with respect to counterpart photoanodes without Au NPs. The enhancement was broadband, as expected for Mie scattering. The plasmonic resonances in their absorption spectra were red-shifted to wavelengths above the hematite absorption edge (600 nm), therefore no plasmonic peaks were observed in the photocurrent action (IPCE) spectra. Small (<18%) enhancement in the plateau photocurrent (at 1.53 V_RHE) was observed, in some cases, whereas in other cases the photocurrent was smaller than that of counterpart photoanodes without Au NPs. The photocurrent enhancement was considerably higher close to the onset potential, reaching up to 124% at 1.23 V_RHE, but the photocurrents were quite low (<0.5 mA/cm²) at these low potentials. No obvious correlation was observed between the absorption and photocurrent gains in photoanodes with different hematite film thicknesses and Au NP sizes, except for 4 photoanodes (out of 14 specimens that were examined) with hematite film thickness of 75 nm. Therefore, we conclude that the photocurrent enhancement observed in our hematite photoanodes with embedded Au NPs was largely due to electrochemical effects rather than optical ones. This study highlights the intricate nature of several effects, both optical and electrochemical, of the Au NPs on hematite photoanodes, which come together to produce different contributions to the photocurrent. Depending on the device structure, some effects may enhance the water photo-oxidation current but other ones may not, and some effects may even suppress it. Therefore, careful design and optimization must be carried out in order to take advantage of the beneficial effects and mitigate the deleterious ones.

INTRODUCTION

Iron oxide (α-Fe₂O₃, hematite) is a promising photoanode candidate for solar water splitting. It is an abundant material with a unique combination of properties that are highly advantageous for water photo-oxidation: stability in alkaline solutions, high catalytic activity for water oxidation, and favorable band gap (2.1 eV) for sunlight harvesting. However, it is also known for having short lifetime of photo-generated charge carriers that gives rise to very short (few nanometers) diffusion length of minority charge carriers, that is holes. Consequently, under illumination the excess charge carriers can be collected only from a very short distance from the surface, whereas charge carriers generated deeper within the hematite layer are lost to nonradiative recombination. The collection length of photo-generated carriers in thin film hematite photoanodes produced by PLD or ALD was reported to be about 20 nm. Unlike the short collection length, the optical absorption length in hematite is much longer, about a micron. Thus, on one hand thick (~1 μm) hematite layers are needed for efficient light harvesting, but on the other hand most of the light is absorbed far away from the surface in regions where nonradiative charge recombination prevails.

Two approaches are being pursued to overcome this dilemma. One approach employs mesoporous thick layers wherein the path length for charge transport to the surface is much shorter than the optical path length through the layer. Essentially, this approach aims to orthogonalize the charge transport and optical path lengths. This requires mesoporous structures that often gives rise to deleterious effects such as enhanced surface recombination and internal shunts. The other approach employs compact (non-porous) thin films that are sensitized for efficient...
light harvesting by employing different photon management schemes that aim to trap the light in films much thinner than the light absorption length. Because of their simple design and the ability to tailor the light intensity profile in subwavelength dimensions, two of the most attractive light trapping schemes are based on resonance or plasmonic effects. This work addresses the latter one.

The plasmonic effect can potentially enhance light absorption in thin film hematite photoanodes by capturing the incident light and localizing it close to metal nanoparticles (NPs) decorating the photoanode or embedded within it. There are several ways in which metal NPs can trap the light, but only two of them: scattering and excitation of localized surface plasmons, are relevant to this study. In the scattering mechanism the incident light is scattered by the metal NPs into the photoanode. The higher the refractive index of the photoanode the stronger the light scatters into it. Hematite has a large refractive index (2.5 < n < 3.1 at wavelengths between 300 and 600 nm) which is beneficial to promote this effect. The scattering cross section of metal NPs is much larger than their geometrical cross section area, therefore small NPs can give rise to high angle scattering. In the second mechanism, the excitation of localized surface plasmons causes enhancement of the electrical field around the NP, thereby enhancing the absorption in the surrounding medium, that is the photoanode.

Various factors influence the resonance frequency of the plasmonic peak: the composition, size and shape of the NP, and the dielectric constant of the environment surrounding it. These factors can be tuned in order to tailor the plasmonic peak as desired to a favorable wavelengths where the absorption spectrum of the photoanode overlaps the solar spectrum. The metal NPs should not absorb the light by themselves but rather trap it in their vicinity in a way that enhances the absorption in the photoanode. Self-absorption by the metal NPs is a wasted loss that should be avoided. In addition, the metallic NPs should not promote charge recombination and they should be stable in the electrolyte solution under pH and potential conditions in which the photoanode operates.

Au NPs are considered as good candidates to explore plasmonic effects in hematite photoanodes. Encouraging results demonstrating enhanced absorption in hematite thin films decorated with Au NPs were reported. Small enhancement in the photocurrent was observed, mostly in the region of the plasmonic frequency, but the photocurrent gain was much smaller than the optical gain in light absorption. Moreover, the root cause underlying the photocurrent gain remains elusive and it is not clear whether it is due to optical effects or perhaps other effects such as electrocatalysis or redox reactions induced by the Au NPs. Indeed, some unusual results were reported in previous studies on hematite photoanodes decorated with Au NPs that are at odds with the expected plasmonic effect. For instance, some studies the photocurrent gain is potential-dependent, and in some reports it extends beyond the hematite absorption edge. Another noteworthy observation is that the photocurrent gain induced by the Au NPs was substantial only in cases where the photocurrent of the pristine hematite photoanodes was very low (below 0.1 mA/cm²) in the first place whereas high-performance hematite photoanodes displayed negligible gain upon sensitization with Au NPs. These observations cast serious questions regarding the root cause of the effect of Au NPs on the photocurrent and whether they can improve high-performance hematite photoanodes. This work investigates these questions, focusing on the first one.

Our guideline was to examine the correlation between the optical gain and the photocurrent gain, considering also non-optical effects that could possibly influence the photocurrent, such as electrocatalysis or redox side reactions. Our strategy was to prepare a series of specimens with and without Au NPs, with different Au NPs size distributions and different hematite film thicknesses, measure their optical and photoelectrochemical properties and carefully examine the correlation between these properties. The photoanodes were made of hematite thin films that were deposited by pulsed laser deposition (PLD) from a 1 cation% Ti-doped Fe₂O₃ target on FTO-coated glass substrates. This provides high reproducibility and ability to tune the hematite film thickness simply by controlling the number of laser pulses shot at the target. The hematite films were decorated with Au NPs produced by dewetting of Au thin films that were deposited either before or after the deposition of the hematite films in order to place the NPs below or above the hematite films, respectively. This method is simple, reproducible and it provides uniform coverage over large area. The size distribution of the Au NPs depends on the initial thickness of the Au layer and the annealing conditions of the dewetting process, providing handles to tailor their optical properties. All in all, we reproducibly controlled the placement of the Au NPs below or above the hematite films, their size distribution and the hematite film thickness. This enabled tailoring the optical and photoelectrochemical properties with minimal spurious side effects because the morphology, microstructure and chemical composition of the photoanodes remained the same. This is the key for a systematic investigation of the correlation between optical and photoelectrochemical properties.

**EXPERIMENTAL SECTION**

**Photoanode preparation**

Au NP decoration was obtained by evaporation of thin Au films with four different thicknesses: 2.5, 5, 10 and 15 nm, onto the samples followed by annealing (in air) 6 h at 600°C in order to induce dewetting of the Au films. The Au films were deposited by electron beam evaporation (Airco Temescal BJD 1800) at ambient temperature at deposition rates of 0.5 Å/s for the 2.5 and 5 nm thick Au films and 1 Å/s for the 10 and 15 nm thick ones. The hematite films
were deposited by PLD before or after the Au deposition and annealing, thereby producing Au NPs embedded above or below the hematite films, respectively. The films were deposited from a 1 cation% Ti-doped Fe₂O₃ target on fluorinated tin oxide (FTO) coated soda-lime glass substrates (TEC 15, Pilkington, Tokyo, Japan). The deposition conditions and substrate cleaning procedure followed our standard PLD process, as described elsewhere.²⁹ The deposition rate was ~0.76 Å/pulse, determined by ex-situ cross section TEM measurements.

**Optical and photoelectrochemical measurements**

Optical transmission and reflection measurements were carried out using a spectrophotometer (Cary 5000 UV-Vis-NIR spectrophotometer, Agilent, USA) equipped with an integration sphere. The absorbance was calculated from the transmittance (T) and reflectance (R) spectra, A(λ) = 100% - T(λ) - R(λ). Photoelectrochemical measurements were carried out with a potentiostat (SP200 potentiostat, Zennium, USA) connected to a potentiostat (SP200 potentiostat, Bio-Logic, France) using the three electrode configuration with Ag/AgCl (in saturated KCl solution) reference electrode and platinum wire counter electrode, using the same electrochemical cell (so-called the “cappuccino cell”) as reported elsewhere.²⁹ The measurements were carried out in 1 M NaOH solution in deionized water (pH = 13.6), in the dark or under illumination with a solar simulator (Model 10500 Low Cost Solar Simulator, Abet Technologies, USA). The irradiance spectrum of the solar simulator is shown in Figure S1 (Supporting Information). The light intensity was tuned to 100 mW/cm² at the position of the photoanode using a calibrated dye solar cell (AK-300 Dye-Sensitized Reference Cell, Konica Minolta, Japan). The measurements were performed with front illumination from the solution side through a 0.28 cm² mask that defines the aperture area of the photoanode as well as the area in contact with the electrolyte solution.

Incident photon-to-current efficiency (IPCE) measurements were carried out by comparing the photocurrent of the photoanode, measured at a certain wavelength (λ) and potential (U), to the short-circuit photocurrent (at the same λ) of a reference photodetector (91150V Reference Cell and Meter, Newport, USA) with a known IPCE spectrum: $IPCE(\lambda, U)_{\text{meas.}} = IPCE(\lambda)_{\text{ref.}} \times \frac{[\text{photo}(\lambda, U)]_{\text{meas.}}}{[\text{light}(\lambda)]_{\text{ref.}}}$.

The measurements were carried out using a high intensity Xe arc lamp (66024 Research Arc Lamp Source, 1000 W Xe, Newport, USA) connected to a power supply (OPS-A100 power supply, Newport, USA) with a radiometer control unit (Merlin, Newport, USA) and coupled to a 1/4 m monochromator (Cornerstone CS-260M, Newport, USA) with 2 exit ports and 3 gratings. The photocurrent of the photoanode, $[\text{photo}(\lambda, U)]_{\text{meas.}}$, was measured using a potentiostat (Zennium, ZAHNER-Electric, GmbH) at a potential U vs. an Ag/AgCl reference electrode. The same optical apparatus and same radiation conditions were used for the measurements of both $[\text{photo}(\lambda, U)]_{\text{meas.}}$ and $[\text{light}(\lambda)]_{\text{ref.}}$.

The photocurrent accounts for the dark current by subtracting the dark current from the measured current under illumination.

**RESULTS AND DISCUSSION**

**Hematite films on TEC15 substrates**

Detailed microstructural characterizations of our thin film hematite photoanodes are reported elsewhere.²⁹ Specific characteristics of the Ti-doped hematite photoanodes without Au NPs that were examined as a reference for comparison are presented in the Supporting Information. These include photographs of hematite photoanodes with 20, 40, 75 and 150 nm thick Ti-doped hematite films on TEC15 substrates (Figure S2); typical top-view HRSEM and cross-section TEM micrographs (Figures S3a and S3b, respectively); and typical XRD diffractograms of TEC15 substrates with and without hematite film (Figure S4). The photoanodes comprised of uniform, polycrystalline hematite films that conformally coated the FTO substrates.

**Au NPs on TEC15 substrates**

The morphological characteristics of Au NPs on TEC15 substrates without hematite films are shown in the Supporting Information. Figure S5 shows photographs of TEC15 substrates coated with Au films of different thicknesses, before and after the dewetting process. The uniform color of the specimens indicates uniform coverage of the Au NPs. Figure S6 shows plan view HRSEM images of the same specimens after the dewetting process. As expected, the size of the NPs increased with increasing Au film thickness, as shown in the size distribution histograms in Figure S7. The spread in the Au NPs size distribution increased with increasing Au film thickness.

The absorption spectra of the respective specimens are shown in Figure 1, together with the spectrum of a pristine TEC15 substrate without Au NPs for comparison. The absorption of the Au NP decorated specimens was higher than that of the pristine TEC15 substrate, and it increased with increasing thickness of the Au film that was evaporated prior to the dewetting process. This is because thicker Au films gave rise to the formation of larger NPs (see Figures S6 and S7) that scattered the light more strongly into the substrate, at all wavelengths.³⁰ There was only one exception from this trend in the absorption spectrum of the specimen with the largest Au NPs near the dipole peak (see blue curve in Figure 1), which is slightly smaller than that with the second largest NPs (green curve). This is due to the size distribution of the respective NPs. The spread in the size of the Au NPs (Figure S7) and the distances between them (Figure S6) gave rise to wide and shallow plasmonic peaks. Since the shape of the NPs was not perfectly spherical, the dipole and quadruple plasmonic peaks at long and short wavelengths, respectively, are clearly seen in the absorption spectra (Figure 1). Parasitic absorption in the specimen that gave rise to optical
loss of wasted photons occurred by interband transition in the Au NPs at wavelengths smaller than 496 nm, as well as in the FTO layer at wavelengths smaller than 350 nm which corresponds to the absorption edge of FTO (the band gap of SnO$_2$ is ~3.6 eV).

Figure 1: Absorption spectra of Au NP decorated TEC15 substrates after dewetting of Au films of different thicknesses: 2.5 nm (violet curve), 5 nm (red curve), 10 nm (green curve) and 15 nm (blue curve). The black curve is the absorption spectrum of a pristine TEC15 substrate, without Au NPs.

**Type 1 photoanodes: Au NPs on hematite-coated TEC15 substrates**

In the first photoanode configuration the Au films were deposited on hematite-coated TEC15 substrates. After the dewetting process the surface of the hematite film was decorated with Au NPs with particle size distribution that depends on the initial thickness of the Au film, as in the previous case with Au films on TEC15 substrates. Figure 2(a) shows photographs of 40 nm thick hematite photoanodes with and without Au NPs (right and left specimens, respectively), and Figure 2(b) shows an HRSEM image of the hematite photoanode that was decorated with Au NPs. The Au NPs were obtained by dewetting of a 15 nm thick Au film that was evaporated on the 40 nm thick hematite film. The size distribution of the Au NPs was nearly the same as for the uncoated TEC15 substrate without hematite (Figure S6d). Note that in this configuration the Au NPs were in direct contact with the electrolyte. Consequently, they gave rise to substantial redox reaction, as shown below.

Figure 2: (a) Photographs of 40 nm thick hematite photoanodes with and without Au NPs (right and left specimens, respectively). (b) Plan view HRSEM image of the hematite photoanode that was decorated with Au NPs obtained by dewetting of a 15 nm thick Au film.

Figure 3 shows absorption spectra of the same photoanodes (from Figure 2a). The absorptance of the Au NP decorated hematite photoanode was considerably higher than that of the counterpart hematite photoanode without the Au NPs, at all wavelengths. The spectral enhancement, defined as the difference between the absorptance of the Au NP decorated hematite photoanode and that of the counterpart photoanode without Au NPs, normalized by the absorptance of the latter photoanode (without Au NPs), is shown in the inset of Figure 3. It varied mildly from ~25% at short wavelengths (350-430 nm) to ~50% at long wavelengths (480-540 nm). This behavior suggests that the enhanced absorption in this spectral range was largely due to Mie scattering, induced by the Au NPs, into the photoanode, because Mie scattering mildly increases with increasing wavelengths. At even longer wavelengths, above 560 nm, the spectral enhancement rose sharply, probably due to plasmonic resonance. However, the prominent enhancement at long wavelengths did not contribute much to the useful absorption in the hematite layer but mostly to wasted absorption elsewhere in the specimen.

Figure 3: Absorption spectra of 40 nm thick hematite photoanodes with and without Au NPs (red full line and black dashed line curves, respectively). The absorption enhancement in the Au NP decorated hematite photoanode with respect to the counterpart photoanode without Au NPs is shown in the inset.

The salient question is whether the enhanced absorptance induced by the Au NPs also enhances the rate of water photo-oxidation, that is the water photo-oxidation current. To answer this question, Figure 4 shows typical cyclic voltammograms (CVs) of the Au NP decorated 40 nm thick
hematite photoanode. The CVs were measured in the dark (red dotted line curve) or under illumination (red full line curve). The results of control measurements obtained with a counterpart 40 nm thick hematite photoanode without Au NPs are shown by the black dotted line (in the dark) and full line curves (under illumination). At high potentials there was no enhancement in photocurrent. In the plateau region at potentials around 1.5 $V_{\text{RHE}}$ (V vs. the reversible hydrogen electrode), the photocurrent of the hematite photoanode that was decorated with Au NPs (red full line curve) was actually lower than that of the counterpart photoanode without Au NPs (black full line curve). At low potentials, below 1.4 $V_{\text{RHE}}$, there seems to be an apparent enhancement in photocurrent induced by the Au NPs, but the origin of the apparent enhancement is unclear. Some observations point to a non-optical origin for the enhancement. First, the shift in the photocurrent onset to lower potential, induced by the Au NPs, is observed also in the dark current (compare the red and black dotted line curves in Figure 4). Second, there was prominent hysteresis between the forward and backward scans of the Au NP decorated hematite photoanode, much more than in the counterpart photoanode without Au NPs, both in the dark and under illumination. And third, the Au NPs gave rise to prominent anodic and cathodic peaks at potentials of 1.3 and 1.06 $V_{\text{RHE}}$, respectively. These peaks were not observed in the counterpart photoanode without Au NPs, indicating that they were induced by the Au NPs. It is noteworthy that similar peaks were observed also in the dark, see Figure 5 below. These observations suggest that the effect of the Au NPs on the current was electrochemical, for the most part, rather than optical.

In order to gain further insight into the electrochemical effect of the Au NPs we carried out CV measurements of an uncoated TEC15 substrate (without hematite) that was decorated with Au NPs by dewetting of a 15 nm thick Au film. The measurements were carried out in 1M NaOH solution in deionized water, the same as in the previous measurements presented in Figure 4. Figure 5 shows the dark CV of the Au NP decorated TEC15 substrate. The potential was cycled from 1.15 to 0.8 $V_{\text{RHE}}$, then to 1.6 $V_{\text{RHE}}$ and finally back to 0.8 $V_{\text{RHE}}$, as indicated by the arrows in Figure 5, at a scan rate of 20 mV/s. In the first leg, from 1.15 to 0.8 $V_{\text{RHE}}$, there was very small cathodic current. In the second leg, from 0.8 to 1.6 $V_{\text{RHE}}$, the current was small below 1.2 $V_{\text{RHE}}$ where it started to grow, reaching an anodic peak at 1.46 $V_{\text{RHE}}$ that merged into an exponential anodic current growth that started at ~1.55 $V_{\text{RHE}}$. In the third leg the anodic current decayed from 1.6 to 1.55 $V_{\text{RHE}}$, and there was a prominent cathodic peak at 1.06 $V_{\text{RHE}}$ that was well separated from the exponential increase of the cathodic current at potentials lower than 0.7 $V_{\text{RHE}}$. The anodic current at potentials higher than 1.55 $V_{\text{RHE}}$ originated from water oxidation, for the most part. However, the anodic and cathodic peaks at 1.46 and 1.06 $V_{\text{RHE}}$, respectively, and the cathodic current at potentials lower than 0.7 $V_{\text{RHE}}$ originated from electrochemical side reactions that did not contribute to the water splitting process. The anodic peak at 1.46 $V_{\text{RHE}}$ originated from oxidation of the Au NPs to gold trihydroxide ($\text{Au} + 3\text{OH}^- = \text{Au(OH)}_3^+ + 3^-$, $E^\circ = 1.457 V_{\text{RHE}}$), forming a passivation layer at the surface of the NPs. The cathodic peak at 1.06 $V_{\text{RHE}}$ originated from the reduction of the Au(OH)$_3^+$ passivation layer back to Au. Supporting this assignment is the fact that on the first leg of the CV scan from 1.15 to 0.8 $V_{\text{RHE}}$ the cathodic current was very small, whereas on the third leg there was a prominent cathodic peak at 1.06 $V_{\text{RHE}}$.

Figure 4: Cyclic voltammograms (CVs) of a 40 nm thick hematite photoanode decorated with Au NPs obtained by dewetting of a 15 nm thick Au film, measured in the dark (red dotted line curve) or under illumination (red full line curve). The results of control measurements of a counterpart 40 nm thick hematite photoanode without Au NPs are shown in the black dotted line (dark measurement) and full line curves (under illumination). The measurements were carried out in 1M NaOH solution in deionized water. The potential was cycled from 0.8 to 1.8 $V_{\text{RHE}}$ and then back to 0.8 $V_{\text{RHE}}$ at a scan rate of 20 mV/s.

Figure 5: Cyclic voltammograms (measured in the dark) of a TEC15 substrate decorated with Au NPs obtained by dewetting of a 15 nm thick Au film. The scan started from a potential of 1.18 $V_{\text{RHE}}$ and was first scanned cathodically to 0.8 $V_{\text{RHE}}$ (1st leg), then anodically to 1.7 $V_{\text{RHE}}$ (2nd leg), and finally back to 0.8 $V_{\text{RHE}}$ (3rd leg), as indicated by the numbered arrows. The scan rate was 20 mV/s.
Thus, there are strong evidences that Au redox took place, giving rise to parasitic current that predominated the overall current at potentials below the onset of the water oxidation reaction. It is noteworthy that illumination may promote this redox current in a similar way to the promotion of the water oxidation current by generating excess charge carriers with excess chemical potential, i.e., photovoltage,\textsuperscript{33} in the hematite layer. To summarize this section we conclude that the first photoanode configuration in which the Au NPs were above the hematite layer, that is in direct contact with the alkaline solution, gave rise to parasitic current due to redox side reaction of the Au NPs. The parasitic redox current predominated the overall current at low potentials, below the onset of the water oxidation reaction. In addition to the redox side reaction, the Au NPs also shifted the onset of water oxidation to lower potentials by approximately 100 mV. This is an electrocatalytic effect and clearly cannot be attributed to an optical effect since it occurred also in the dark. In order to highlight this fact Figure 6 compares the dark CVs obtained from a pristine TEC\textsubscript{15} substrate (without hematite and Au NPs, green curve), a TEC\textsubscript{15} substrate coated with a 40 nm thick hematite layer (without Au NPs, black curve), a TEC\textsubscript{15} substrate coated with a 15 nm thick Au layer (without hematite and prior to dewetting, blue curve), and a TEC\textsubscript{15} substrate decorated with Au NPs obtained by dewetting of a 15 nm thick Au film (without hematite, red curve). Clearly, the water oxidation reaction in the Au NP decorated specimen preceded the other specimens by several hundred mV, showing that Au NPs have lower overpotential for water oxidation than hematite and FTO.

And last but not least, although the overall absorption in the specimen was enhanced by the Au NPs (see Figure 3), the photocurrent in the plateau region was found to be smaller in the Au NP decorated hematite photoanode than in the counterpart photoanode without Au NPs (see Figure 4). Thus, not only that the enhancement in the overall absorption in the Au NP decorated photoanode was not productive for water photo-oxidation, it actually reduced the plateau photocurrent. This counterintuitive observation suggests that wasted absorption may have occurred in parts of the specimen that do not contribute to the water photo-oxidation reaction, such as absorption by interband transition in the Au NPs or enhanced absorption in the TEC\textsubscript{15} substrate into which the light was scattered by the Au NPs. Alternatively, this could also be due to deleterious electronic effects such as charge recombination induced by the Au NPs.\textsuperscript{17,23,24} In order to suppress the Au redox reaction and the wasted absorption by Au NPs that overshadow the hematite layer, we examined another photoanode configuration in which the Au NPs were embedded under the hematite film.

\textbf{Type 2 photoanodes: Au NPs embedded under hematite films on TEC\textsubscript{15} substrates}

In the second photoanode configuration the Au NPs were embedded under the hematite film in order to eliminate the overshadow effect and to suppress the Au redox side reaction by trying to prevent direct contact with the electrolyte solution. Embedding the Au NPs under the hematite film was achieved simply by reversing the order of the photoanode preparation steps, that is the Au film deposition and dewetting steps preceded the hematite film deposition step. Figure 7(a) shows photographs of 14 photoanode specimens with different Au film thicknesses (2, 5, 10 and 15 nm) and different hematite film thicknesses (20, 40, 75 and 115 nm) that were examined in this work. Figure 7(b) shows a cross-section HRSEM image of one of these specimens with 15 nm thick Au film and 75 nm thick hematite film. Most of the Au NPs were covered by the hematite film, which is expected to suppress the Au redox reaction, at least partially, by reducing their direct contact with the electrolyte solution.

![Figure 6: Cyclic voltammograms (measured in the dark) of a pristine TEC\textsubscript{15} substrate (without hematite and Au NPs, green curve), a TEC\textsubscript{15} substrate coated with a 40 nm thick hematite layer (without Au NPs, black curve), a TEC\textsubscript{15} substrate coated with a 15 nm thick Au layer (without hematite and prior to dewetting, blue curve), and a TEC\textsubscript{15} substrate decorated with Au NPs obtained by dewetting of a 15 nm thick Au film (without hematite, red curve).]
Figure 7: (a) Photograph of 14 specimens of the second photoanode configuration (Au NPs embedded under the hematite film) with different Au and hematite film thicknesses. (b) Cross-section HRSEM image of one of the specimens, with 15 nm thick Au film and 75 nm thick hematite film.

Figure 8 shows the absorption spectra of two of the 14 specimens in Figure 7a, the ones with Au NPs obtained by dewetting of 5 nm thick Au films embedded under 40 or 115 nm thick hematite films (red full or dashed line curves, respectively). For comparison, the figure shows also the absorption spectra of the counterpart hematite photoanodes without Au NPs (black curves) and of an Au NP decorated TEC15 substrate without hematite (blue curve). The Au NPs enhanced the absorption in both the 40 and 115 nm thick hematite photoanodes, but the enhancement was larger for the thinner hematite film. This is expected for this photoanode configuration in which the Au NPs were embedded under the hematite film and therefore the thicker the hematite film was the more light was absorbed in it before reaching the Au NPs, thereby reducing the influence of the Au NPs. The absorption at wavelengths longer than the absorption edge of hematite (600 nm) must have been due to parasitic absorption elsewhere in the specimen, e.g., absorption in the Au NPs or in the TEC15 substrate, and high angle light scattering. It is noteworthy that the plasmonic peak, clearly observed around 560 nm in the Au NP decorated TEC15 substrate without hematite (blue curve), shifted to longer wavelengths (~700 nm) in the embedded configuration (red curves). This was due to the increase in the dielectric constant of the environment that surrounded the Au NPs,18,20 which is much higher in hematite than in air. As a result, the plasmonic peak shifted to longer wavelengths above the absorption edge of hematite, therefore it no longer contributed to the productive absorption in the hematite film. Thus, the enhancement of potentially productive absorption at wavelengths below the absorption edge of hematite was largely due to light scattering backward into the hematite film that was induced by the Au NPs that were embedded under the film, i.e., due to Mie scattering.30

Figure 8: Absorption spectra of photoanodes with Au NPs embedded under 40 or 115 nm thick hematite layers (red full or dashed line curves, respectively), and counterpart hematite photoanodes of the same thickness without Au NPs (black full or dashed line curves for 40 or 115 nm thick hematite films, respectively). The Au NPs were obtained by dewetting of 5 nm thick Au films prior to the deposition of the hematite films. The blue curve shows the absorption spectrum of an Au NP decorated TEC15 substrate without hematite in which the Au NPs were obtained by dewetting of a 5 nm thick Au film.

We define the absorption gain induced by the Au NPs as the ratio between the photon flux absorbed in photoanodes with Au NPs and in the counterpart photoanodes without Au NPs. The photon flux absorbed in a photoanode was calculated by integrating the product of the absorbance spectrum of the photoanode (taken from Figure 8) times the irradiance spectrum of the light source (taken from Figure S1) up to the absorption edge of hematite (600 nm). Thus, the absorption gain provides an upper limit estimation of the expected gain in useful absorption in the hematite film. If the enhanced absorption occurred mostly in the hematite film then it would be expected to enhance the photocurrent. But if the enhancement in absorption occurred elsewhere in the specimen, in inactive
regions that do not contribute to the photocurrent, it would not enhance the photocurrent. Figure 9 shows the absorption gain calculated for all the 14 photoanodes of the second configuration.

Figure 9: The absorption gain calculated for photoanodes with different Au film thickness and different hematite film thickness. The thickness of the Au films, before dewetting, is marked on the x axis, whereas the thickness of the hematite films is color coded with black, red, blue and magenta dots for 20, 40, 75 and 115 nm thick films, respectively.

The most prominent trends in Figure 9 are that the absorption gain decreased with increasing hematite film thickness, and it increased with increasing Au film thickness. The former trend is obviously due to absorption in the hematite film above the Au NPs. The latter trend is due to the dependence of the scattering cross section on the particle size. All 14 specimens followed these trends except for one outlier that corresponds to a 40 nm thick hematite film deposited on Au NPs that were obtained by dewetting of a 2.5 nm thick Au film. This outlier may be due to a unique resonance mode of this particular optical stack or from another unknown reason. The fact that the other 13 specimens followed these trends speaks for the solid ground underlying these observations. The salient question is whether the trends in the absorption gain could be correlated with similar trends in the photocurrent gain.

Figures 10(a) and (b) show light and dark CVs and chopped light chronoamperograms, respectively, of the champion photoanode that achieved the highest photocurrent of all the 14 photoanodes of the second configuration with Au NPs embedded under the hematite films. This was the specimen with the thickest hematite and Au films (115 and 15 nm, respectively). CVs of this photoanode measured in the dark and under illumination are shown by the red dashed and full line curves, respectively. For comparison, the black dashed and full line curves show the dark and light CVs of the counterpart photoanode with a 115 nm thick hematite film deposited directly on TEC15 substrate, without Au NPs. The photocurrent of the Au NP sensitized hematite photoanode was slightly larger than that of the counterpart photoanode without Au NPs in the entire range of potentials. This is unlike the CVs of photoanodes of the first configuration in which the Au NPs were on top of the hematite film, wherein in the plateau region the photocurrent of the Au NP decorated hematite photoanode was smaller than that of the counterpart photoanode without Au NPs (see Figure 4). Other unusual features in the CVs of photoanodes of the first configuration (Figure 4) that do not show up so prominently in the CVs of the photoanodes of the second configuration (Figure 10) are the hysteresis and the anodic and cathodic peaks. This indicates that the parasitic current due to Au redox side reaction was substantially suppressed in the second photoanode configuration with embedded Au NPs, as expected. However, some hysteresis still remained and there was a shift in the onset potential of the dark current. This suggests that a small amount of Au reached the surface, either by diffusion or perhaps through micro-cracks in the hematite film. Indeed, a small amount of Au was detected by XPS measurements (see Figure S8). Nevertheless, the amount of Au at the surface was small, certainly much smaller than in the first photoanode configuration wherein the Au NPs were right at the surface. Consequently, the electrochemical effects induced by the Au NPs were suppressed in the second photoanode configuration, increasing the likelihood that the optical effect would become prominent. CVs of other specimens of the second photoanode configuration are presented in Figure S9. Note that in some cases the hematite photoanodes without Au NPs surpassed their counterpart photoanodes with Au NPs.
Figure 10: (a) Cyclic voltammograms, measured in the dark or under illumination (red dashed or full line curves, respectively), of the champion photoanode that achieved the highest photocurrent of all the 14 specimens of the second photoanode configuration (that is the one with 115 nm thick hematite film on Au NPs obtained by dewetting of a 15 nm thick Au film). The black curves show cyclic voltammograms of a 115 nm thick hematite photoanode without Au NPs. (b) Chopped light chronoamperograms of the same photoanodes, with or without Au NPs (red or black curves, respectively). The blue curve shows the potential steps, expressed in $V_{RHE}$.

Examining the IPCE spectrum of the champion photoanode from Figure 10 shows no plasmonic peaks in the entire spectrum (see Figure S10). This is commensurate with the absorption spectrum of this photoanode that shows no plasmonic peaks up to 700 nm (see Figure S11). Nevertheless, the Au NPs gave rise to broadband enhancement in absorption due to Mie scattering, resulting in an absorption gain of 1.39 for this specimen. The photocurrent gain was 1.52 or 1.12 at potentials of 1.23 or 1.53 $V_{RHE}$, respectively. Similarly to the absorption gain, the photocurrent gain is defined as the ratio between the photocurrent obtained in photoanodes with Au NPs and in the counterpart photoanodes without Au NPs, extracted from chopped light chronoamperograms such as the one shown in Figures 10(b). The lack of agreement between absorption and photocurrent gains and the inconsistency of the photocurrent gain at different potentials raises questions regarding the correlation between absorption and photocurrent gains. In order to address these questions, we examine the correlation between the absorption gain (Figure 9) and the photocurrent gain induced by the Au NPs for all 14 specimens of the second photoanode configuration. Figure 11 shows the photocurrent gain of all the specimens at two potentials: 1.23 $V_{RHE}$, close to the photocurrent onset (Figure 11a); and 1.53 $V_{RHE}$, in the photocurrent plateau region (Figure 11b). The photocurrent gain was much higher at 1.23 $V_{RHE}$ than at 1.53 $V_{RHE}$, which is difficult to relate to an optical effect and is much more consistent with an electrocatalytic or other electrochemical effect (e.g., Au redox side reaction).

Figure 11: Photocurrent gain obtained for all 14 specimens of the second photoanode configuration with Au NPs embedded under hematite films of different thicknesses (as indicated in the color-coded legend) as a function of the thickness of the Au film from which the NPs were obtained by dewetting. The photocurrent gain is presented for two potentials: (a) 1.23 and (b) 1.53 $V_{RHE}$.

The trends in the photocurrent gain as a function of the thickness of the hematite and Au films were quite different than the respective trends in the absorption gain. While the absorption gain displayed consistent trends for 13 out of the 14 specimens: it decreased with increasing hematite film thickness and increased with increasing Au film thickness (see Figure 9); the trends in the photocurrent gain were not consistent. Referring to Figure 11, the photocurrent gain did not exhibit a consistent trend with respect to the thickness of the Au film, and the sensitivity of the gain to hematite film thickness was dependent on potential. For a potential of 1.23 $V_{RHE}$ (Figure 11a), the photocurrent gain of the thicker hematite photoanodes tended to decrease with increasing hematite film thickness, whereas for 1.53 $V_{RHE}$ (Figure 11b) the photocurrent gain was less than unity for the 40 nm thick hematite photoanode, which reached the highest gain at 1.23 $V_{RHE}$ (Figure 11a). The unusually low gain of the thinnest (20 nm) hematite photoanodes, in
both potentials (Figures 1a and 1b) is likely because of incomplete coverage of the Au NPs by hematite.

In order to examine the correlation between absorption and photocurrent gains, Figure 12 presents plots of the photocurrent gain at 1.23 and 1.53 V_RHE (Figure 12a and 12b, respectively) as a function of the absorption gain for all 14 specimens of the second photoanode configuration. Looking at all the specimens altogether one cannot find obvious correlation between the absorption and photocurrent gains. However, dividing the whole collection of data into sub-groups according to the hematite film thickness shows that the photoanodes with 75 nm thick hematite films (blue symbols) display similar trends at both potentials, 1.23 and 1.53 V_RHE. Despite the poor statistics, it seems that for these specimens the photocurrent gain was proportional to the absorption gain, at least for 3 out of the 4 photoanodes in this sub-group (except for the one with the largest Au NPs).

![Photocurrent gain plotted against the absorption gain for all 14 specimens of the second photoanode configuration with Au NPs embedded under hematite films of different thicknesses (as indicated in the color-coded legend). The photocurrent gain is presented for two potentials: (a) 1.23 and (b) 1.53 V_RHE. The arrows show the direction in which the thickness of the Au film from which the NPs were obtained by dewetting increases.](image)

The lack of obvious correlation between photocurrent and absorption gains for most of the specimens suggests that the photocurrent enhancement originated largely from electrochemical rather than optical effects. The presence of Au at the surface (see Figure S8) reduced the overpotential for water oxidation (see Figure 6), thereby shifting the photocurrent onset to lower potentials which resulted in higher photocurrents at low potentials in comparison to the counterpart photoanodes without Au NPs. This is purely an electrocatalytic effect, and is not related to the capture of light. While it had quite a substantial influence at low potentials close to the photocurrent onset, the effect became weaker at higher potentials in the photocurrent plateau region. It is noteworthy that in this range (~1.4 to 1.5 V_RHE) there might have been a contribution to the current from Au redox reaction, as was observed in photoanodes of the first configuration. Since the photocurrent gain at high potentials was so small it is difficult to tell how much of it was due to water oxidation and how much originated from the Au redox reaction. However, the exact makeup of the photocurrent gain in this range is not of crucial importance to this study, since the photocurrent gain in this potential range was so small (< 18% at 1.53 V_RHE) as to be negligible.

### CONCLUSIONS

The first part of this study shows that Au NPs in direct contact with alkaline solutions (1M NaOH in water) underwent a redox side reaction that preceded the water oxidation reaction by several hundred mV. Furthermore, the Au NPs may absorb light and scatter it into parts of the photoanode that do not contribute to the desired reaction, that is water (photo)oxidation. Therefore, the Au NPs should rather be embedded under the hematite layer in order to suppress these spurious effects. Indeed, in the second part of this work that examines the embedded configuration, it was shown that the Au redox side reaction was suppressed and the absorbance was enhanced in comparison to counterpart photoanodes without Au NPs. However, embedding the Au NPs under the hematite red-shifted their plasmonic resonances to wavelengths above the hematite absorption edge, therefore the plasmonic effect became irrelevant to the photocurrent. The enhancement in absorption in the visible range was largely due to Mie scattering. Most of the photoanodes in the embedded configuration displayed higher photocurrents than the counterpart photoanodes without Au NPs. However, the photocurrent enhancement was substantial only at low potentials whereas at high potentials it was very small and some photoanodes displayed the opposite trend, namely, hematite photoanodes without Au NPs reached higher photocurrents than their counterpart photoanodes with Au NPs.
A detailed examination of the trends of the absorption and photocurrent gains as a function of the size of the Au NPs and the thickness of the hematite films shows no obvious correlation between the respective gains for most of the specimens. Only 4 out of 14 specimens, the ones with 75 nm thick hematite films, were found to show a plausible correlation between absorption and photocurrent gains. These observations cast serious doubts as to whether the root cause of the photocurrent enhancement was optical at all. Revisiting the first part of this work, where a cathodic shift in the onset potential of water oxidation in the dark was observed in the presence of Au NPs, we can now conclude that the photocurrent enhancement observed in the photoanodes with embedded Au NPs originated primarily from electrochemical effects rather than from optical ones. Since the photocurrent enhancement was substantial mostly at rather low potentials close to the photocurrent onset where the photocurrents were rather small, it is difficult to tell how much of it actually contributed to the desired reaction, that is water oxidation, and how much contributed to spurious side reactions such as the redox reaction of the Au NPs.

This work shows the intricate nature of several effects, both optical and electrochemical, of the Au NPs on hematite photoanodes, which come together to produce different contributions to the photocurrent. Depending on the device structure, some effects may enhance the water photo-oxidation current but other ones may not, and some effects may even suppress it (e.g., recombination). Therefore, careful design and optimization must be carried out in order to take advantage of the beneficial effects and mitigate the deleterious ones. This requires precise control of the size and shape of the NPs as well as their location, which then leads to 2D patterning at small dimensions. This is a critical challenge for large area devices such as solar cells.

**AUTHOR INFORMATION**

**Corresponding Author**

* Email: avner@mt.technion.ac.il ; Phone: +972-(0)4-8294576

**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**ASSOCIATED CONTENT**

**Supporting Information**

The irradiance spectrum of the lamp that was used to measure the photocurrent; photographs and microstructural characterizations (HRSEM, TEM, XRD) of hematite films on FTO coated glass substrates (without Au NPs); photographs, HRSEM images and particle size distribution of Au NPs on FTO coated glass substrates (without hematite); XPS of a photoanode of the second configuration with Au NPs embedded under a 115 nm thick hematite film; cyclic voltammograms of photoanodes of the second configuration; IPCE spectra of the champion hematite photoanode with or without Au NPs; absorption spectra of the champion photoanodes with and without Au NPs embedded under the hematite layer.

**ACKNOWLEDGMENT**

The research leading to these results has received funding from the European Research Council under the European Union’s Seventh Framework Programme (FP/2007-2013) / ERC Grant Agreement n. [67516]. Some of the experiments reported in this work were carried out using central facilities at the Technion’s Photovoltaic Laboratory supported by the Nancy & Stephen Grand Technion Energy Program (GTEP) and the Russell Berrie Nanotechnology Institute (RBNI), the Micro and Nano Fabrication Unit (MNFU), and the Hydrogen Technologies Research Laboratory (HTRL) supported by the Nancy and Stephen Grand Technion Energy Program (GTEP), Adelis Foundation, and the Solar Fuels I-CORE program of the Planning and Budgeting Committee and the Israel Science Foundation (Grant No. 152/11).

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