

An Integrated Device for the Solar-Driven Electrochemical Conversion of CO<sub>2</sub> to CO

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# 1 An Integrated Device for the Solar-Driven Electrochemical 2 Conversion of CO<sub>2</sub> to CO

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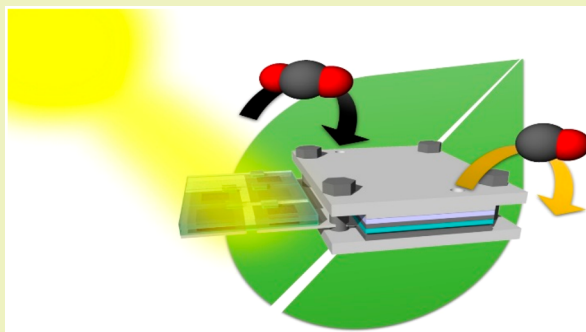
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Supporting Information

5 **ABSTRACT:** The conversion of carbon dioxide into value-added  
6 products using sunlight, also called artificial photosynthesis, represents a  
7 remarkable and sustainable approach to store solar energy, transforming  
8 it into chemical energy. There are mainly two strategies to carry out this  
9 process: the photocatalytic reduction of carbon dioxide (CO<sub>2</sub>) or the  
10 photovoltaic-powered electrochemical reduction of CO<sub>2</sub>. Herein, we  
11 focus on the latter route, i.e., the development of a device coupling a  
12 solar cell to an electrochemical reactor for CO<sub>2</sub> reduction. Different  
13 literature works demonstrated the possibility to achieve such a coupling,  
14 but no evidence of a real integration between the two systems has been  
15 given up to now. In this work, we present an integrated device  
16 constituted by a dye-sensitized solar module (based on a mesoporous  
17 titanium dioxide photoanode) and an electrochemical cell (based on a copper–tin cathode). The integration of the two systems is  
18 accomplished through a common platinum-based electrode, which acts either as a cathode for the photovoltaic module and as an  
19 anode for the electrochemical reactor. The integrated system was characterized by a stable current of 3.6 mA under continuous solar  
20 irradiation, enabling the production of 80 mmol of carbon monoxide per day, with a solar-to-fuel efficiency equal to 0.97%.

21 **KEYWORDS:** Artificial photosynthesis, Integrated device, Dye-sensitized solar cells, Photovoltaic module, CO<sub>2</sub> reduction reaction,  
22 Electrochemical conversion



## 23 ■ INTRODUCTION

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

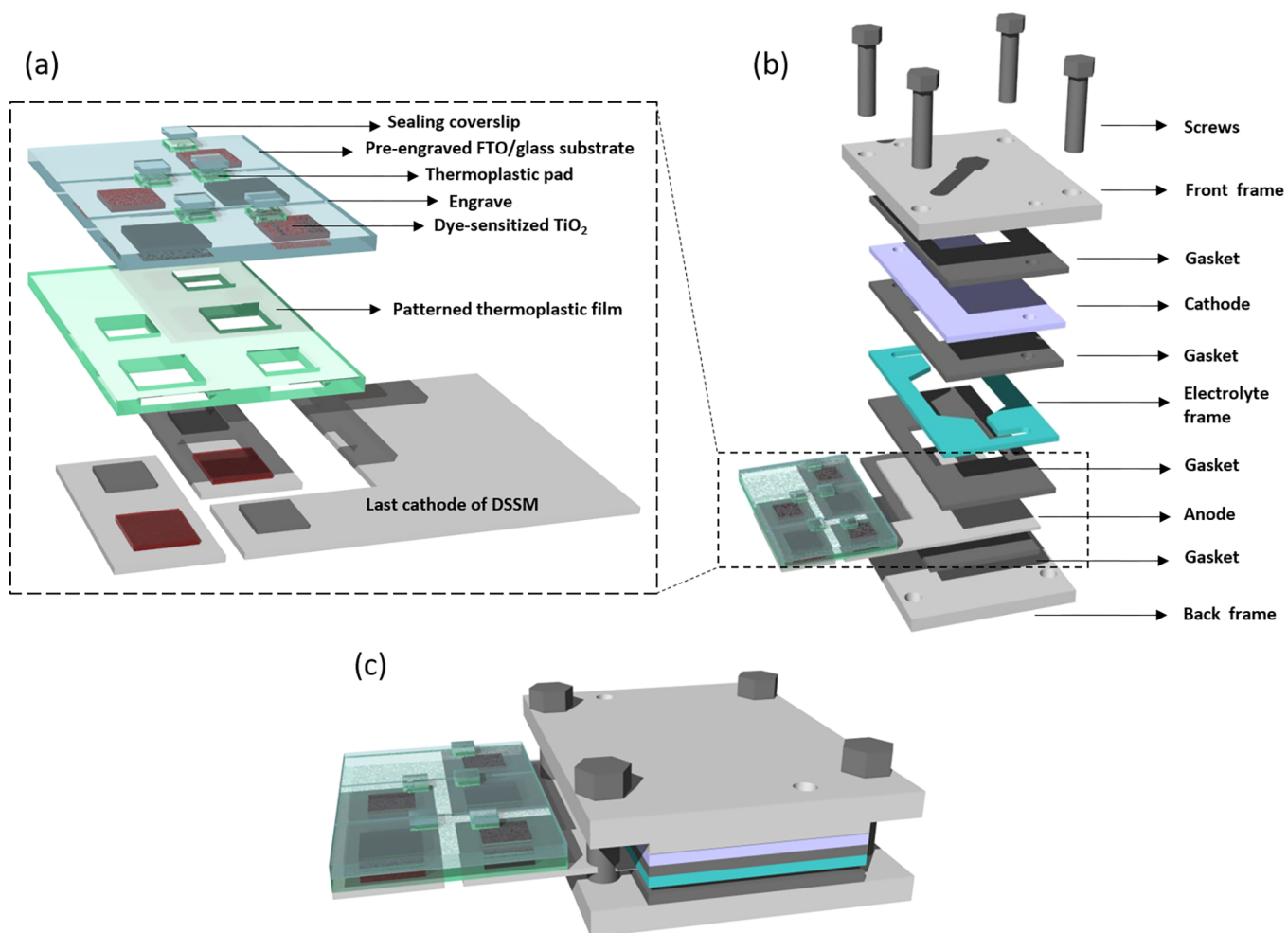
38 Apart from systems employing photoelectrodes,<sup>7–9</sup> there are  
39 different examples in the literature dealing with solar-driven  
40 CO<sub>2</sub> electroreduction obtained by coupling a photovoltaic  
41 (PV) device with an electrochemical cell (EC).<sup>10–17</sup> As an  
42 example, Kauffman et al. used a commercial 6 V Si solar  
43 module to power a two-chamber electrochemical reactor with a  
44 gold (Au) cathode and a platinum (Pt) anode which was able  
45 to produce more than 400 L/(g<sub>Au</sub> h) of carbon monoxide  
46 (CO) with a selectivity of about 96%.<sup>10</sup> Schreier and co-

workers employed three series-connected perovskite solar cells 47  
to power a single-chamber electrolyzer with a Au cathode<sup>11</sup> 48  
and studied a triple-junction GaInP/GaInAs/Ge PV device 49  
coupled with a dual-chamber EC based on a SnO<sub>2</sub>-coated CuO 50  
cathode and anode.<sup>12</sup> In both cases, a selectivity toward CO 51  
larger than 80% was reached, with solar-to-CO efficiencies 52  
equal to 6.5% and 13.4% for perovskite- and triple-junction- 53  
based systems, respectively. A 1.4% solar-to-formate efficiency 54  
was obtained by White et al. employing a poly-Si solar panel 55  
and a three-cell electrolyzer stack composed of indium (In)- 56  
based cathodes and iridium oxide (IrO<sub>2</sub>)-based anodes.<sup>13</sup> 57  
Moreover, hydrocarbons and oxygenates can be produced by 58  
solar-driven CO<sub>2</sub> reduction,<sup>16</sup> with a conversion efficiency 59  
larger than 5% by using a III–V/Si tandem PV cell and a two- 60  
chamber reactor with a nanostructured copper–silver (Cu– 61  
Ag) bimetallic cathode and IrO<sub>2</sub> anode. A lower solar-to- 62  
hydrocarbons efficiency equal to 2.3% was obtained by a low- 63

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

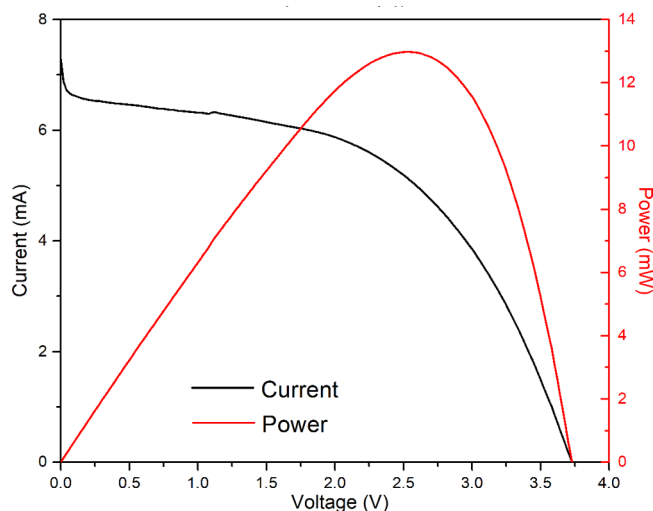
cost all-Earth-abundant system, composed of a perovskite PV minimodule and a two-chamber EC based on nanostructured CuO for both the cathode and anode.<sup>17</sup> In all of the above-mentioned and other works,<sup>14,15,18,19</sup> the PV cell/module is coupled to the electrochemical reactor through 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<sub>2</sub> 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;<sup>20</sup> at the same time, Pt is widely used as the anode material in EC for CO<sub>2</sub> conversion.<sup>3,6,10</sup> 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<sub>2</sub> 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,<sup>21</sup> 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<sub>2</sub> 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).<sup>11,22</sup> A Cu–Sn electrocatalyst recently proposed by our group,<sup>23,24</sup> 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<sub>2</sub>-saturated 0.1 M KHCO<sub>3</sub> aqueous solution was chosen as the electrolyte. The

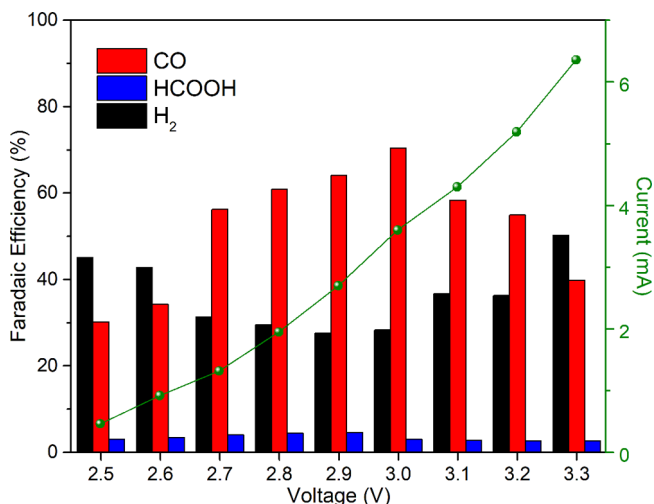
114 volume of the electrolyte was 7 mL, with a 3 mL headspace. A  
 115 scheme of the integrated device is depicted in Figure 1.  
 116 The performance of the two components of the system was  
 117 first investigated individually. Figure 2 shows the current–



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

118 voltage characteristic of the PV model acquired under AM1.5G  
 119 illumination. By comparing the curve in Figure 2 with the data  
 120 reported for our previously published DSSM,<sup>21</sup> it can be  
 121 observed that the addition of the fifth solar cell in the PV  
 122 module leads to a boost of the voltage with respect to the four-  
 123 cell module, with an open circuit value of 3.73 V, i.e., almost a  
 124 1 V increase. This improvement cannot be simply justified with  
 125 the addition of a cell since it is larger than the open circuit  
 126 voltage ( $V_{oc}$ ) of a traditional DSSC (based on the combination  
 127 of  $\text{TiO}_2$ , Ru-based dye and  $\text{I}^-/\text{I}_3^-$ ). Therefore, it must be  
 128 ascribed to the different architectures of the two DSSM.  
 129 Indeed, in the present study, Ti foils are used as current  
 130 collectors on one side of the module to allow integration with  
 131 the electrochemical reactor for  $\text{CO}_2$  reduction, while fluorine-  
 132 doped tin oxide (FTO)-coated glasses were used by Scalia et  
 133 al.<sup>21</sup> This variation induces two main effects: (i) the reduction  
 134 of the series resistance (accounting for the transport resistance  
 135 of the substrate) due to a higher conductivity of Ti with  
 136 respect to FTO and (ii) the *in situ* formation of a  $\text{TiO}_2$   
 137 blocking layer on the Ti surface during the thermal treatment  
 138 for photoanode preparation. While the former can influence  
 139 the photogenerated current, the latter can be considered as the  
 140 main reason responsible for the increased  $V_{oc}$  of the present  
 141 DSSM. In fact, it is well known that the introduction of a very  
 142 thin  $\text{TiO}_2$  layer between the current collector and the  
 143 nanostructured photoanode film allows for preventing electron  
 144 recombination with a positive effect on the  $V_{oc}$ .<sup>25</sup> For what  
 145 concerns the other parameters, both the PV modules exhibit  
 146 similar currents (short circuit value of about 7 mA) and fill  
 147 factors (0.48), thus leading to an enhanced photoconversion  
 148 efficiency of 2.68% for the novel five-cell device. It is worth  
 149 noting that a maximum power of 13 mW is produced by the  
 150 DSSM at 2.54 V and that power larger than 10 mW can be  
 151 obtained in the wide voltage range of 1.7–3.2 V.  
 152 The performance of the EC was assessed through 1 h  $\text{CO}_2$   
 153 electrolysis tests at different voltages. A micro-gas chromato-

graph ( $\mu\text{GC}$ ) was used for the online measurements of the  
 gaseous products, and a high-performance liquid chromato-  
 graph (HPLC) was used for the analysis of the liquid products  
 at the end of each test.<sup>26</sup> During the experiments, a constant  
 $\text{CO}_2$  flow of 10 mL/min was maintained in order to saturate  
 the electrolyte and to carry the gaseous products to the  $\mu\text{GC}$ .  
 Figure 3 reports the faradaic efficiency (FE) for the different

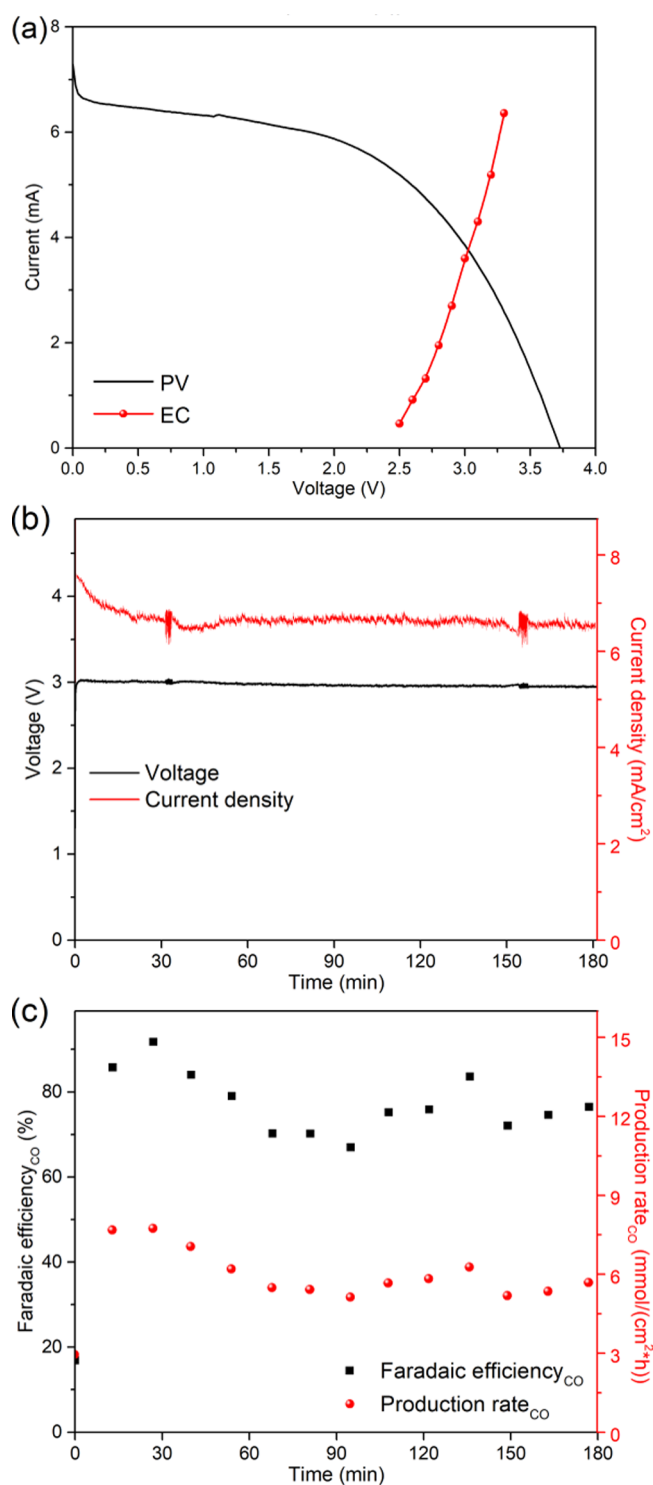


**Figure 3.** Faradaic efficiencies for  $\text{CO}$ ,  $\text{HCOOH}$ , and  $\text{H}_2$  formation in EC at various applied voltages during 1 h electrolysis (left axis) and corresponding measured currents (right axis).

reaction products as a function of the applied voltage. Only  
 $\text{CO}$  and  $\text{H}_2$  were detected as gaseous products, while just  
 formic acid ( $\text{HCOOH}$ ) was identified as the liquid product.  
 With the exception of low ( $\leq 2.6$  V) and high ( $\geq 3.3$  V)  
 voltages, the  $\text{CO}_2\text{RR}$  outperforms the competing hydrogen  
 evolution reaction, thus confirming the goodness of our Cu-  
 based electrocatalyst.<sup>23,24</sup> A maximum FE for  $\text{CO}$  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  $6.4 \text{ mA}/\text{cm}^2$ ). 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 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  $\text{CO}$   
 production is equal to 2.6 mA ( $4.7 \text{ mA}/\text{cm}^2$ ). 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  $\mu\text{GC}$  (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  $3.00 \pm 0.06$  V for all the period of investigation and a by  
 corresponding stable current density equal to  $6.5 \pm 0.4 \text{ mA}/\text{cm}^2$  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.<sup>7,14,18</sup> 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





**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.

stable during 3 h of operation, thus proving that sunlight and  $\text{CO}_2$  can be efficiently and continuously converted by our integrated device, similarly to PV–EC coupled systems present in the literature.<sup>11,12,17</sup> 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  $\eta_{\text{STC}}$  of our integrated system, according to the formula

$$\eta_{\text{STC}} = \frac{E_{\text{CO}_2/\text{CO}}^0 \cdot J \cdot \text{FE}_{\text{CO}}}{W_{\text{sol}}} \quad (1)$$

where  $E_{\text{CO}_2/\text{CO}}^0$  is the standard cell potential when the EC conducts the  $\text{CO}_2$ RR to CO (equal to 1.34 V),  $J$  is the current density of the PV module,  $\text{FE}_{\text{CO}}$  is the faradaic efficiency for CO, and  $W_{\text{sol}}$  is the solar irradiance.<sup>11</sup> 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  $\text{H}_2$  as a secondary product (for example, for the production of syngas),<sup>27</sup> 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.<sup>14</sup> Better results have been also reported.<sup>11,17,18</sup> However, it has to be highlighted that the performance of our integrated PV–EC system can be improved since different aspects can be optimized:

- 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.
- 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  $\text{CO}_2$ .

## CONCLUSION

An integrated system composed of a third-generation PV module and an EC for the electroreduction of  $\text{CO}_2$  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  $\text{CO}_2$ RR. This represents the first integrated artificial photosynthesis device for the solar-driven electrochemical conversion of  $\text{CO}_2$ . 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>.

cathode.<sup>23,24</sup> In accordance with the analysis conducted on the bare EC, only CO and HCOOH were detected as  $\text{CO}_2$ 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

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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