Selective Catalytic Electrocatalytic Reduction of CO₂ at Silicon Nanowires (SiNWs) Photocathodes Using Non-Noble Metal-Based Manganese Carbonyl Bipyridyl Molecular Catalysts in Solution and Grafted onto SiNWs

Encarnación Torralba-Penalver, Yun Luo, Jean-Daniel Compain, Sylvie Chardon-Noblat, and Bruno Fabre

1. INTRODUCTION

With the rising atmospheric CO₂ levels, a large variety of strategies have been developed to efficiently convert this molecule to high value-added compounds. Nevertheless, one of the main issues related to the challenge of CO₂ molecule conversion is its extreme stability. As a matter of fact, CO₂ is highly thermodynamically stable. Reactions involving CO₂ formic acid (HCOOH) for instance. produce useful chemicals, such as carbon monoxide (CO) or...
reports devoted to the electrocatalytic reduction of CO\textsubscript{2} at traditional electrodes, the use of SCs as photocathodes has been much less explored. As an example, Kubiak\textsuperscript{9,26,27} Sato\textsuperscript{8,20} and Ishitani\textsuperscript{30} groups have demonstrated from cyclic voltammetry experiments that the electrocatalytic potential corresponding to the reduction of CO\textsubscript{2} with noble metals (Re, Ru)-based carbonyl molecular catalysts in solution or attached to SC surfaces can be lowered on noble metals (Re, Ru)-based carbonyl molecular catalysts in Kubiak cathodes has been much less explored. As an example, traditional conducting electrodes, the use of SCs as photoelectrochemical systems studied. The CO\textsubscript{2} electrocatalysts, Mn non-noble-metal-based complexes, which have been demonstrated from cyclic voltammetry experiments that the electrocatalytic potential corresponding to the reduction of CO\textsubscript{2} with noble metals (Re, Ru)-based carbonyl molecular catalysts in solution or attached to SC surfaces can be lowered on illuminated p-type Si, InP and NiO photocathodes when compared to the electrocatalysis on “classical” glassy carbon electrodes.

In the present work, p-type hydrogen-terminated silicon(100) nanowires (SiNWs–H) is used as a photocathode for the electroreduction of CO\textsubscript{2} in the presence of different non-noble metal (Mn)-based carbonyl bipyridyl complexes, acting as homogeneous catalysts for the reduction process. Compared with planar hydrogen-terminated silicon (Si–H), SiNWs–H can produce larger photocurrents and establish charge transfer at less-negative potentials, due to the multi-faceted nature of the nanowires.\textsuperscript{31} As a matter of fact, in an array of high-aspect-ratio nanostructures such as SiNWs, light can be absorbed effectively along the long axis of the structure. Furthermore, they are easy to prepare\textsuperscript{32} and highly stable under reductive conditions.\textsuperscript{33} Regarding molecular electrocatalysts, Mn non-noble-metal-based complexes, which have been first prepared and studied in our group\textsuperscript{17,34} and since then have received careful attention from other research groups,

![Diagram](image-url)

Scheme 1. Mn(I)-Based Carbonyl Bipyridyl Molecular Catalysts Used in This Study

In this work, cyclic voltammetry combined with electrochemical impedance spectroscopy, chronoamperometry measurements, and exhaustive electrolysis allow qualitative and quantitative description of the performances of the different photoelectrochemical systems studied. The CO\textsubscript{2} electrocatalyst at both planar and nanostructured silicon photocathodes was performed using various Mn-based complexes (Scheme 1). This report also includes the discussion of the general voltammetric features related to the electrocatalytic process and the analysis of the stability of the different interfaces during controlled-potential preparative-scale electrolysis. Key parameters characterizing the physical properties of the different semiconductor/liquid junctions, such as the built-in voltage, the barrier height, or the depletion width within the space-charge layer, have been determined. Moreover, the energy conversion characteristics of each investigated system (fill factor and energy conversion efficiency) have also been quantified. Herein, we demonstrate that SiNWs–H stands as an efficient photocathode to perform the CO\textsubscript{2} electroreduction with respect to planar Si–H, showing better stability, double built-in voltages, and space-charge layer widths under electrocatalytic conditions, as well as higher fill factors and better energy conversion efficiencies.

Finally, as an ongoing work, we also present preliminary results on Mn-based modified SiNWs photocathodes prepared by electropolymerization of a new Mn molecular complex incorporating an N-functionalized pyrrole derivative (Scheme 1). Indeed, it is worth emphasizing that the transfer of the catalyst from the solution phase to solid interfaces is an essential prerequisite for technologically viable future applications related to electrocatalysis at photocathodes.

2. RESULTS AND DISCUSSION

2.1. Cyclic Voltammetry Studies. Electrochemical measurements were performed in CH\textsubscript{3}CN + 0.1 M Bu\textsubscript{4}NClO\textsubscript{4} under different conditions: argon, CO\textsubscript{2}, and CO\textsubscript{3} + 5% v/v H\textsubscript{2}O at Si–H and SiNWs–H photocathodes. Same experiments were also carried out at a glassy carbon electrode (GCE) considered as reference. Typical cyclic voltammograms (CVs) corresponding to the reduction of the Mn(I) tricarbonyl complex [Mn(bpy) (CO)\textsubscript{3}(CH\textsubscript{3}CN)]\textsubscript{2} (bpy = 2,2′-bipyridine) at flat Si–H and SiNWs–H in the dark and under irradiation through a red filter (λ > 600 nm; fluence: 20 mW cm\textsuperscript{2}) are shown in Figure 1. The CVs obtained with the two other investigated Mn-based complexes, [Mn(bpy) (CO)Br] and [Mn(dmbpy) (CO)\textsubscript{2}(CH\textsubscript{3}CN)]\textsubscript{2} (dmbpy = 4,4′-dimethyl-2,2′-bipyridine) are given in Figures S2 and S3 (Supporting Information).

The electrochemical behavior of these Mn(I) tricarbonyl complexes at GCE has already been reported by us.\textsuperscript{17,34} Briefly, the CVs of a solution of [Mn(bpy) (CO)\textsubscript{3}(CH\textsubscript{3}CN)]\textsubscript{2} (bpy = 2,2′-bipyridine) at 1 mM in CH\textsubscript{3}CN + 0.1 M Bu\textsubscript{4}NClO\textsubscript{4} at flat Si–H (left side panel) and SiNWs–H (right side panel) in the dark (dotted red lines) and under illumination through a red filter (20 mW cm\textsuperscript{2}; solid red lines) under Ar (a, d), CO\textsubscript{2} (b, e) and CO\textsubscript{3} + 5% v/v H\textsubscript{2}O (c, f). Black lines correspond to the CVs obtained at GCE. Potential scan rate: 0.1 V s\textsuperscript{-1}. 

![Figure 1: CVs](image-url)
in the cathodic potential range, they undergo two successive irreversible one-electron reduction waves (Figure 1a,b; black lines), leading to the formation of a dimer \([\text{Mn}^0(L)\text{(CO)}_3]_2\) (L: ligand) and the anionic mononuclear species \([\text{Mn}(L)\text{(CO)}_3]^-\), respectively, following eqs 1–3.

\[
\text{[Mn}(L)\text{(CO)}_3]\text{(CH}_3\text{CN})^+ + e^- \rightarrow \text{[Mn}(L)\text{(CO)}_3]\text{(CH}_3\text{CN})
\]

(1)

\[
\text{[Mn}(L)\text{(CO)}_3\text{CH}_3\text{CN})] \rightarrow 1/2\text{[Mn}(L)\text{(CO)}_3]_2 + \text{CH}_3\text{CN}
\]

(2)

\[
\text{[Mn}(L)\text{(CO)}_3]_2 + 2e^- \rightarrow 2\text{[Mn}(L)\text{(CO)}_3]^-
\]

(3)

The addition of water to the \(\text{CO}_2\)-saturated electrolyte solution of \([\text{Mn}(bpy)\text{(CO)}_3\text{(CH}_3\text{CN})]\text{(PF}_6)\) causes an enhancement in the cathodic current (Figure 1c), which indicates the involvement of the reduced Mn dimer in the electrocatalytic process.

A similar electrochemical behavior was observed at illuminated flat Si–H and SiNWs–H (Figure 1). The redox processes ascribed to the Mn complex are observed at less-negative potentials on SiNWs–H. We also notice the presence of a shoulder between the two principal cathodic peaks, which was observed only at flat Si–H (Figure 1a,b). The origin of this feature is thought to be due to a redox-active species like \([\text{Mn}(bpy)\text{(CO)}_3X]\) wherein an acetonitrile ligand would have been exchanged by a better electron-donating ligand, such as water, halogen, or also hydride, which could be present on the Si–H surface at the photoelectrode interface. This hypothesis seems reasonable because such features were not observed on the CVs of the Mn complex at either GCE or SiNWs–H electrode which were subjected to different surface treatment than flat Si–H.

The cathodic photocurrent density was slightly increased under \(\text{CO}_2\) and more strongly increased under \(\text{CO}_2\) in the presence of water. It must be underlined that the CVs at either GCE or SiNWs–H for \(\text{CO}_2\) +5% \(\text{H}_2\text{O}\) are, respectively, 0.48 and 0.75 mA cm\(^{-2}\), leading to an accentuated S-shaped response. The electrode potential for which there is no space-charge region in the semiconductor. Toward this goal, impedance spectroscopy analysis was performed on illuminated silicon electrodes. It is worth noting that the cathodic current corresponding to the reduction of the Mn complex at GCE is nearly zero at this potential (≈1.0 V) in all media. These results actually support an activation of the electrocatalytic process by photogenerated minority charge carriers (namely, electrons) at illuminated silicon electrodes.

<table>
<thead>
<tr>
<th>medium</th>
<th>GCE</th>
<th>Si–H</th>
<th>SiNWs–H</th>
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<tbody>
<tr>
<td>Ar</td>
<td>(-1.07)</td>
<td>(-1.47)</td>
<td>(-0.82)</td>
</tr>
<tr>
<td>(\text{CO}_2)</td>
<td>(-1.07)</td>
<td>(-1.50)</td>
<td>(-0.77)</td>
</tr>
<tr>
<td>(\text{CO}_2 + 5% \text{H}_2\text{O})</td>
<td>(-1.10)</td>
<td>(-0.83)</td>
<td>(-0.95)</td>
</tr>
</tbody>
</table>

*Values in V vs saturated calomel electrode (SCE). The semiconducting surfaces were irradiated through a red filter (20 mW cm\(^{-2}\)).

Table 1. Redox Peak Potentials for the Different Mn Carbonyl Complexes at 1 mM in CH\(_3\)CN + 0.1 M Bu\(_4\)NClO\(_4\) (Figures 1, S2, and S3)

Efficiency to decouple minority carrier generation and collection. It is worth noting that the cathodic current corresponding to the reduction of the Mn complex at GCE is nearly zero at this potential (≈1.0 V) in all media. These results actually support an activation of the electrocatalytic process by photogenerated minority charge carriers (namely, electrons) at illuminated silicon electrodes.

Similar features were observed for \([\text{Mn}(dmbpy)\text{(CO)}_3\text{(CH}_3\text{CN})]\text{(PF}_6)\) and \([\text{Mn}(bpy)\text{(CO)}_3\text{Br}]\) complexes, with higher photocurrent densities for the bpy analogue (Figure S2 and S3). The spectra showed the characteristic absorbance bands already reported for these complexes, including a shift in the absorbance band of \([\text{Mn}(bpy)\text{(CO)}_3\text{Br}]\) due to the formation of the corresponding Mn acetonitrile derivative by a solvolysis process eq 4.17

\[
\text{[Mn}(L)\text{(CO)}_3\text{Br}] + \text{CH}_3\text{CN} \rightarrow \text{[Mn}(L)\text{(CO)}_3\text{(CH}_3\text{CN})]^+ + \text{Br}^-
\]

(4)

No degradation of the complexes over moderate irradiation periods (~90 min) was inferred from the spectra.

2.2. Energy Diagram of the Semiconductor/Electrolyte Interface at Equilibrium. To build the energy diagram of Si–H and SiNWs–H interfaces in equilibrium with the different molecular catalyst solutions, it is essential to estimate the flatband potential \(V_b\) of the silicon surface, that is, the electrode potential for which there is no space-charge region in the semiconductor. Toward this goal, impedance spectroscopy measurements were performed in the dark under depletion conditions (i.e., depletion of valence band holes in the space charge region of the p-type surface). Under these conditions, \(V_b\) can be estimated from the commonly used Mott–Schottky (MS) plot (\(C^2\) vs \(E\)) that gives the space-charge capacitance C.
as a function of the electrode potential $E$ (see Appendix in the SI). From the intercept and the slope of a linear MS plot, the dopant density $N_D$ and $V_{fb}$ of a given semiconductor can be easily determined.

Figure 2 shows the different MS plots obtained for the molecular catalyst $[\text{Mn(dmbpy)}\ (\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$ in the three investigated media. For the sake of simplicity, only the MS plots measured at 50 kHz are shown, though several frequencies were applied giving comparable values of $V_{fb}$ and $N_D$ (SI).

Two slopes can be distinguished in the $C^{-2}$ vs $E$ plots, as already reported for other $p$-type silicon surfaces. These deviations from ideality are attributed to the critical dependence that $p$-type silicon exhibits on the initial surface treatment, in contrast to the case of $n$-type silicon. The average $V_{fb}$ values estimated from the first slope of the linear MS plot at higher potentials, together with the open circuit potential values, OCP, measured in each medium are gathered in Table 2.

$V_{fb}$ was also estimated from the second slope of the MS plots, but the highly positive values obtained ($>0.8$ V vs SCE) were considered to be not relevant and therefore immediately discarded. An average value for the dopant density $N_D$ of $(1.8 \pm 0.2) \times 10^{15}$ cm$^{-3}$ was obtained from the first slope of the linear MS plot, which matched adequately the resistivity value provided by the distributor.

Some trends can be drawn from such data. First, the $V_{fb}$ values calculated for SiNWs–H in contact with $[\text{Mn(dmbpy)}\ (\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$ are slightly more positive than those obtained with flat Si–H. This was not the case for the other two Mn-based complex homologues (Table 2) for which $V_{fb}$ was found to not depend significantly on the structuring state of the silicon electrode. Second, a systematic decrease in both OCP and $V_{fb}$ values when adding $5\%$ of $\text{H}_2\text{O}$ under CO$_2$ atmosphere was observed for all the tested systems with both silicon surfaces. For instance, the addition of water into a CO$_2$-saturated solution of $[\text{Mn(dmbpy)}\ (\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$ led to a decrease in OCP of ca. 100 and 260 mV on Si–H and SiNWs–H, respectively, whereas the $V_{fb}$ values decreased around 200 mV for both silicon electrodes. The first phenomenon (decrease in OCP) clearly indicates a change in the potential of the redox couple of the catalyst at equilibrium with the silicon surface, consistent with the involvement of a different intermediate between the Mn complex and CO$_2$ in the presence or absence of water. The second phenomenon (decrease in $V_{fb}$) might be attributed to a partial oxidation of the silicon surface upon water addition, with the consequent generation of surface states leading to the nonideal situation of Fermi Level pinning. All the OCP values obtained at SiNWs–H were systematically more negative than those obtained at Si–H, which implies the creation of a higher built-in voltage at the interface SiNWs/catalyst solution (Figure 3 and Table S1) and in agreement with the higher cathodic photocurrent density observed for SiNWs–H (Figure 1, S2 and S3). From the OCP, $N_D$ and $V_{fb}$ values gathered in Table 2, the different interfacial energetic parameters which characterize the semiconductor/solution system at electrochemical equilibrium can be calculated and be used to depict the corresponding energetic diagram (see Appendix for any detail). As an example, Figure 3 shows the energy diagram at the interface formed between a solution of $[\text{Mn(bpy)}\ (\text{CO})_3\text{Br}]$ and Si–H or SiNWs–H under argon, CO$_2$ and CO$_2$ + 5\% v/v H$_2$O.

<table>
<thead>
<tr>
<th>medium</th>
<th>OCP/V</th>
<th>$V_{fb}$/V</th>
<th>OCP/V</th>
<th>$V_{fb}$/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>$-0.25$</td>
<td>$0.10$</td>
<td>$-0.35$</td>
<td>$0.20$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>$-0.24$</td>
<td>$0.02$</td>
<td>$-0.32$</td>
<td>$0.13$</td>
</tr>
<tr>
<td>CO$_2$ + $5%$ H$_2$O</td>
<td>$-0.36$</td>
<td>$-0.11$</td>
<td>$-0.49$</td>
<td>$-0.01$</td>
</tr>
</tbody>
</table>

Table 2. Flatband Potentials $V_{fb}$ and Open Circuit Potentials OCP (V vs SCE) Obtained from Solutions of the Different Mn Carbonyl Complexes at 1 mM in CH$_3$CN + $0.1$ M Bu$_4$NClO$_4$.

$a$The $V_{fb}$ values correspond to the average values determined from Mott-Schottky plots at three different frequencies: 50, 40, and 30 kHz. Relative uncertainty: $\pm 0.02$ V.
obtained for the three different molecular catalysts are gathered in Table S1 for both silicon electrodes. The knowledge of such parameters allows for a complete quantitative description of the energetics of each system under equilibrium conditions and is particularly useful to assess the suitability of the different systems for performing the photoelectrochemical reduction of CO₂. From the degree of band bending shown in Figure 3 and the values reported in Table S1, it is clear that the electric field inside the semiconductor is stronger for SiNWs−H compared with Si−H, even more in the presence of water, for which the space-charge region extends almost double inside the silicon bulk for SiNWs−H (compare Figure 3c and 3f). Moreover, by comparing the values of $V_{bi}$, $\phi_b$, and $W$ for both kinds of surfaces and following the reasoning given above, it can be concluded that under the condition selected for this study, SiNWs−H are always preferable to Si−H as photoelectrodes for the electroreduction of CO₂ in terms of efficiency in decoupling minority carriers generation and collection. On the other hand, for a given kind of surface, the $V_{bi}$, $\phi_b$, and $W$ values are similar for the three studied molecular catalysts (Table S1), which would indicate a comparable catalytic efficiency toward the CO₂ reduction.

2.3. Light to Electrical Energy Conversion Efficiency for CO₂ Photoelectroreduction. Figure 4 shows the photocurrent density−voltage and power−voltage plots obtained with the three molecular catalysts, under CO₂ + 5% v/v H₂O at Si−H and SiNWs−H (left and right side panels, respectively). The values of the short-circuit photocurrent density $J_{sc}$, open-circuit potential under illumination $V_{oc}$, and maximum power drawn for the photoelectrochemical cell $P_{max}$ for each system were calculated by following the procedure described in the SI. The photocurrent density values required for building these plots were obtained by subtracting the first scan of the CVs recorded in the dark from that recorded under illumination for each system. Moreover, the potential of the second reduction peak of the Mn complexes at GCE was taken as the zero potential for the energy conversion calculations, because at this potential value, we can state that the light saturation regime (yielding the maximum photocurrent) has been reached within 5% error at the interface silicon/molecular catalyst solution, so it coincides with the potential of short-circuit photocurrent within this error. The fill factor FF and energy conversion efficiency $\eta$ values calculated from these plots are gathered in Table S3.

Figure 3. Energy diagrams at the interface formed between a solution of [Mn(bpy) (CO)₃Br] at 1 mM and Si−H (left side panel) or SiNWs−H (right side panel) under argon (a, d, blue lines), CO₂ (b, e, red lines) and CO₂ + 5% v/v H₂O (c, f, green lines). $E_{cb}$, $E_{vb}$, $E_{F}$, and $E_{Ox/Red}$ are defined in the Supporting Information (SI). SC: semiconductor, E: electrolytic solution.

Figure 4. Photocurrent density−voltage (red lines) and power−voltage (green lines) plots corresponding to solutions of [Mn(bpy) (CO)₃Br] (a, d), [Mn(dmbpy) (CO)₃(CH₃CN)](PF₆) (b, e) and [Mn(bpy) (CO)₃(CH₃CN)](PF₆) (c, f) at 1 mM in CH₃CN + 0.1 M Bu₄NClO₄ under CO₂ + 5% v/v H₂O, at Si−H (left side panel) and SiNWs−H (right side panel). See SI for symbols and details. Note that the power is given by $P = J \times V$, though it has been plotted in the negative j axis for the sake of simplicity.

Table 3. Fill Factor FF and Energy Conversion Efficiency $\eta$ Values Obtained from the Photocurrent Density−Voltage Plots Given in Figure 4 for the Different Silicon/Molecular Catalyst Solution Interfaces under Electro catalytic Conditions (CO₂ + 5% v/v H₂O)
The FF and η values obtained from these systems are in very good agreement with those reported for Ni or Pt nanoparticles coated p-type silicon photocathodes or for p-type dyesensitized solar cells.48 As expected, the interface SiNWs–H Mn complex solution exhibited higher FF and η with respect to Si–H, which is consistent with better electrocatalytic performances of this interface for the CO₂ reduction. Moreover, a greater catalytic efficiency of the complex [Mn(bpy) (CO)₃(CH₃CN)](PF₆) can be noticed, as evidenced by a higher catalytic efficiency, in fact, the electrocatalytic reduction of CO₂ using the dmbpy complexes could proceed through two distinct pathways depending on the catalysis potential, as previously demonstrated.17

2.4. Stability of the Silicon/Electrolyte Interface under Photoelectrocatalytic Conditions. In order to test the stability of the different silicon/electrolyte interfaces, chronoamperometric experiments in which the light source was successively switched ON/OFF during periods of 60 and 120 s, respectively, were performed at different reduction potentials, under CO₂ + 5% v/v H₂O with vigorous stirring. Figure 5 shows the chronoamperometric curves obtained under ON/OFF (120 s/60 s) illumination cycles for the complex [Mn(bpy) (CO)₃Br] at Si–H and SiNWs–H, together with the corresponding chronocoulometric responses.

The photocurrent densities measured at SiNWs–H were higher and more stable than those measured at Si–H. It must be noticed that at moderately cathodic potentials (until −1.0 V vs SCE), for which small or no photocurrent was observed at Si–H, appreciable photocurrent values could be measured on SiNWs–H. Similar behavior was observed with [Mn(bpy) (CO)₃(CH₃CN)](PF₆) and [Mn(dmbpy) (CO)₃(CH₃CN)](PF₆), with photocurrent density values slightly higher for the dmbpy analogue. Therefore, on the basis of these observations and electrochemical data (vide supra), we can state that SiNWs–H is a more efficient photocathode than Si–H for the CO₂ electrocatalytic reduction with Mn-carbonyl molecular catalysts in solution.

2.5. Preparative Scale Electrolysis. To obtain further insights on the catalytic activity of the investigated Mn-based complexes, preparative-scale electrolysis was carried out by using the most efficient photocathode, namely SiNWs–H, as the working electrode. Thus, controlled-potential electrolysis experiments were carried out at −1.10 V vs SCE with [Mn(bpy) (CO)₃Br] or [Mn(dmbpy) (CO)₃(CH₃CN)](PF₆) at 1 mM in CH₃CN + 0.1 M Bu₄NClO₄ under CO₂ + 5% v/v H₂O in a tightly closed electrochemical cell. The gas composition inside the cell was analyzed at regular time intervals by gas chromatography (GC) to follow the selectivity of the electrocatalytic process. Additionally, analysis of the electrolyte solution by HPLC was carried out at the end of the electrolysis to determine the possible presence of formate.

Both bpy and dmbpy derivatives led to quantitative faradaic efficiency toward the selective production of CO without generation of H₂ or formate. The measured photocurrents remained stable during the electrolysis time (3 h for the bpy analogue and 5 h for the dmbpy derivative). Nevertheless, the UV–vis spectra of the Mn complexes before and after electrolysis evidenced partial degradation of the catalysts, possibly caused by a long exposition to light, particularly for the bpy derivative. For this catalyst, approximately half of the catalyst was lost after 3 h electrolysis, whereas no significant degradation was observed after 5 h electrolysis for the dmbpy analogue. The turnover frequency (TOF) corresponding to these two systems was calculated following two expressions to take into account both the role of the semiconductor as photocatalyst as well as that of the molecular electrocatalyst in solution. The first expression uses the formalism available for heterogeneous catalysts, as previously reported for the CO₂ catalytic reduction at a silicon surface (see SI for more information). The corresponding TOF numbers are given in Figure 6 as a function of the electrolysis time.

The TOF, available for homogeneous catalysts, was based on the amount of produced CO during the electrolysis experiment. In this context, the amount of generated CO (determined by GC) was found to be 0.663 and 0.415 mol × mol⁻¹ of catalyst × h⁻¹ for the bpy and dmbpy analogues, respectively. The lack of expressions characterizing the surface concentrations of the electroactive catalytic species at the semiconductor/liquid junction impedes a more accurate calculation of the TOF, as proposed by Costentin et al.15,52 It must be underlined here that, up to date, there is no expression for the TOF number taking into account together the contributions of both semiconductor and molecular electrocatalyst.

Therefore, from the analytical and preparative electrochemical studies, it can be concluded that the bpy analogues are molecular catalysts more efficient than the dmbpy one to perform the electroreduction of CO₂ at −1.10 V at illuminated
CO₂ reduction, we report here an original modification incorporating Mn-based bipyridyl carbonyl complexes for the considerable step toward the design of catalytic interfaces in the range of 0.0−1.0 V (Figure 7a). The current densities associated with the two redox processes of the Mn center (cathodic peaks around −1.4 and −1.0 V) decreased slightly in the course of electropolymorization during the four first scans and then became stable. The SEM images of Mn catalyst-modified SiNWs−H showed a granular morphology for the polymer (Figure 7c), covering homogeneously the vertical sidewalls of SiNWs. This type of homogeneous globular deposit is in agreement with the morphology observed for a nonfunctionalized ppyr coating onto silicon nanotrees and recently reported by Aradilla et al.57 The electrochemical properties of the SiNWs−H photoelectrode modified by the Mn-ppy functionalized film were analyzed in a monomer-free electrolytic solution (Figure 8a). In the anodic range, a stable quasi-reversible redox system at ca. 0.6 V was observed. It corresponds to the reversible oxidation of the ppyr matrix (doping/undoping process) of the electrogenerated film. This provides further evidence for the presence of a durably attached electroactive deposit.

In the cathodic range, the voltammetric responses of the two successive redox systems of immobilized Mn³⁺ species were maintained under argon, as observed for the similar complex in solution (Figure 1a,d, Figure S2a,d and Figure S3a,d). Upon the addition of CO₂ and then H₂O, an enhancement in the cathodic photocurrent density was observed, in agreement with a catalytic activity of the modified photoelectrode. These preliminary results are promising and demonstrate the validity of the electropolymerization approach to elaborate hybrid molecular SiNWs−H-modified photocathodes for catalytic applications. We are now pursuing this research by studying in detail the electropolymerization process in view of developing Mn complex-functionalized ppyr-modified Si−H and SiNWs−H cathodes, as effective as possible, for photo-assisted electrocatalytic reduction of CO₂.

3. CONCLUSIONS

The electrochemical reduction of CO₂ at illuminated flat Si−H and SiNWs−H photocathodes has been investigated in CH₃CN medium by cyclic voltammetry, in the presence of three Mn-
based carbonyl bipyridyl molecular complexes acting as homogeneous catalysts. The electrochemical data have clearly demonstrated the higher efficiency of the semiconducting photoelectrodes versus conventional working electrodes (e.g., GCE) in terms of energy consumption. From the energetic diagrams of the different semiconductor/liquid junctions, it can be concluded that the degree of band bending and the depth of the space-charge layer is always greater for SiNWs–H than for flat Si–H, being double under electrocatalytic conditions (\(\text{CO}_2 + 5\% \text{v/v H}_2\text{O}\)). Interestingly, the efficiency of the light to electrical energy conversion and fill factor calculated under catalytic conditions have been higher for the nanostructured surface, owing to the higher electrochemically active surface area of SiNWs and its higher capacity to decouple minority carrier generation and collection. Bulk electrolysis at controlled potential has shown the quantitative conversion of \(\text{CO}_2\) to \(\text{CO}\), with no significant and 50% light-induced degradation for the dmbpy and bpy derivatives, respectively, at the end of photoassisted electrolysis. Finally, the electropolymerization of a new Mn-based pyrrole monomer onto the SiNWs–H photocathode has been successfully performed. The film has been found to be homogeneously electrodeposited along the wires of SiNWs and has retained the electrochemical activity of the Mn complex in hydro-organic solution under Ar and in the presence of \(\text{CO}_2\). Work is currently in progress in order to study the selectivity of the electrocatalytic reduction of \(\text{CO}_2\) with these novel modified photoelectrodes.


