An Integrated Device for the Solar-Driven Electrochemical Conversion of CO2 to CO

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Letter

# An Integrated Device for the Solar-Driven Electrochemical Conversion of $CO_2$ to CO

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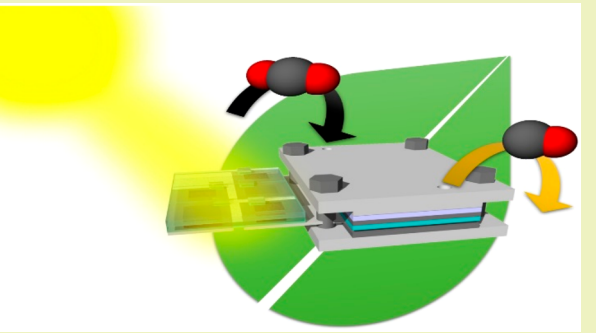
**ABSTRACT:** The conversion of carbon dioxide into value-added products using sunlight, also called artificial photosynthesis, represents a remarkable and sustainable approach to store solar energy, transforming it into chemical energy. There are mainly two strategies to carry out this process: the photocatalytic reduction of carbon dioxide ($CO_2$) or the photovoltaic-powered electrochemical reduction of $CO_2$. Herein, we focus on the latter route, i.e., the development of a device coupling a solar cell to an electrochemical reactor for $CO_2$ reduction. Different literature works demonstrated the possibility to achieve such a coupling, but no evidence of a real integration between the two systems has been given up to now. In this work, we present an integrated device constituted by a dye-sensitized solar module (based on a mesoporous titanium dioxide photoanode) and an electrochemical cell (based on a copper−tin cathode). The integration of the two systems is accomplished through a common platinum-based electrode, which acts either as a cathode for the photovoltaic module and as an anode for the electrochemical reactor. The integrated system was characterized by a stable current of 3.6 mA under continuous solar irradiation, enabling the production of 80 mmol of carbon monoxide per day, with a solar-to-fuel efficiency equal to 0.97%.



**KEYWORDS:** *Artificial photosynthesis, Integrated device, Dye-sensitized solar cells, Photovoltaic module, $CO_2$ reduction reaction, Electrochemical conversion*

## INTRODUCTION

Artificial photosynthesis, i.e., the conversion of solar energy to chemical energy, mimicking the plants' process of natural photosynthesis, has attracted a lot of interest in the scientific community.[1] Essentially, two types of artificial photosynthesis processes are studied by scientists, namely, photocatalytic water splitting,[2] i.e., the conversion of water into oxygen and hydrogen, and the solar-driven carbon dioxide reduction reaction ($CO_2$RR), i.e., the conversion of $CO_2$ to carbon-based value-added products.[3] The latter is of particular interest because it would allow attaining a triple goal: (1) storing the excess energy coming from the Sun that is not put in the electric grid,[4] (2) reduction of atmospheric $CO_2$, i.e., the major greenhouse gas, which can be used as a raw material,[5] and (3) production of valuable chemicals.[6]

Apart from systems employing photoelectrodes,[7−9] there are different examples in the literature dealing with solar-driven $CO_2$ electroreduction obtained by coupling a photovoltaic (PV) device with an electrochemical cell (EC).[10−17] As an example, Kauffman et al. used a commercial 6 V Si solar module to power a two-chamber electrochemical reactor with a gold (Au) cathode and a platinum (Pt) anode which was able to produce more than 400 L/($g_{Au}$ h) of carbon monoxide (CO) with a selectivity of about 96%.[10] Schreier and co-workers employed three series-connected perovskite solar cells to power a single-chamber electrolyzer with a Au cathode[11] and studied a triple-junction GaInP/GaInAs/Ge PV device coupled with a dual-chamber EC based on a $SnO_2$-coated CuO cathode and anode.[12] In both cases, a selectivity toward CO larger than 80% was reached, with solar-to-CO efficiencies equal to 6.5% and 13.4% for perovskite- and triple-junction-based systems, respectively. A 1.4% solar-to-formate efficiency was obtained by White et al. employing a poly-Si solar panel and a three-cell electrolyzer stack composed of indium (In)-based cathodes and iridium oxide ($IrO_2$)-based anodes.[13] Moreover, hydrocarbons and oxygenates can be produced by solar-driven $CO_2$ reduction,[16] with a conversion efficiency larger than 5% by using a III−V/Si tandem PV cell and a two-chamber reactor with a nanostructured copper−silver (Cu−Ag) bimetallic cathode and $IrO_2$ anode. A lower solar-to-hydrocarbons efficiency equal to 2.3% was obtained by a low-

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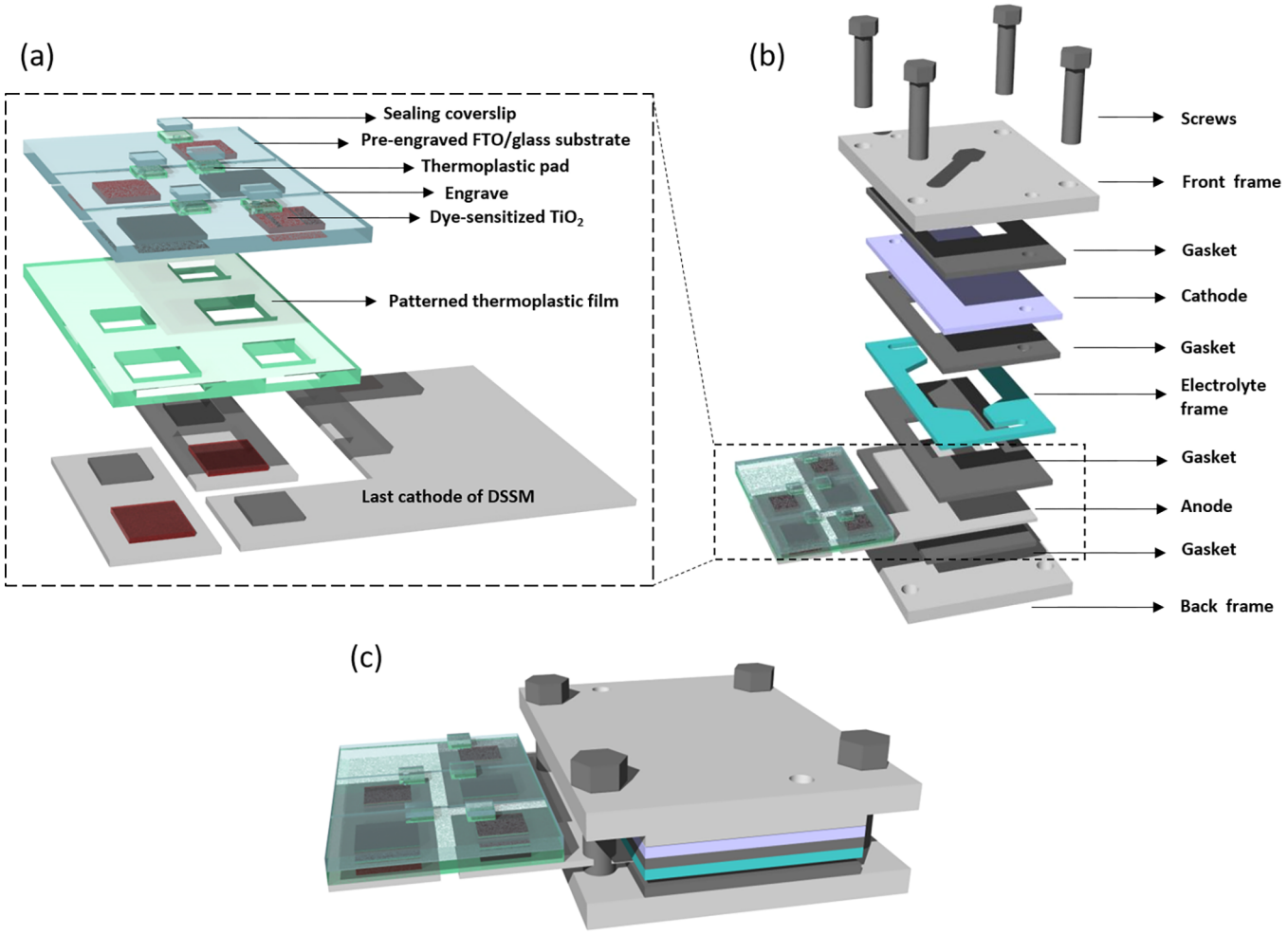


**Figure 1.** Scheme of the integrated PV−EC system: (a) solar module, (b) electrochemical reactor, and (c) integrated device.

cost all-Earth-abundant system, composed of a perovskite PV minimodule and a two-chamber EC based on nanostructured CuO for both the cathode and anode.[17] In all of the above-mentioned and other works,[14,15,18,19] the PV cell/module is coupled to the electrochemical reactor through electrical wire connections, since the solar cell is external or attached to the electrolyzer. In this sense, we can speak of connected systems, but no real integrated systems (i.e., with shared electrodes between the PV and the EC) have been proposed in the literature so far.

In this work, we present, for the first time, an integrated device for the solar-driven electrochemical conversion of $CO_2$ to value-added products. To carry out the integration, we concluded that a third-generation PV technology, namely, dye-sensitized solar cell (DSSC), makes use of Pt as the cathodic electrode;[20] at the same time, Pt is widely used as the anode material in EC for $CO_2$ conversion.[3,6,10] With these premises, we fabricated an integrated system in which the Pt electrode is shared between the dye-sensitized solar module (DSSM) and the electrochemical reactor, acting at the same time both as cathode for the solar device and as anode for the EC. The integrated system was able to carry out the unassisted $CO_2$ reduction to CO under simulated solar irradiation for more than 3 h.

## RESULTS AND DISCUSSION

The PV module is composed of five series-connected DSSCs, similar to our previous work,[21] with an increase in the cell number to five in order to achieve an operating voltage higher than 2.5 V. The module employed a nanocrystalline $TiO_2$ photoanode, Ru-based sensitizer, iodide/tri-iodide electrolyte, and Pt cathode. Two different current collectors were selected for module fabrication: transparent conductive substrate as the front side (top of the device) and titanium foils as the back side (bottom of the device). Details of the fabrication procedure are reported in the Supporting Information. The dimension of the last cathode of the cell series was chosen in order to overpass the PV module footprint and act as the anode for the EC. Concerning the EC, a single-chamber configuration was employed, in which no membrane was used to separate the anode and the cathode, as shown in Figure 1. This configuration has been adopted in order to reduce the total cell overpotential by eliminating the proton exchange membrane (see Supporting Information for details).[11,22] A Cu−Sn electrocatalyst recently proposed by our group,[23,24] characterized by a good selectivity toward CO, was used as the cathodic material. The Cu−Sn cathode was prepared through a cost-efficient electrodeposition route, as detailed in the Supporting Information. The already mentioned Ti-supported Pt was employed as the anode. A $CO_2$-saturated 0.1 M $KHCO_3$ aqueous solution was chosen as the electrolyte. The


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volume of the electrolyte was 7 mL, with a 3 mL headspace. A scheme of the integrated device is depicted in Figure 1.

The performance of the two components of the system was first investigated individually. Figure 2 shows the current−voltage characteristic of the PV model acquired under AM1.5G illumination. By comparing the curve in Figure 2 with the data reported for our previously published DSSM,[21] it can be observed that the addition of the fifth solar cell in the PV module leads to a boost of the voltage with respect to the four-cell module, with an open circuit value of 3.73 V, i.e., almost a 1 V increase. This improvement cannot be simply justified with the addition of a cell since it is larger than the open circuit voltage ($V_{oc}$) of a traditional DSSC (based on the combination of $TiO_2$, Ru-based dye and $I^-/I_3^-$). Therefore, it must be ascribed to the different architectures of the two DSSM. Indeed, in the present study, Ti foils are used as current collectors on one side of the module to allow integration with the electrochemical reactor for $CO_2$ reduction, while gluorine-doped tin oxide (FTO)-coated glasses were used by Scalia et al.[21] This variation induces two main effects: (i) the reduction of the series resistance (accounting for the transport resistance of the substrate) due to a higher conductivity of Ti with respect to FTO and (ii) the *in situ* formation of a $TiO_2$ blocking layer on the Ti surface during the thermal treatment for photoanode preparation. While the former can influence the photogenerated current, the latter can be considered as the main reason responsible for the increased $V_{oc}$ of the present DSSM. In fact, it is well known that the introduction of a very thin $TiO_2$ layer between the current collector and the nanostructured photoanode film allows for preventing electron recombination with a positive effect on the $V_{oc}$.[25] For what concerns the other parameters, both the PV modules exhibit similar currents (short circuit value of about 7 mA) and fill factors (0.48), thus leading to an enhanced photoconversion efficiency of 2.68% for the novel five-cell device. It is worth noting that a maximum power of 13 mW is produced by the DSSM at 2.54 V and that power larger than 10 mW can be obtained in the wide voltage range of 1.7−3.2 V.

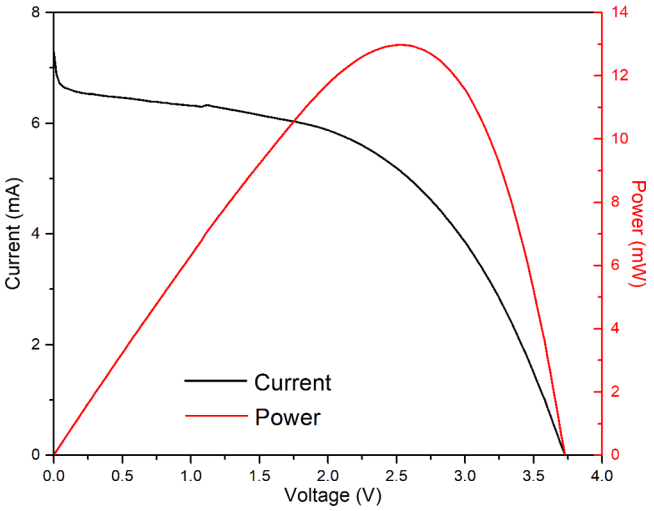


**Figure 2.** Current−voltage characteristic of the five-cell PV module under 1 sun illumination (left axis) and corresponding produced power (right axis).

The performance of the EC was assessed through 1 h $CO_2$ electrolysis tests at different voltages. A micro-gas chromatograph ($\mu$GC) was used for the online measurements of the gaseous products, and a high-performance liquid chromatograph (HPLC) was used for the analysis of the liquid products at the end of each test.[26] During the experiments, a constant $CO_2$ flow of 10 mL/min was maintained in order to saturate the electrolyte and to carry the gaseous products to the $\mu$GC. Figure 3 reports the faradaic efficiency (FE) for the different reaction products as a function of the applied voltage. Only CO and $H_2$ were detected as gaseous products, while just formic acid (HCOOH) was identified as the liquid product. With the exception of low (≤2.6 V) and high (≥3.3 V) voltages, the $CO_2$RR outperforms the competing hydrogen evolution reaction, thus confirming the goodness of our Cu-based electrocatalyst.[23,24] A maximum FE for CO production of about 73% was obtained at 3.0 V, where the total measured current is 3.6 mA (corresponding to a cathodic current density of 6.4 mA/cm$^2$). By comparing this data with those of the PV module, an optimal operating point at 3.0 V can be envisaged for the integrated system since the solar device produces a similar current of 3.7 mA at this voltage.

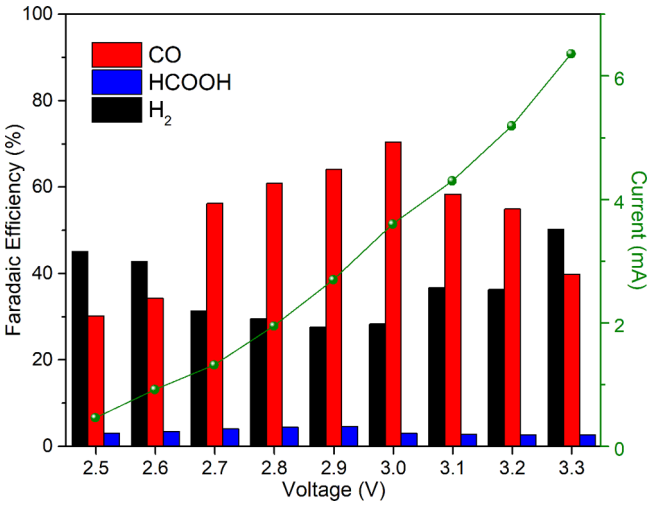


**Figure 3.** Faradaic efficiencies for CO, HCOOH, and $H_2$ formation in EC at various applied voltages during 1 h electrolysis (left axis) and corresponding measured currents (right axis).

Figure 4a shows the measured current−voltage characteristic of the PV module under 1 sun illumination superimposed to that of the EC. As anticipated above, the theoretical operating point, given by the intersection of the two curves, can be found at 3.0 V. At this potential, the power produced by the PV module is 11.5 mW, and the partial current (density) for CO production is equal to 2.6 mA (4.7 mA/cm$^2$). The electrolysis experiment on the integrated PV−EC system was carried out under 1 sun illumination for more than 3 h, during which the produced gases were measured by $\mu$GC (the liquid products were measured after the test through HPLC). The results of this measurement are reported in Figure 4b and c. The integrated device is characterized by a constant voltage of 3.00 ± 0.06 V for all the period of investigation and a by corresponding stable current density equal to 6.5 ± 0.4 mA/cm$^2$ after 30 min of operation (Figure 4b). It is worth noting that such a stability is in line with or even better than those reported for nonintegrated PV−EC systems.[7,14,18] In the initial phase of the electrolysis, the decrease in the current density is associated with the reduction of oxide species in the Cu−Sn


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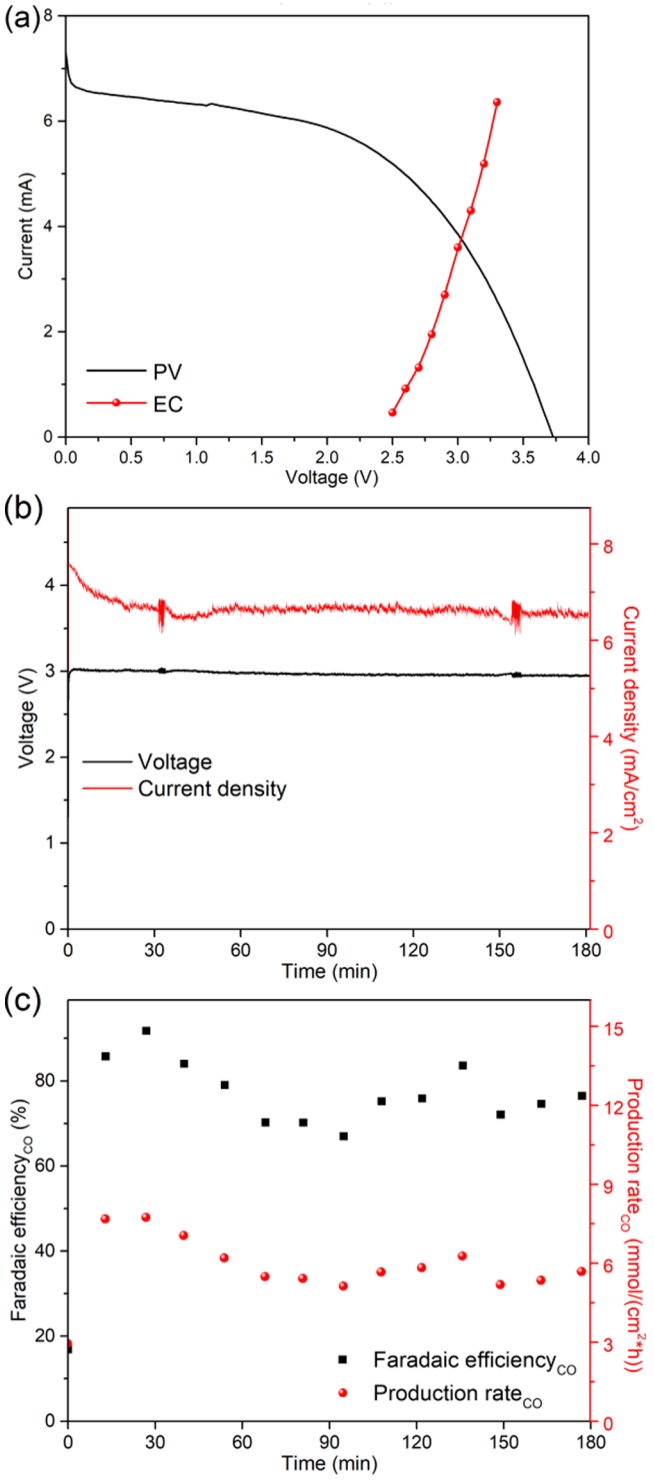


**Figure 4.** (a) Current–voltage characteristic of the five-cell PV module under 1 sun illumination and of the EC. (b) Voltage (left axis) and current density (right axis) during a 3 h test of the integrated PV–EC system under 1 sun illumination. (c) FE (left axis) and production rate (right axis) for CO during a 3 h test of the integrated PV–EC system under 1 sun illumination.

cathode.[23,24] In accordance with the analysis conducted on the bare EC, only CO and HCOOH were detected as $CO_2$RR products, with average FE values equal to about 78% and 2%, respectively. The FE for CO is plotted as a function of the electrolysis time in Figure 4c. It can be observed that it remains stable during 3 h of operation, thus proving that sunlight and $CO_2$ can be efficiently and continuously converted by our integrated device, similarly to PV–EC coupled systems present in the literature.[11,12,17] A CO production rate of about 80 mmol/day (considering 24 h of continuous operation) was obtained along the 3 h test.

The obtained data was employed to calculate the solar-to-CO efficiency $\eta_{STC}$ of our integrated system, according to the formula

$$\eta_{STC} = \frac{E^0_{CO_2/CO} \cdot J \cdot FE_{CO}}{W_{sol}} \quad (1)$$

where $E^0_{CO_2/CO}$ is the standard cell potential when the EC conducts the $CO_2$RR to CO (equal to 1.34 V), $J$ is the current density of the PV module, $FE_{CO}$ is the faradaic efficiency for CO, and $W_{sol}$ is the solar irradiance.[11] A solar-to-CO efficiency equal to 0.79% is found for our integrated PV–EC system. This efficiency can be further increased considering also $H_2$ as a secondary product (for example, for the production of syngas),[27] leading to a total solar-to-fuel efficiency of 0.97%. The obtained values are comparable to the efficiencies presented in the literature for coupled PV–EC systems.[14] Better results have been also reported.[11,17,18] However, it has to be highlighted that the performance of our integrated PV–EC system can be improved since different aspects can be optimized:

(i) An additional PV cell can be added to the module in order to enlarge the voltage window of the module and shift the operating point in a region of higher cell efficiency.

(ii) Adapting the active area of the PV module to the electrocatalyst one can be done in order to match the two currents.

These aspects have already been taken into consideration in a new work which is in progress in our lab. Nevertheless, the present work demonstrates the feasibility of an integrated PV–EC system that enables the solar-driven electrochemical conversion of $CO_2$.

## CONCLUSION

An integrated system composed of a third-generation PV module and an EC for the electroreduction of $CO_2$ under solar illumination has been presented here. The PV module is based on a series of five DSSCs, while the EC is based on a Cu–Sn electrocatalyst. The integration of the two devices has been achieved through a common Pt-based electrode, which works both as a cathode for the PV module and as an anode for the EC.

A stable voltage of 3 V has been obtained from the integrated system under 1 sun illumination for 3 h, during which CO production with a FE of 78% was achieved as a result of the unassisted $CO_2$RR. This represents the first integrated artificial photosynthesis device for the solar-driven electrochemical conversion of $CO_2$. This system is currently under optimization in our laboratory in order to improve the overall device efficiency.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c02088.



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Experimental section, measurements of membrane overpotential, scheme of DSSM, scheme of EC, and pictures of the integrated PV−EC device (PDF)

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### Author Contributions

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

### Notes

The authors declare no competing financial interest.

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