Photocurrent polarity switching in electrochemical cells with light via an excited state proton transfer mechanism

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Abstract

Light is a common source of energy in sustainable technologies for photocurrent generation. To date, in such light-harvesting applications, the excited electrons generate the photocurrent. Here, we introduce a new mechanism for photocurrent generation that is based on excited state proton transfer (ESPT) of photoacids and photobases that can donate or accept a proton, respectively, but only after excitation. We show that the formed ions following ESPT can either serve as electron donors or acceptors at the electrodes, which are dependent on the electric potential, or modify the properties of the electrochemical interface, both resulting in photocurrent generation. We further show that control of the current polarity is obtained by switching the irradiation between the photoacid and the photobase. Our study represents a new approach in photoelectrochemistry by introducing ESPT processes, which can be further utilized in light-responsive energy production or energy storage.

Keywords: Photoacids, Photobases, Electrochemical cell, 2-naphthol-6-sulfonate, 6-aminoquinoline.
Introduction

The road to sustainable clean energy technologies is of prime importance to our planet, with light being one of the most commonly used sustainable sources of energy. Among the different light-harvesting technologies, our study here is concerning photoelectrochemistry. Photoelectrochemical cells are usually designed to either generate hydrogen by electrolysis or to generate photocurrent, i.e., they can be analogous to photovoltaic cells,[1-3] such as dye-sensitized photoelectrochemical cells that make use of light-sensitive organic dyes (photosensitizers) for photocurrent generation.[4-7] Other common applications of photoelectrochemical cells are taking advantage of the photocurrent polarity for sensing and logic operation.[8-10]

An important parameter in electrochemical processes is their dependence on the local pH,[11-17] meaning the local concentration of protons next to the electrode. Here, we use Brønsted photoacids (PAs) and photobases (PBs) that can behave as strong acids and bases only as a response to light absorption, thus, they can transiently manipulate the proton concentration using light as an energy source. This property of PAs and PBs is due to their fundamental change in $pK_a$ that drops or rises, respectively, upon excitation, thus resulting in an excited state proton transfer (ESPT) event.[18-21] Therefore, in their electronically excited state, a PA dissociates and transfers the proton to a proton acceptor, such as water or another solvated molecule, while a PB acts in a reverse mode by abstracting a proton from a proton donor, which similarly can be water or another donor. This ability of Brønsted PAs and PBs has been used before to transiently control dynamic processes that are dependent on the protonation or deprotonation of molecules, such as self-assembly processes, enzymatic activities, self-propulsion, and protonic transport.[22-29] It is worth mentioning that other types of molecules are also termed PAs, which are not the type used here, but rather a photochromic molecule that undergoes a light-induced structural change in which a proton is released, with the spiropyran-merocyanine system being the common representative of such PAs.

In this work, we show a new application of Brønsted PAs and PBs for light-driven photoelectrochemical photocurrent generation. We demonstrate that the ESPT of PAs and PBs can be utilized for photocurrent production and polarity switching in an electrochemical cell, both in single-cell and H-cell configurations. Unlike common photoelectrochemical devices for photocurrent generation, the use of PAs and PBs results in a fundamentally different mechanism for photocurrent generation. In common photoelectrochemical cells, photocurrent
generation is a result of an electron transfer process between the electronically excited state and the electrode. In the system presented here, the photocurrent generation is due to an ESPT process. While the goal of this work is to introduce a new mechanism for harvesting light in photoelectrochemical cells, the new knowledge discussed here can be utilized in future devices, either for photocurrent generation or for energy storage.

Results and Discussion

Spectroscopic characterization of the ESPT process

In this study, we have chosen the common 2-naphthol-6-sulfonate (2N6S) as the PA and 6-aminoquinoline (6AQ) as the PB (Figure 1a). The hallmark of the ESPT process is the deprotonation of the PA (ROH) to RO⁻ and the protonation of the PB (RN) to RNH⁺ only upon light excitation, which is due to the different pKₐ values between the ground and excited states (Figure 1a). The ESPT process can be observed spectroscopically since the protonated and deprotonated states of both the PA and the PB absorb and emit at different wavelengths. Indeed, while the UV-Vis ground state absorption spectra of 2N6S and 6AQ show that 2N6S is in its ROH state and 6AQ is in its RN state (Figure 1b, black curves), the emission spectra, which probe the excited state, show that 2N6S is in its RO⁻* state and 6AQ is in its RNH⁺* state (Figure 1b, red curves). Importantly, the emergence of the ionic forms following PA and PB excitation is only in the excited state. Thus, upon returning to the ground state, the ESPT will be followed by a recombination process that will eventually result in the molecules returning to their initial ROH/RN states.
Figure 1. The ESPT mechanism of the 2N6S PA and the 6AQ PB and its spectroscopic signature. (a) molecular structures and reactions of 2N6S (ROH) and 6AQ (RN), showing also the $pK_a$ change between ground and excited states. (b) and (c) Absorption (black curves) and emission (red curves) spectrum of 2N6S and 6AQ, respectively. $\lambda_{ex}$=340 nm for the emission spectra.

**Photocurrent production of 2N6S**

In the first part of our study, we used a photoelectrochemical cell composed of a single cell setup using a screen-printed electrode with a graphite working electrode (WE), platinum counter electrode (CE), and silver coated with a silver chloride reference electrode (RE). To study the photoelectrochemical properties of 2N6S we performed cyclic voltammetry (CV) in dark and under UV irradiation using a LED with $\lambda_{ex}$=340 nm (Figure 2). We observed that only under irradiation, a positive peak with a maximum at +0.5V and a negative peak at -0.5V were formed. In addition, between -1 and -0.5V the photocurrent became less negative. As none of these peaks appeared in the dark measurements, or in measurements of pure electrolyte (Figure S1a), it implies that these peaks are due to the formation of the ionic forms: RO$^-$ and H$^+$. Since H$^+$ can only accept electrons, we ascribed it to the new peak at -0.5V. To pinpoint
the formation of the peak at +0.5V to the formation of RO', we performed both CV and chronoamperometry (CA) measurement of 2N6S solution (without irradiation) but at different pH values covering the two sides of its pKₐ while comparing it to a buffer at the same pH without the PA (see Figure S1b and c and text within).

Figure 2. Cyclic voltammetry of aqueous solution containing the 2N6S PA: in dark (black curve) and under irradiation (red curve), λₑₓ=340 nm.

In the next step, we followed photocurrent generation of 2N6S with CA under applying -1V, -0.5V, and +0.5V on the WE (the marked areas in the CV presented in Figure 2). Under a negative -1V on the WE with dark/light irradiation intervals (Figure 3a), we can clearly observe a light response of the measured current, exhibiting a decrease in cathodic current upon light irradiation with a measured absolute photocurrent density of 0.97 ± 0.22 µA/cm². While turning off the light, the current density has returned to its initial value (prior to irradiation). Unlike the decrease in cathodic current upon light irradiation observed upon applying -1V, when -0.5V was applied we observed an increase in the cathodic current upon irradiation with a measured photocurrent density of 0.48±0.14 µA/cm² (Figure 3b). Upon switching to the positive +0.5V regime, we observed an increase in the anodic current upon irradiation with a measured photocurrent density of 0.07±0.02 µA/cm² (Figure 3c). As before, upon turning off the irradiation, the current density decreased back to the baseline level (prior to irradiation) in both bias regimes.
Figure 3. The dynamicity of the photocurrent generation and suggested mechanisms at different bias regimes. (a), (b) and (c) chronoamperometry of aqueous solution containing the 2N6S PA taken at -1V, -0.5V, and +0.5V, respectively, on the WE upon light/dark intervals ($\lambda_{ex}$=340 nm) marked by the purple rectangles. (d), (e), and (f) show a schematic model of the system under -1V, -0.5V, and +0.5V, respectively.

To explain our results, we will refer to the scheme of the electrochemical cell (Figure 3d-3f), at the different voltage regimes. In general, the current generated on the WE is influenced by both a direct charge transfer between the electrode to/from a species in solution as well as by mass transport across the diffuse layer, whereas each one of the processes can determine the rate limiting step of the reaction. As shown in the scheme, during the reaction, the reactant diffuses to the electrode, where charge transfer takes place, followed by the diffusion of the product into bulk solution.

At -1V, we observed a change in the magnitude of the current upon light irradiation without the emergence of a new redox peak. Accordingly, in this relatively high value of the applied...
potential, we suggest that mass transport is the rate-limiting step of the electrochemical reaction due to the extremely fast charge transfer (Figure 3d). The diffusion mode of mass transport is expressed by Fick’s law:[30]

\[
J_{\text{diffusion}} = -\frac{D(c_b-c_s)}{\delta}
\]  
(Eq. 1)

where \( J \) is the flux, \( D \) is the diffusion coefficient, \( \delta \) is the diffusion layer thickness, and \( C \) is concentration of the reactants in the bulk (\( C_b \)) and surface (\( C_s \)). Our electrochemical system is multicomponent including \( \text{Na}^+, \text{Cl}^- \), ROH, water and the products of its reduction. All the components are related to each other and can affect mass transport. Consequently, a change in one of the components will affect the diffusion layer thickness of the entire system.[31] Accordingly, upon light irradiation, the \( \text{RO}^- \cdots \text{H}^+ \) ion pairs are formed, thus changing the composition of the diffuse layer, and resulting in an increase in the thickness of the diffusion layer, which eventually decreases the cathodic current (Eq. 1).

As observed in our results, the direction of the photocurrent generation is flipped upon moving from -1V to -0.5V, thus implying a different mechanism. Moreover, unlike at -1V, at -0.5V we observed the emergence of a new reduction peak. Accordingly, we suggest here that in the -0.5V bias regime, the charge transfer at the electrode/electrolyte interface is the reaction rate-limiting process (Figure 3e). Upon light irradiation, the \( \text{RO}^- \cdots \text{H}^+ \) ion pairs are formed, resulting in the attraction of \( \text{H}^+ \) toward the negatively charged cathode followed by their reduction, which eventually increases the cathodic current.

To explain our findings in the +0.5V bias regime, i.e., the formation of a new oxidation peak following irradiation, we should also refer to the charge transfer at the electrode/electrolyte interface as a reaction rate-limiting process (Figure 3f). Unlike the behavior of the cell in the negative bias regime, in the positive one, the negatively charged photoacid is attracted to the positively charged anode. Upon light irradiation and the formation of an \( \text{RO}^- \cdots \text{H}^+ \) ion pair, the \( \text{RO}^- \) anions are now attracted to the positively charged anode and can undergo oxidation, resulting in an increase in the anodic current. To support this hypothesis regarding the positive (+0.5V) regime, we conducted a control experiment where the electrolyte without the PA was titrated with the addition of \( \text{RO}^- \) (from an alkaline condition) during the CA measurement, which resulted in an increase of the current density (Figure S1d and text within).

As discussed above, in most photocurrent generation types of devices, such as in electrochemical dye-sensitized solar cells, the photocurrent is obtained via a direct electron (or hole) transfer between the photoexcited molecule in its higher energetic level and the electrode.
In most cases, the photoexcited molecule forms a layer (either single or multi-layers) on the WE. In our system, we suggest a different mechanism for photocurrent generation that originates from a photo-dissociation reaction of the PA and an electrochemical reaction between the formed ions in the excited state and the electrodes. To support this mechanism, i.e., to exclude the direct electron transfer mechanism from the excited PA (ROH*) to the electrode without the involvement of the ESPT process, we turned to another common PA, which is 8-hydroxypyrene-1,3,6-trisulfonic acid (HPTS), and its non-photoacid methylated analog, 8-methoxypyrene-1,3,6-trisulfonic acid (MPTS) (Figure 4a and b). We did not use the HPTS PA in the previous experiments due to its propensity to undergo bleaching upon prolonged exposure to light. In common with the 2N6S PA, HPTS also exhibits a predominate 405 nm ROH peak in the absorption spectrum, corresponding to the ground state form, and a predominant 530 nm RO- peak in the emission spectrum, corresponding to the excited state form (Figure 4a), which is due to the ESPT process. In contrast, methylation of HPTS, (MPTS) exhibits only the ROCH3 405 nm peak in the absorption spectrum, and the 450 nm peak in the emission spectrum (Figure 4b). Since MPTS is not dissociated upon irradiation, any photocurrent generation would be possible only via a direct electron transfer mechanism. Thus, we followed the CA of HPTS and MPTS in dark/light irradiation (at λex=405 nm) intervals with a similar applied positive potential of +0.5V on the WE as is shown above (Figure 4c). As shown in the figure, a maximal photocurrent production of 0.06 µA/cm² was obtained for HPTS following light irradiation, which decayed to the baseline level in dark, while no photocurrent production was detected for MPTS. In line with the CA results, the CV measurements also show that the CV response of MPTS is identical in both dark and light conditions, whereas HPTS shows a photocurrent generation upon light irradiation with +0.5V being the onset of the photocurrent (Figure S3). These results support our hypothesis that the photocurrent production from PAs derives from electrochemical reactions of the photo-dissociated ions in the excited state and not from a direct electron transfer to the electrode.
**Figure 4.** The role of ESPT in photocurrent generation. (a) and (b) absorption (black curves) and emission (red curves) spectrum of HPTS and MPTS, respectively. $\lambda_{ex}=405$ nm for the emission spectra. The figures also show the molecular structures and reactions of HPTS and MPTS. (c) The changes in the measured CA upon light/dark intervals ($\lambda_{ex}=405$ nm) of HPTS (black line) and MPTS (red line) under +0.5V.

**Photocurrent production of 6AQ**

In this section, we shift from having a PA in the single cell configuration to having a PB in this configuration. As before, we first identified the electrochemical reactions of the 6AQ PB by CV measurements in dark and under UV irradiation (**Figure 5a**). The unique electrochemical feature that appears under light irradiation is a negative peak with a maximum around -1V that is absent in the dark. Unlike the case of having a PA in the solution, here, having a PB resulted in the increase of cathodic current upon the irradiation of 6AQ at the negative (-1V) bias regime (**Figure 5a**). Accordingly, while measuring the CA at this potential, we observed an increase in cathodic current with an absolute measured photocurrent density of $0.05\pm0.01 \mu A/cm^2$. 

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**Figure 5a**
(Figure 5b). Upon turning off the irradiation, the current density returned back to the baseline level. In line with the mechanism suggested for the PA under the applied bias of -1V (Figure 3d), here the reaction rate is limited by mass transfer (Figure 5c). However, since the PB is uncharged prior to the irradiation, it is not depleted from the negatively charged electrode. Accordingly, upon irradiation, the formed RNH⁺ can now be attracted to the electrode and accept electrons from the WE. Hence, both water and RNH⁺ reduction processes are possible and the addition of RNH⁺ reduction under irradiation is causing the observed changes in both CV and CA measurements. To pinpoint the contribution of RNH⁺ to the measured photocurrent, we have performed CA upon titrating RNH⁺ at a low pH solution (Figure S2 and text within).

Figure 5. The use of a photobase for photocurrent generation and suggested mechanism. (a) Cyclic voltammetry of aqueous solution containing the 6AQ PB in dark (black curve) and under irradiation (red curve). (b) Chronoamperometry under -1V bias on the WE upon light/dark intervals. λₑₓ=340 nm for both (a) and (b). (c) A schematic model of the system under -1V bias.
Switching current polarity by irradiation of 2N6S and 6AQ.

Until now, we have explored the photocurrent response of either a PA or a PB in a single-cell configuration. We suggested that due to the interaction of ions (formed upon the irradiation) with the interface, the rate of reaction could be modified. In this context, pH is an important factor.\cite{17, 32-34} To explore the effect of pH, we introduce in this section a different design of a photoelectrochemical cell, which is an H-type cell made of glass with 2 quartz optical windows, separated by a Nafion membrane (Figure 6a). Before describing the electrochemical measurements, we used this configuration without the electrodes, while having the 2N6S PA and 6AQ PB in separate cells, to explore the proton transfer between the two half-cells. As before, upon light irradiation, the 2N6S will result in proton dissociation and 6AQ will result in proton association. One of the challenges in using Brønsted PA and PB is the competition with the proton recombination process, meaning the return of the proton to the PA or the deprotonation of the PB upon returning to their ground state. In some cases, other processes can influence this recombination, such as proton transfer to/from another proton acceptor/donor that is not water. In our study, the participation of the formed ions (RO⁻/H⁺/RNH⁺) in the electrochemical process competes with the recombination process. In this section, in the absence of the electrochemical setup, we are targeting the ability of the Nafion membrane to capture and pump protons from one half-cell to the other, which also competes with the recombination process. To explore this, we have used the H-cell configuration while measuring the concentration of protons, i.e., the pH of the solution, in each half-cell. While placing the pH electrode in the half-cell containing the 6AQ PB, a pH increase was measured upon irradiation of 2N6S that continued also in dark, while only upon irradiation of the 6AQ, a decrease in the pH was observed that also continued in the dark until the start of the next cycle (Figure 6b). The opposite trend was obtained while placing the pH electrode in the half-cell containing the 2N6S PA, where the pH decreased upon irradiation of 2N6S and continued to decrease in dark, while upon irradiation of 6AQ, the pH increased and continued to increase in dark (Figure 6b). The mirror image of the two independent experiments indicates a proton transport through the Nafion membrane of the H-cell, resulting in a light-induced modulation of the pH by switching the irradiation between 2N6S and 6AQ. To explain these results, we suggest the following mechanism (Figure 7): (I) First, PA is present in the CE compartment in its protonated form (ROH), while PB is present in its deprotonated form (RN) in the WE compartment. The compartments are separated by Nafion membrane, composed of a hydrophobic tetrafluoroethylene backbone with pending ether groups terminated with
sulfonate groups. As shown in previous studies of Nafion, the sulfonic groups are present both in their protonated and deprotonated states.\[35-36\] (II) Upon the irradiation of the CE compartment, RO$^-$ ions are formed in the excited state, followed by a recombination in the ground state. Far from the Nafion membrane, this H$^+$ recombination will be from the bulk water solution. However, adjacent to the membrane interface, the RO$^-$ ions can recombine with H$^+$ coming from the sulfonic groups, hence, deprotonate them. This, in turn, will induce a cascade of proton transfer reactions that will eventually deprotonate some of the water molecules on the other side of the membrane, thus, generating a proton flux from the WE towards the CE compartment. (III) Following proton transport from one side of the membrane to another, the CE compartment becomes more acidic, while the WE compartment becomes more basic. (IV) Upon the irradiation of the WE compartment, the PB molecules in their excited state (RN$^*$) act as strong bases and they can abstract protons from a proton donor. Away from the membrane, water acts as the donor. However, next to the membrane interface, the sulfonic groups can act as proton donors. As above, this will induce a cascade of proton transfer reactions that will eventually abstract protons from the solution on the other side of the membrane, thus, generating proton flux from the CE towards the WE compartment. Accordingly, the pH in the WE and CE compartments drops and rises back again, respectively, to its initial value.

To explore the light-induced modulation of the pH on the generated photocurrent, we turned to photoelectrochemical measurements where a platinum CE was inserted into the half-cell containing the 2N6S PA and a graphite WE and an Ag/AgCl RE were inserted to a joint half-cell containing the 6AQ PB (Figure 6a). We used this H-cell setup to follow the CA at the negative (-1V) bias regime on the WE (Figure 6c) while irradiating the different half cells in the following sequence: irradiation the 6AQ PB → dark → irradiation the 2N6S PA → dark. As seen in the figure, upon irradiation of 6AQ, a negative photocurrent was obtained, and by turning off the light, a positive current trend was obtained that brought the current close to its initial value. Following the latter, irradiation of 2N6S has induced increased positive photocurrent, which then decreased back to the initial baseline level upon turning off the light. In terms of photocurrent magnitude, in the H-cell configuration, we received a negative photocurrent of ~40 µA/cm$^2$ upon the excitation of the PB and a positive photocurrent of ~20 µA/cm$^2$ upon the excitation of the PA. We suggest that the absolute magnitude of the generated photocurrent upon the excitation of PB is larger than the one of PA due to the direct reduction of the former by the WE (in addition to the effect of pH), in a similar manner to the single-cell setup (Figures 5b and c). On the other side, the PA present in the CE compartment can only
‘interact’ with the WE compartment by proton pumping. In summary, as indicated by our results using the H-cell setup, the pH jump in the WE environment upon applying a bias of -1V induces the decrease in cathodic current, while the pH drop induces the opposite.

**Figure 6.** Manipulating proton shuttling with a photoacid and a photobase in an H-cell configuration. (a) A schematic representation of the photoelectrochemical H-cell setup. (b) The monitored pH in the photobase (top figure) and photoacid (bottom figure) compartments upon alternate irradiation of the PA and PB compartments without the electrochemical setup. (c) Chronoamperometry under -1V bias on the WE upon alternate irradiation of the 6AQ and 2N6S compartments having dark intervals between irradiations ($\lambda_{ex}=340$).
Figure 7. Schematic representation of proton pumping through Nafion membrane. In the schemes, the Nafion membrane separates aqueous solutions of 2N6S PA (on the left side) and 6AQ PB (on the right side).

Conclusions

In this study, we show the potential of using PAs (2N6S) and PBs (6AQ) in a photoelectrochemical setup for light-induced current generation. By using several electrochemical techniques (CV and CA) acquired before and during the irradiation of the solution in both single-cell and two-compartment H-cell configurations, we observed photocurrent generation and discussed the role of ESPT from/to the PA/PB in the electrochemical process. Our results indicate that the formed ions in the excited state (RO⁻/H⁺/RNH⁺) have a crucial role in the electron transfer processes involving the WE and CE in both the negative and positive bias regimes. By using a methylated derivative of a photoacid that cannot undergo the ESPT process, we validated that the observed photocurrent generation...
is not due to the direct sensitization of the electrode by the excited PA. The H-cell configuration allowed to photo-modulate the electrical current intensity and polarity by irradiating a specific half-cell, either the one of the PB or the one of the PA, while the proton-conducting membrane separating the half-cells is serving as a proton pump between the cells. Our study here represents a new concept in photoelectrochemistry and shifts the discussion from purely electronic processes to processes involving proton transfer. The concepts initiated in this study can be further utilized in devices targeting light-responsive energy production, energy storage, and hydrogen formation applications.

Experimental section

**Electrochemical measurements.** All electrochemical measurements were conducted using a PalmSens3 potentiostat. The electrolyte solution in all measurements contained 0.1 M NaCl. In the cyclic voltammetry measurements, the scan rate was 0.02 V/s for the 2N6S and 6AQ measurements and 0.035V/s for the HPTS/MPTS measurements. In chronoamperometry measurements, the time interval was set to 2 s, $E_{DC}$ was -1 V for the experiments at negative potential bias, and 0.5 V for the experiments at positive potential bias. The single-cell configuration was based on a screen-printed electrode with a graphite working electrode with a surface area of 0.079 cm$^2$, platinum counter electrode, and silver coated with silver chloride reference electrode. The concentrations of the photoacids/photobases used in the single-cell configuration were: 0.5 mM for 2N6S and 6AQ and 0.2 mM for HPTS and MPTS. The light irradiation in the single-cell configuration was above the sample using a 340 nm LED with a maximum power output of 60 mW (M340L4, ThorLabs) for the excitation of 2N6S and 6AQ or a 405 nm LED with a maximum power output of 540 mW (M405L4, ThorLabs) for the excitation of HPTS and MPTS. Both LEDs were controlled by a T-cube LED driver (LEDD1B, ThorLabs). The H-cell configuration was based on a home-built glass design with a bottom quartz window. The electrodes in the H-cell configuration were graphite working electrode with a surface area of 0.28 cm$^2$ and the same counter and reference electrodes as described for the single-cell configuration. The concentration of the photoacids/photobases used in the H-cell configuration was 3 mM for both 2N6S and 6AQ. The light irradiation in the H-cell configuration was below the quartz window using a 340 nm LED with a maximum output power of 130 mW (CUD4AF1B, SETi) with a home-built controller.
**UV-Vis and fluorescence spectroscopy.** UV-Vis measurements were performed using Cary 60 spectrophotometer (Agilent) and the fluorescence measurements were performed using Fluorolog fluorometer (HORIBA). A quartz cuvette with a pathlength of 0.5 cm was used for both the UV-Vis and fluorescence measurements. The slit size in the fluorescence measurements was adjusted to 2 nm. The concentration of photoacids/photobases used in the spectroscopy measurements was 0.1mM.

**Acknowledgments**

A.Y. is supported by the Ariane de Rothschild Fellowship. Y.S. is supported by fellowships of the Nancy & Stephen Grand Technion Energy Program (GTEP) and by a Schulich Graduate fellowship. N.Am. thanks the US-Israel Binational Science Foundation (number 2018239), and the Ministry of Science and Technology (number 3-16243), for financial support. N.Ad. thanks the “Nevet” grant from GTEP and a Technion VPR Berman Grant for Energy Research. Some of the results reported in this work were obtained using central facilities at the Technion’s Hydrogen Technologies Research Laboratory (HTRL) supported by the Nancy & Stephen GTEP, the ADELIS Foundation, and the Solar Fuels I-CORE as well as the Russel Berrie Nanotechnology Institute (RBNI). We thank Dr. Rachel Edrei for technical support.

**Conflicts of interest**

There are no conflicts to declare.

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