

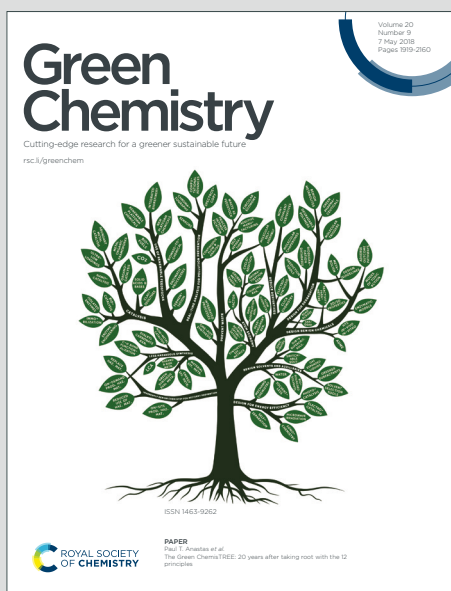
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1. This work advances green chemistry by developing a sacrificial-anode-free photoelectrochemical (PEC) system that enables the direct dicarboxylation of alkenes with CO<sub>2</sub> under mild conditions, offering a sustainable route to valuable dicarboxylic acids.
2. The Ni/p-Si photocathode achieves a Faradaic efficiency of 77.7% toward phenylsuccinic acid without sacrificial metals or toxic reagents. It exhibits broad substrate scope, reduced energy input, and enhanced charge separation, minimizing waste and improving atom economy.
3. The greenness of this system could be further enhanced by integrating earth-abundant, fully recyclable cocatalysts and coupling PEC processes with solar-driven anodic oxidation to eliminate the need for external bias, moving toward fully self-sustained artificial photosynthesis.



# Photoelectrochemical Dicarboxylation of Styrene with CO<sub>2</sub> to Phenylsuccinic Acid on Ni-Decorated Silicon Photocathode

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**KEYWORDS:** Carbon Fixation, Dicarboxylation, CO<sub>2</sub> Reduction, Phenylsuccinic Acid, Photoelectrochemical Cell, Photocathode

## ABSTRACT

The conversion of CO<sub>2</sub> into value-added chemicals is highly critical for sustainable development. Among the various strategies, the dicarboxylation of alkenes with CO<sub>2</sub> offers a highly attractive route to access synthetically valuable dicarboxylic acids, which serve as key intermediates in the production of polymers and pharmaceuticals. Photoelectrochemical (PEC) catalysis carboxylation represents an efficient and sustainable carboxylation strategy, offering distinct advantages including mild reaction conditions, cost-effectiveness, and environmental compatibility. In this study, an efficient PEC system is presented for the carboxylation of styrene using a Ni-modified p-type micro-pyramid silicon (Ni/p-Si) photocathode. The incorporation of Ni catalyst significantly suppresses charge recombination and accelerates charge transfer at the electrode-electrolyte interface, thereby enhancing the overall photoelectrochemical performance. The optimized Ni/p-Si photocathode achieved 77.7% Faradaic efficiency (FE) for phenylsuccinic acid at -2.4 V vs. Ag/AgCl, with a photocurrent density of -4.5 mA cm<sup>-2</sup>. Moreover, this PEC platform demonstrates moderate FEs across a range of substituted styrenes, indicating good



functional group tolerance. Mechanistic studies reveal that the reaction proceeds via single-electron reduction of styrene to generate radical anions, which undergo CO<sub>2</sub> addition followed by further reduction and subsequent attack on a second CO<sub>2</sub> molecule to yield succinic acid. These findings broaden the scope of CO<sub>2</sub> utilization through selective and sustainable C-C bond formation processes.

## INTRODUCTION

Carbon dioxide (CO<sub>2</sub>) is widely regarded not only as a notorious greenhouse gas but also as an inexpensive, abundant, nontoxic, and ideal C1 building block.<sup>1-3</sup> The conversion and utilization of CO<sub>2</sub> into value-added chemicals have been recognized as a promising way to mitigate energy shortages and environmental problems caused by the greenhouse effect.<sup>4</sup> Beyond its direct reduction to small-molecule fuels,<sup>5, 6</sup> the incorporation of CO<sub>2</sub> into organic molecules (such as ketones,<sup>7</sup> alkynes,<sup>8</sup> alkenes,<sup>9</sup> and alkyl halides<sup>10</sup>) enables the synthesis of carboxylic acids, which are critical ingredients for the synthesis of pharmaceuticals, cosmetics, pesticides, dyes, and other highly valuable chemicals.<sup>11, 12</sup> Among these substrates, alkenes have attracted particular attention due to their wide availability and structural diversity.<sup>13</sup> The carboxylation of alkenes with CO<sub>2</sub> enables direct access to structurally diverse carboxylic acids, avoiding conventional multistep formylation/oxidation processes.<sup>14</sup> This approach represents an efficient and sustainable carboxylation strategy, offering distinct advantages including mild reaction conditions, cost-effectiveness, and environmental benignity for green chemical synthesis.<sup>12</sup>

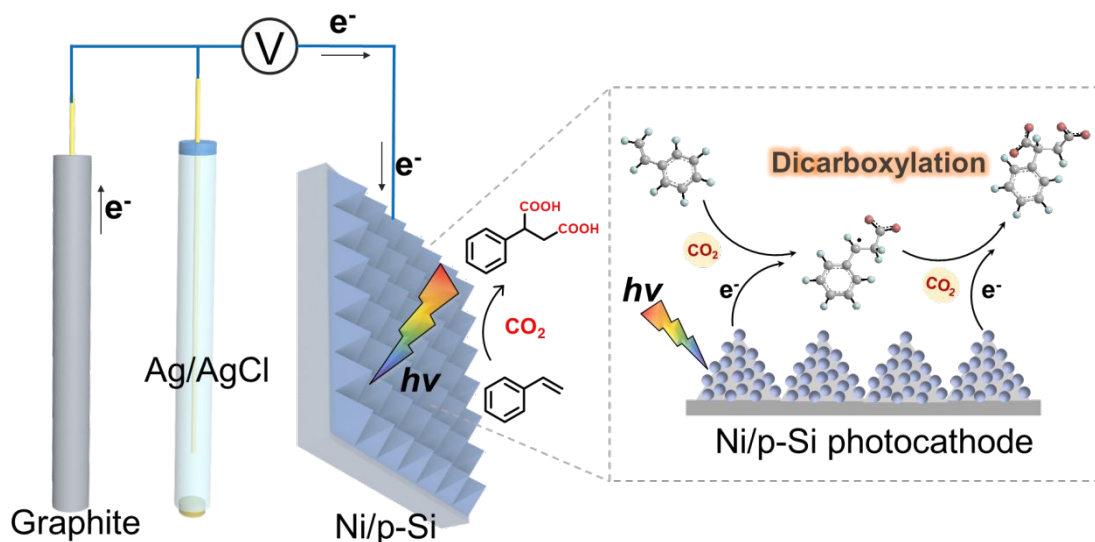
Significant efforts have been made to achieve the carboxylation of alkenes with CO<sub>2</sub> through traditional transition-metal catalysis, electrochemical, photocatalysis, and photoelectrocatalysis methods.<sup>15-20</sup> Among these methods, photoelectrochemical catalysis (PEC), combining the advantages of both photocatalysis and electrocatalysis, offers a compelling platform for converting and storing solar energy in chemical substances under mild conditions.<sup>21, 22</sup> Specifically, PEC carboxylation directly utilizes solar energy to generate electron hole pairs over electrocatalysis, which effectively reduces the overpotential and enhances energy conversion



efficiency enabling carboxylation reactions to proceed under milder potentials with higher energy efficiency and superior selectivity.<sup>23</sup> The successful implementation of PEC carboxylation of alkenes with CO<sub>2</sub> critically depends on the rational design and fabrication of the photocathode. Silicon (Si) stands out as one of the most promising semiconductor materials for photocathode applications, owing to its earth abundance, narrow band gap (1.12 eV) with efficient light harvesting, low cost, high carrier mobility, and streamlined large-scale production.<sup>24-26</sup>

Silicon photocathodes have emerged as particularly promising materials for PEC applications, demonstrating excellent performance in both PEC hydrogen evolution and CO<sub>2</sub> reduction reactions.<sup>27, 28</sup> Notably, the PEC hydrocarboxylation with CO<sub>2</sub> as substrate was first achieved using silicon-nanowires (SiNWs) photocathode with a sacrificial Al anode, enabling the synthesis of  $\alpha$ -hydroxy acids from aromatic ketones.<sup>29</sup> This approach was successfully extended to  $\alpha,\beta$ -unsaturated ketones using unmodified SiNWs.<sup>30</sup> While these studies established the viability of light-driven PEC hydrocarboxylation, the reaction efficiency remains fundamentally constrained by the limited catalytic activity of bare Si. To enhance the reaction kinetics, a homogeneous nickel-based molecule was subsequently employed in the PEC carboxylation system,<sup>31</sup> which improved reaction kinetics but introduced new challenges, including metal toxicity, difficult product separation, and low catalyst utilization efficiency. As an alternative, heterogeneous catalyst-modified photoelectrodes have shown great potential. For instance, a recent study demonstrated that Ag nanoparticle-decorated Si photocathode paired with Al sacrificial anode enabled selective CO<sub>2</sub> fixation for the synthesis of profen drug intermediate.<sup>32</sup> Despite these advances, the development of highly selective, broadly applicable catalyst-modified photocathodes, particularly in nonsacrificial metal PEC systems, remains an unmet challenge in PEC carboxylation. Moreover, the use of silicon-based PEC platforms for alkene dicarboxylation has been largely unexplored, highlighting a critical gap in current CO<sub>2</sub> valorization strategies.





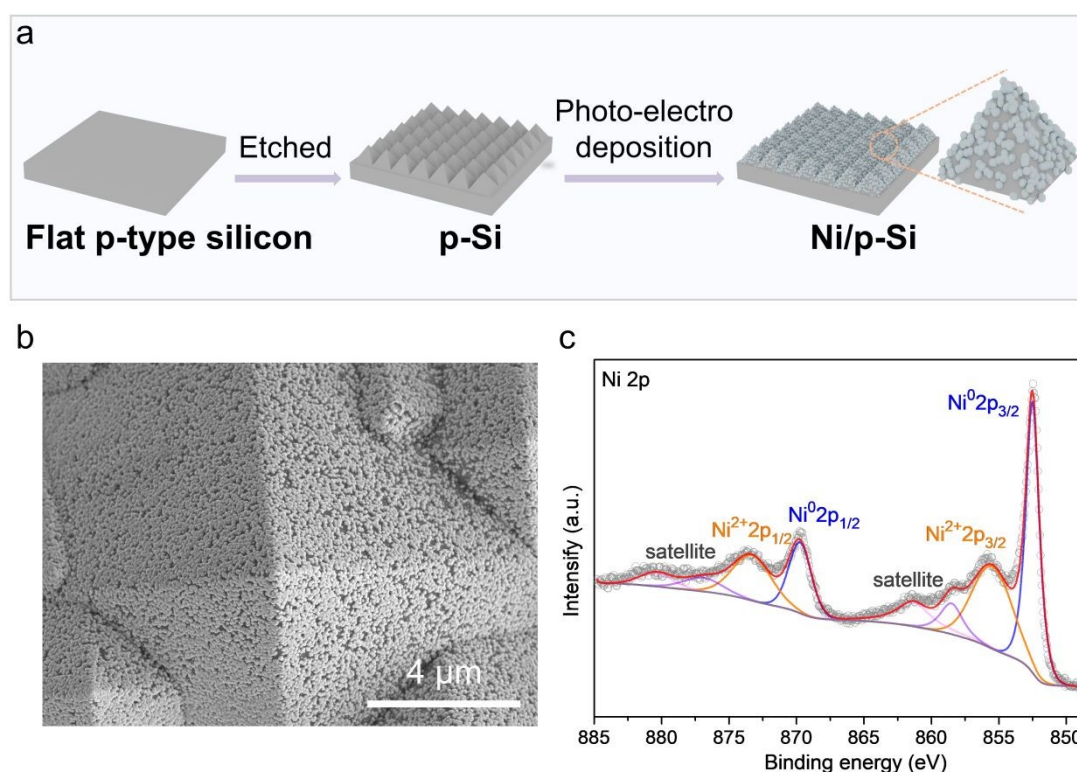
**Figure 1.** Schematic diagram of the PEC dicarboxylation on Ni/p-Si photocathode.

In this study, we demonstrate an efficient and nonsacrificial PEC system for the dicarboxylation of styrene with  $\text{CO}_2$ , utilizing a Ni-modified micro-pyramidal Si photocathode (Ni/p-Si) in conjunction with a graphite anode (**Figure 1**). The rationally designed micro-pyramid array architecture simultaneously suppresses optical reflectance and enhances photon capture efficiency. The incorporation of a Ni cocatalyst significantly improves the PEC performance by effectively suppressing electron-hole recombination and significantly promoting interfacial charge transfer, resulting in a remarkable enhancement of photocurrent. The Ni/p-Si photocathode achieves a maximum Faradaic efficiency (FE) of 77.7% for the reductive dicarboxylation of styrene to phenylsuccinic acid at  $-2.4$  V vs. Ag/AgCl. Moreover, this photocathode exhibits broad substrate tolerance, delivering FEs ranging from 43.6% to 65.8% across a series of electronically diverse styrene derivatives, including both electron-rich and electron-deficient substrates, as well as trans-stilbene. This study establishes a catalyst-modified silicon photocathode as a robust and highly efficient platform for PEC dicarboxylation, providing an economical and scalable route to value-added succinic acid derivatives from  $\text{CO}_2$  and simple alkenes.

## RESULTS AND DISCUSSION



The preparation of the Ni/p-Si photocathode is schematically illustrated in **Figure 2a**. The planar p-type silicon wafer is structured by a rapid anisotropic etching treatment to generate a light-trapping micro-pyramidal structure on the surface.<sup>33</sup> Subsequently, the Ni catalyst is decorated on the p-Si by photoelectrodeposition. The surface morphologies of p-Si and Ni/p-Si electrodes are characterized by scanning electron microscopy (SEM). The SEM images of the etched p-Si substrate reveal a densely packed array of micro-pyramidal structures with a polydisperse size distribution, uniformly covering the silicon surface (**Figure S1**).



**Figure 2.** (a) Schematic illustration of the preparation process for Ni/p-Si. (b) SEM image of Ni/p-Si. (c) High-resolution XPS spectrum of Ni 2p region for the as-fabricated Ni/p-Si electrode.

As shown in **Figure 2b** and **Figure S2**, SEM images confirm the successful deposition of the Ni catalyst on the surface of the p-Si substrate, clearly revealing a uniform distribution of Ni catalyst with an average size of approximately 100 nm. The elemental mappings and energy-dispersive X-ray (EDX) spectroscopy (**Figure S3**) further reveal a uniform distribution of Ni across the photocathode surface. The surface composition and chemical states of the as-



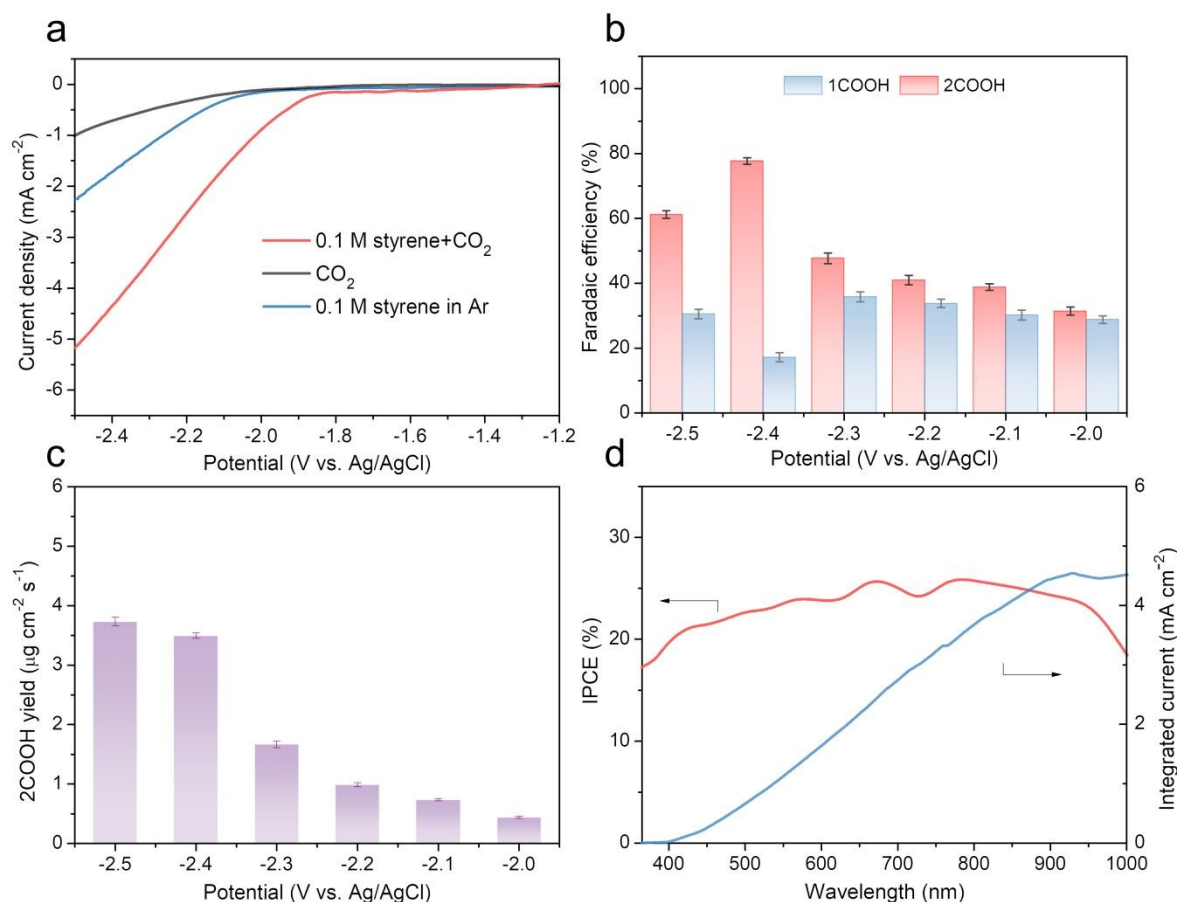
prepared Ni/p-Si were analyzed by X-ray photoelectron spectroscopy (XPS) (**Figure S4a**), confirming the presence of Ni on the silicon surface. The high-resolution XPS spectrum of the Ni 2p region for Ni/p-Si (**Figure 2c**) reveals that the deposited nickel catalyst is composed of both metallic Ni and Ni<sup>2+</sup> species. The peaks with binding energies of 852.5 and 869.7 eV correspond to Ni 2p<sub>3/2</sub> and Ni 2p<sub>1/2</sub> of metallic nickel, respectively, while the peaks at 855.5 and 873.3 eV are attributed to the Ni<sup>2+</sup> species.<sup>34, 35</sup> Additionally, the Si 2p spectrum indicates the presence of a thin layer of silicon dioxide on the surface (**Figure S4b**). X-ray diffraction (XRD) analysis shows no discernible diffraction peaks for Ni (**Figure S5**), suggesting that the deposited nickel catalyst is amorphous.

Following the successful fabrication and structural characterization of the Ni/p-Si photocathode, its photoelectrochemical carboxylation performance was evaluated using styrene as a model substrate. To investigate the influence of the styrene concentration, PEC carboxylation reactions were conducted with varying initial concentrations of styrene in CO<sub>2</sub>-saturated 0.1 M tetrabutylammonium bromide (TBAB) anhydrous acetonitrile solutions. Linear sweep voltammetry (LSV) scans were recorded at a scan rate of 20 mV s<sup>-1</sup> under simulated 1-sun illumination (100 mW cm<sup>-2</sup>), without *IR* compensation. Styrene concentrations ranging from 0 to 0.2 M were examined. As shown in **Figure S6**, the photocurrent density increased significantly with increasing styrene concentration up to 0.1 M, indicating enhanced electron consumption by substrate availability. Beyond this concentration, the photocurrent reached a saturation plateau as the mass transfer limitation was eliminated. Therefore, 0.1 M was selected as the optimal styrene concentration for subsequent PEC dicarboxylation studies.

The performance of PEC carboxylation on Ni/p-Si photocathode was evaluated in a three-electrode single cell. The electrolyte was composed of 10 mL CO<sub>2</sub>-saturated acetonitrile solution containing 0.1 M styrene and TBAB. As shown in **Figure 3a**, a relatively low photocurrent density was observed in the CO<sub>2</sub>-saturated electrolyte without styrene, indicating limited PEC CO<sub>2</sub> reduction activity under these conditions. In contrast, the introduction of 0.1 M styrene under the Ar atmosphere generated an apparent photocurrent response, predominantly attributed to



radical polymerization under anhydrous conditions.<sup>36</sup> Remarkably, when both CO<sub>2</sub> and styrene were present, the photocurrent density increased significantly, accompanied by a notable positive shift in the onset potential. These results strongly suggest that the carboxylation reaction is initiated only when both reactants are simultaneously available, consistent with the proposed reaction precesses.<sup>12</sup>



**Figure 3.** (a) LSV curves of the Ni/p-Si photocathode under different reaction conditions. (b) Faradaic efficiencies (%) of products from PEC carboxylation of styrene under different potentials. (c) Yield rates of **2COOH** production for Ni/p-Si at different applied potentials. (d) IPCE of Ni/p-Si photocathode at -2.4 V vs. Ag/AgCl under monochromatic light at different wavelengths.

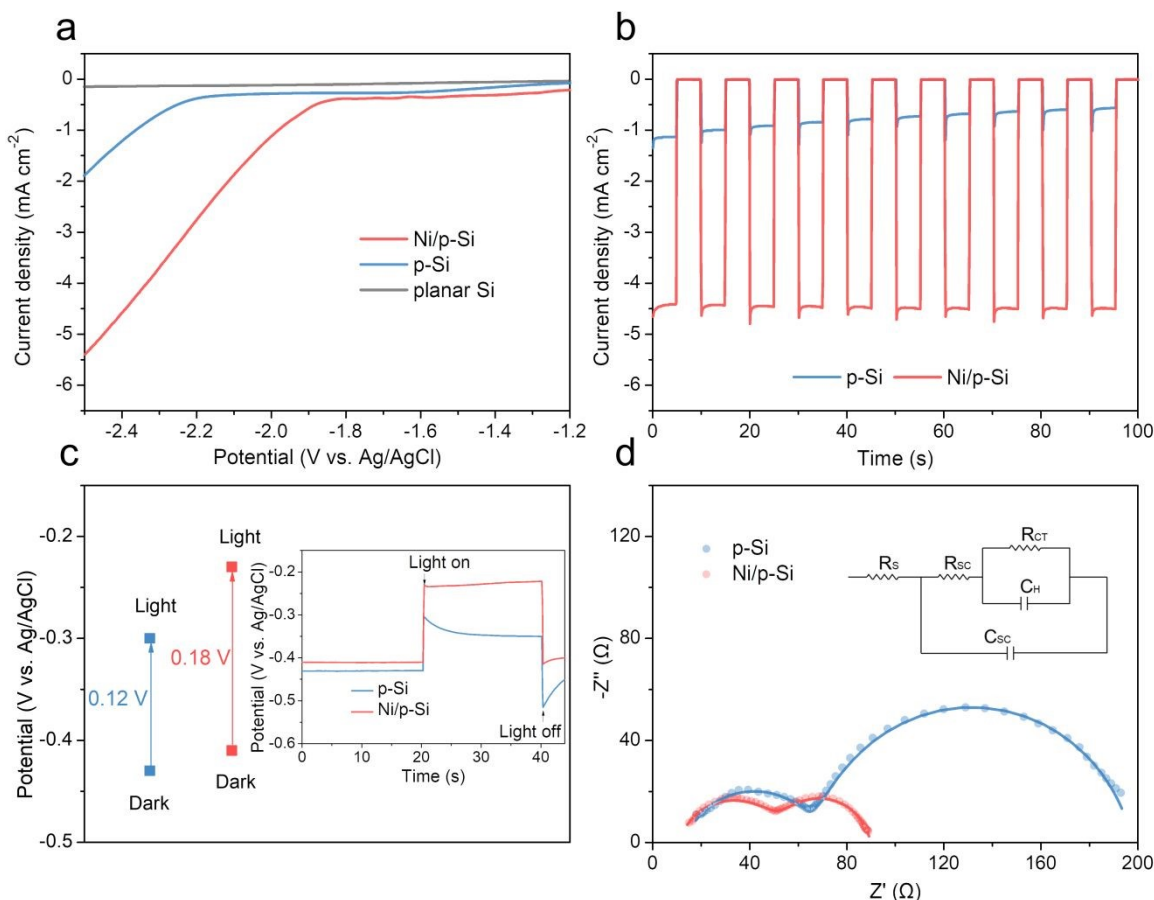
The effect of applied potential on the PEC carboxylation performance of Ni/p-Si photocathode was systematically investigated. Two primary liquid-phase products were identified: phenylsuccinic acid (**2COOH**, dicarboxylation product) and hydrocinnamic acid



(**1COOH**, hydrocarboxylation product). Reversed-phase high-performance liquid chromatography (HPLC) was employed for qualitative and quantitative analysis of both products (**Figure S7**), with retention times of 4.5 min for **2COOH** and 8.3 min for **1COOH**, respectively.<sup>37</sup>  
<sup>38</sup> Chronoamperometric measurements were conducted at different applied potentials, followed by acidification with 2 M HCl to protonate carboxylate intermediates prior to product extraction and detection (**Figure S8**). The corresponding FEs, selectivity and average yield rates were calculated according to **Eq. S1-3** in **Supporting Information**. As shown in **Figure 3b**, the optimal applied potential for the production of **2COOH** was found to be  $-2.4$  V vs. Ag/AgCl with a remarkable FE as high as  $77.7 \pm 1.0\%$ . Notably, the carboxylation reaction achieved an overall FE of 90%, confirming the viability of this PEC carboxylation strategy rather than the reduction of  $\text{CO}_2$  or styrene alone. The selectivity of **2COOH** on Ni/p-Si is  $79.4 \pm 1.7\%$  at  $-2.4$  V vs. Ag/AgCl (**Figure S9**). As illustrated in **Figure 3c**, the production rate of **2COOH** showed a clear potential dependence, with the yield rate progressively increasing at more negative potentials. The Ni/p-Si photocathode attained a maximum **2COOH** production rate of  $3.7 \pm 0.1 \mu\text{g cm}^{-2} \text{s}^{-1}$  at  $-2.5$  V vs Ag/AgCl.

The incident-photon-to-current efficiency (IPCE) of the Ni/p-Si photocathode was measured under monochromatic light irradiation at an applied potential of  $-2.4$  V vs. Ag/AgCl (**Figure 3d**). The Ni/p-Si photocathode reached a maximum IPCE of 25.6% at 670 nm. In addition, by integrating the IPCE curve over the AM 1.5G solar irradiation (ASTM G173-03) spectrum, a photocurrent of  $4.5 \text{ mA cm}^{-2}$  at  $-2.4$  V vs Ag/AgCl was obtained, which was consistent with the measured LSV curve photocurrent value, confirming the consistency and reliability of the PEC performance data.





**Figure 4.** (a) LSV curves of the planar Si, p-Si, Ni/p-Si photocathodes in CO<sub>2</sub>-saturated 0.1 M tetrabutylammonium bromide (TBAB) acetonitrile solution containing 0.1 M styrene under AM 1.5 G illumination (100 mW cm<sup>-2</sup>). (b) *I*-*t* curves of the p-Si and Ni/p-Si photocathodes under chopped illumination at -2.4 V vs. Ag/AgCl. (c) Open-circuit potential (OCP) measurements of p-Si and Ni/p-Si under dark and light conditions. (d) Nyquist plots of p-Si and Ni/p-Si at -2.4 V vs. Ag/AgCl under light. Inset: corresponding equivalent circuit model.

These findings further prompted an investigation into the role of the Ni cocatalyst in enhancing the PEC performance of the microstructured silicon electrode. As shown in **Figure 4a**, the PEC carboxylation activity of planar Si, etched p-Si, and Ni/p-Si photocathodes was systematically compared. The planar Si photocathode presented a negligible photocurrent due to its high surface reflectivity, resulting in poor intrinsic catalytic activity.<sup>39, 40</sup> In contrast, the p-Si photocathode demonstrated a significantly enhanced photocurrent response, which can be attributed to the improved light-harvesting capability of the micro-pyramidal surface structure (**Figure S10**). This result highlights the importance of morphological engineering in promoting



PEC performance. Remarkably, the Ni/p-Si photocathode exhibited the most positive onset potential ( $-1.9$  V vs. Ag/AgCl) and the highest photocurrent density for the PEC carboxylation of styrene with  $\text{CO}_2$ . These enhancements are attributed to the accelerated interfacial charge-transfer kinetics facilitated by the Ni cocatalyst. Furthermore, the onset potential for styrene carboxylation on the Ni/p-Si photocathode showed a positive shift of approximately  $0.5$  V compared to that observed on a glassy carbon electrode (**Figure S11**), highlighting the catalytic superiority and synergistic effect of the PEC system.

Further insight into the photoelectrochemical behavior was obtained by analyzing the transient photocurrent responses of p-Si and Ni/p-Si photocathodes at a constant bias of  $-2.4$  V vs Ag/AgCl (**Figure 4b**). The Ni/p-Si photocathode achieved a remarkably enhanced photocurrent density of  $-4.5 \text{ mA cm}^{-2}$ , representing a four-fold enhancement compared to that of the bare p-Si photoanode. Additionally, the Ni/p-Si photocathode presented much smaller transient spikes than the p-Si electrode during each on-off cycle, suggesting more efficient charge transfer and reduced charge recombination facilitated by the Ni cocatalyst.<sup>41</sup> To further evaluate the interfacial photoresponse, the photovoltage ( $V_{\text{ph}}$ ) at the photocathode/electrolyte interface was determined from the open-circuit potential (OCP) difference between illuminated and dark conditions (**Figure 4c**). The Ni/p-Si photocathode exhibited an increased photovoltage of  $0.18$  V, compared to  $0.12$  V for p-Si, demonstrating that the Ni catalyst enhanced the interfacial electric field. This strengthened band bending at the semiconductor/electrolyte interface promoted charge separation and suppressed recombination, thereby contributing to the observed improvements in both onset potential and photocurrent density.<sup>42, 43</sup>

To gain further insights into the charge transfer behavior, photoelectrochemical impedance spectroscopy (PEIS) measurements were conducted to investigate charge transfer kinetics across the semiconductor/catalyst/electrolyte interfaces. The PEIS responses of bare p-Si and Ni/p-Si photocathodes at  $-2.4$  vs Ag/AgCl under illumination are displayed in **Figure 4d**. The resulting Nyquist plots exhibit two well-defined semicircle features, which were fitted using a resistor-capacitor equivalent circuit model (inset, **Figure 4d**). In this model,  $R_s$  corresponds to

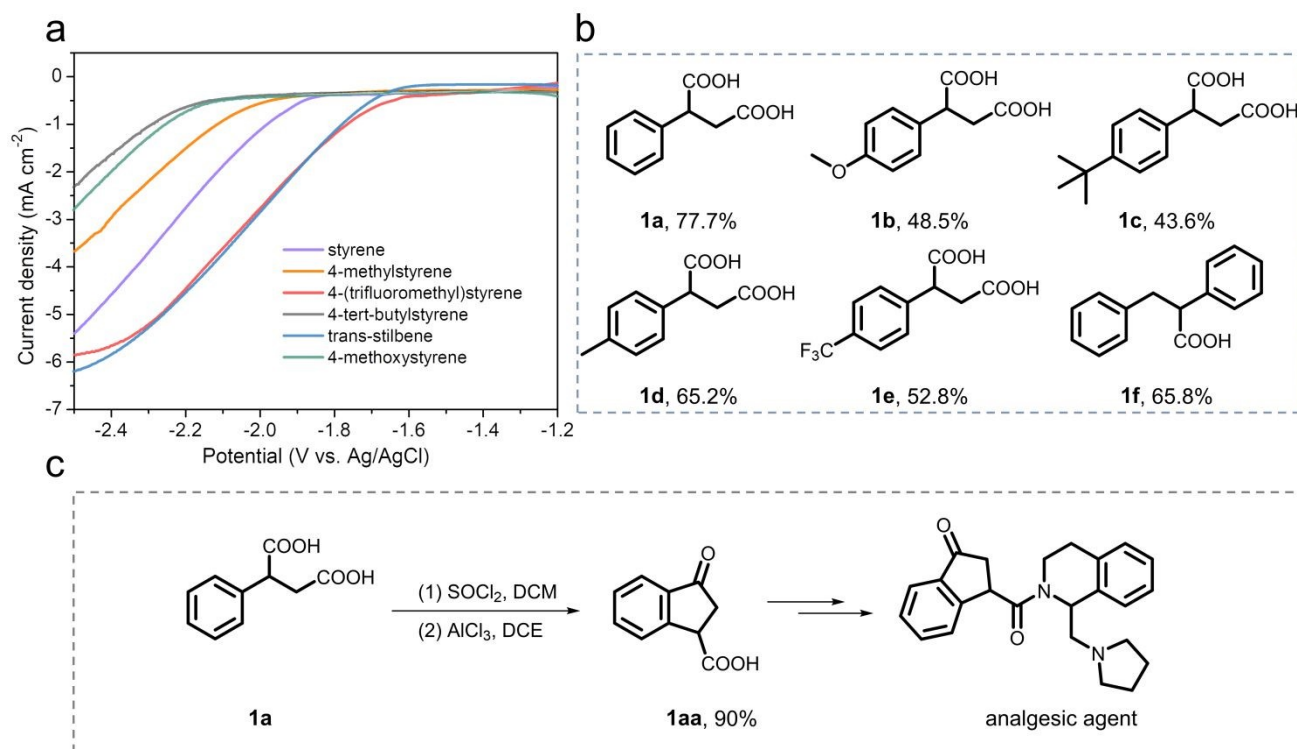


the series resistance of the circuit, modeling the Cu substrate and Si semiconductor interface at high frequencies.  $R_{sc}$  represents the bulk resistance between the Si and Ni catalyst, while  $C_{sc}$  accounts for the capacitive behavior of the electrodes. Additionally, the surface-state capacitance ( $C_H$ ) and charge-transfer resistance ( $R_{ct}$ ) at the electrode/electrolyte interface reflect the properties of the Helmholtz layer.<sup>44, 45</sup> The fitted parameters derived from this model are summarized in **Table S1**. Compared to the bare p-Si electrode, the Ni/p-Si electrode displays significantly smaller semicircle diameters, indicating lower interfacial resistances. Specifically, the Ni/p-Si electrode demonstrates significantly reduced resistances ( $R_{sc} = 44.48 \, \Omega$ ,  $R_{ct} = 34.53 \, \Omega$ ) compared to bare p-Si ( $R_{sc} = 56.35 \, \Omega$ ,  $R_{ct} = 128.50 \, \Omega$ ). These reductions confirm enhanced bulk charge transport and accelerated charge transfer facilitated by the Ni catalyst, consistent with the electrochemical performance trends observed in LSV measurements (**Figure 4a**). In summary, the Ni catalyst serves as highly efficient catalytic sites for the CO<sub>2</sub> carboxylation reaction, promoting efficient separation of photogenerated charge carriers and enhancing charge transfer across the electrode/electrolyte interface, thereby significantly enhancing the PEC carboxylation efficiency observed in the Ni/p-Si system.

Long-term stability and reusability are critical factors in evaluating the PEC performance and practical applicability of photocathode materials. The operational stability of Ni/p-Si was assessed under a constant potential of  $-2.4 \, \text{V}$  vs. Ag/AgCl. As shown in **Figure S12**, the FE for **2COOH** maintained >90% of its initial value over four consecutive PEC carboxylation cycles, demonstrating excellent cycling stability of the Ni/p-Si photocathode. To further examine the structural and chemical stability of the photocathode, post-reaction characterizations were conducted. As illustrated in **Figure S13a**, the SEM image showed that the post-carboxylation Ni/p-Si electrode retained its pristine micro-pyramidal morphology after long-term PEC operation, with the Ni catalytic sites remaining well-dispersed across the textured silicon surface. The XRD pattern of the tested Ni/p-Si electrode revealed the appearance of distinct SiO<sub>2</sub> diffraction peaks at  $2\theta = 20.8^\circ$  and  $26.6^\circ$  (JCPDS No. 46-1045), confirming the formation of a surface oxide layer during PEC operation (**Figure S13b**). The chemical states of Ni/p-Si after PEC carboxylation



were measured by XPS (**Figure S14**). XPS analysis confirmed that the valence state of Ni remained relatively unchanged after the long-time stability test, suggesting that the Ni catalyst was chemically stable. However, a significant increase in the SiO<sub>2</sub> peak intensity was observed, indicating photocorrosion of the underlying silicon, which likely contributed to the slight degradation of the photoelectrocatalytic performance during extended use.<sup>46, 47</sup>



**Figure 5.** Scope of styrene derivatives for PEC carboxylation. (a) LSV curves of 0.1 M styrene derivatives. (b) FE of products, determined by <sup>1</sup>H NMR. The PEC carboxylation of styrene derivatives was conducted on the Ni/p-Si photocathode in CO<sub>2</sub>-saturated 0.1 M TBAB acetonitrile containing 0.1 M substrate. (c) Demonstration of the synthetic utility of the PEC dicarboxylation strategy.

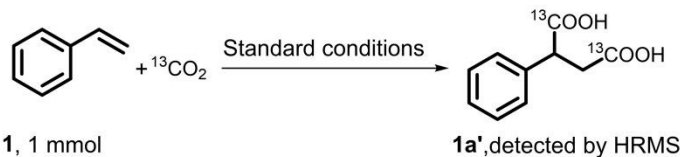
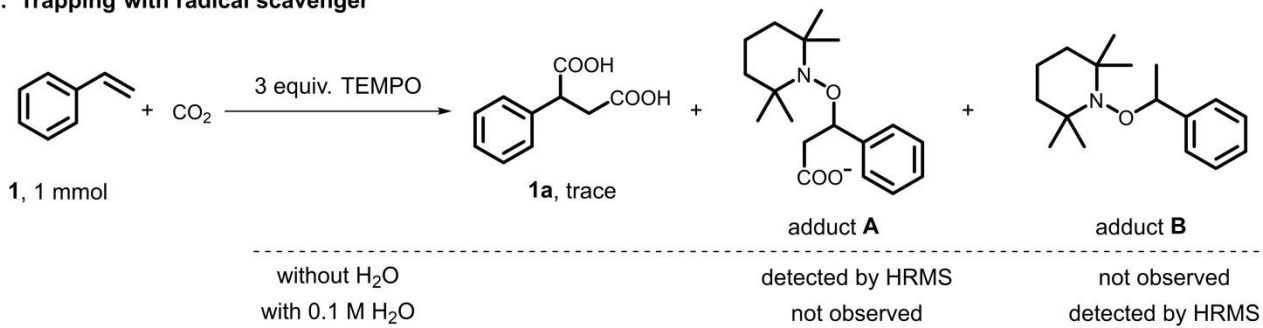
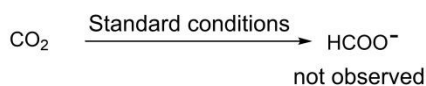
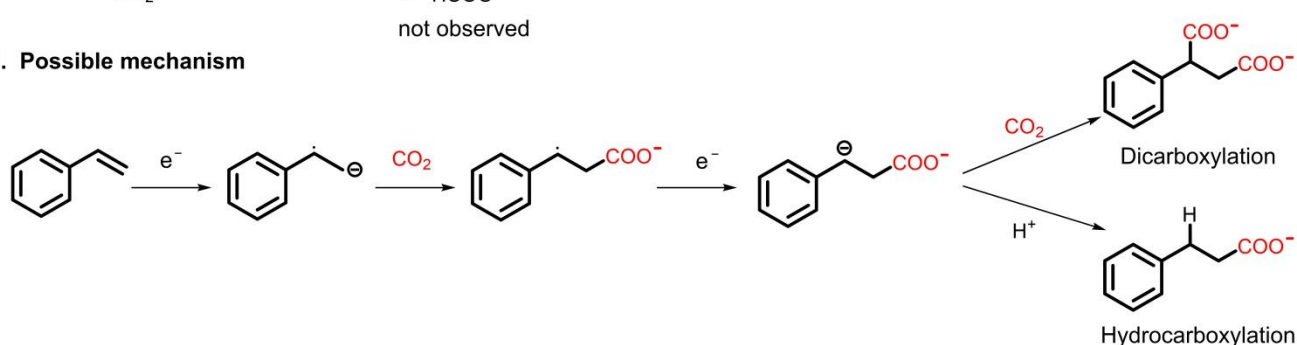
The substrate scope of the PEC carboxylation protocol was systematically investigated using a range of styrene derivatives under identical reaction conditions, and the results are summarized in **Figure 5**. The initial electrochemical behavior of these substrates was assessed by LSV measurements. As demonstrated in **Figure 5a**, the observed reactivity trends can be explained by the electronic effect of substituents on the C=C double bond. Styrene derivatives bearing electron-donating groups (such as methoxy, methyl, and tert-butyl substituents) showed



increased electron density at the C=C bond, thereby hindering reduction and resulting in higher reduction potentials. In contrast, the derivative bearing an electron-withdrawing group (such as a trifluoromethyl substituent) exhibited decreased electron density at the C=C bond, facilitating electron acquisition and consequently displaying a positively shifted potential. Notably, trans-stilbene with an extended  $\pi$ -conjugation system showed significantly earlier onset potentials compared to unsubstituted styrene. Under optimized electrolytic potentials, the maximum FEs for PEC carboxylation of various substrates are presented in **Figure 5b**. The PEC carboxylation of 4-methoxystyrene, 4-tert-butylstyrene, 4-methylstyrene, and 4-trifluoromethylstyrene produced the corresponding dicarboxylic acids with max FE of 48.5%, 43.6%, 65.2%, and 52.8%, respectively, demonstrating the method's tolerance for diverse electronic substituents. In contrast, trans-stilbene preferentially underwent hydrocarboxylation with an FE of 65.8%, likely due to steric hindrance impeding the second CO<sub>2</sub> insertion.<sup>48</sup> The synthetic utility of this PEC carboxylation strategy was further demonstrated through the preparation of pharmaceutically relevant compounds from succinic acid derivatives. Using 2-phenylsuccinic acid (**2COOH**, **1a**) obtained via PEC carboxylation as the starting material (**Figure 5c**), intramolecular Friedel-Crafts cyclization efficiently afforded compound **1aa** in 90% yield. Notably, compound **1aa** is a key intermediate for the synthesis of an analgesic agent.<sup>49</sup>

To gain deeper insight into the reaction mechanism, a series of mechanistic investigations were performed. To confirm the C1 sources and elucidate the C-C bond formation mechanism, a <sup>13</sup>C labeling experiment was conducted using <sup>13</sup>CO<sub>2</sub> (**Figure 6a**). The results revealed complete <sup>13</sup>C incorporation into the dicarboxylation product **2a** (**Figure S15**), confirming that both carboxyl groups originated exclusively from CO<sub>2</sub>, thereby eliminating the possibility of alternative carbon sources contributing to the carboxylation process. Additionally, LSV revealed similar onset potentials for CO<sub>2</sub> and styrene reduction, suggesting that both reductions may occur competitively under PEC carboxylation conditions.<sup>50</sup> This overlap complicates the direct identification of the initial activation step, thereby necessitating further radical-trapping and intermediate-probing experiments to clarify the mechanistic pathway.



**a. Detection of  $^{13}\text{C}$ -involving product****b. Trapping with radical scavenger****EPR measurement****c. Detection of formate****d. Possible mechanism**

**Figure 6.** Investigation of the reaction mechanism. (a)  $^{13}\text{CO}_2$  labelling experiment. (b) Radical trapping experiment. (c) Detection of formate. (d) Proposed mechanism for PEC carboxylation of styrene with  $\text{CO}_2$  on Ni/p-Si photocathode.

The involvement of radical intermediates in the PEC carboxylation mechanism was



supported by radical-trapping experiments. The addition of radical scavenger (e.g., 2,2,6,6-tetramethylpiperidine-1-oxyl, TEMPO) effectively suppressed the formation of the dicarboxylation product, strongly indicating that radical species are key intermediates in the reaction pathway (**Figure 6b**). Meanwhile, two radical-derived adducts, designated as **A** and **B**, were identified by HPLC-APCI-TOF/MS analysis (**Figure S16**), providing additional evidence for the generation of a benzylic carbanion intermediate during the reaction. Moreover, the control experiment demonstrated only trace amounts of formate ( $\text{HCOO}^-$ ) generation from  $\text{CO}_2$  reduction in the absence of styrene (**Figure 6c** and **Figure S17**), further demonstrating that the initial electron transfer to  $\text{CO}_2$  is less favored than electron transfer to styrene under the reaction conditions.<sup>49</sup> Electron paramagnetic resonance (EPR) spectroscopy further supported the reduction of styrene to generate alkyl radicals in this system (**Figure 6b** and **Figure S18**).<sup>51, 52</sup>

Based on the above experiments, the possible mechanism for the PEC carboxylation is proposed in **Figure 6d**. Upon light irradiation, the p-Si photocathode produces photogenerated electrons, which migrate to the electrode surface. These electrons are transferred to styrene and  $\text{CO}_2$ , forming a  $\beta$ -carboxylate radical intermediate through a single-electron reduction process. Subsequently, a second electron transfer converts the radical into a  $\beta$ -carboxylate carbanion intermediate. This nucleophilic intermediate can then follow two competing pathways: it either attacks a second molecule of  $\text{CO}_2$  to yield the dicarboxylated product (**2COOH**), or undergoes protonation to form the hydrocarboxylated product (**1COOH**).

In terms of product separation, the isolation of phenylsuccinic acid is straightforward despite the use of TBAB/acetonitrile solutions under dilute conditions. After the completion of the PEC carboxylation reaction, the acetonitrile solvent is first removed by rotary evaporation under reduced pressure to concentrate the reaction mixture. The concentrated solution is then acidified to convert the phenylsuccinate salt into the free phenylsuccinic acid. Due to the significantly lower solubility of phenylsuccinic acid compared to its salt form in water, the product can efficiently precipitate as a high-purity solid, enabling straightforward separation and purification via simple suction filtration. This simple precipitation-filtration process avoids the need for



complex extraction or energy-intensive purification steps, thereby enhancing the overall sustainability of the methodology.

## CONCLUSION

In summary, we have developed a Ni-modified p-type micro-pyramid silicon (Ni/p-Si) photocathode for efficient PEC carboxylation of styrene with CO<sub>2</sub>. The Ni catalyst plays a crucial role in enhancing the PEC carboxylation performance by effectively promoting charge carrier separation and transfer while simultaneously suppressing charge recombination. The Ni/p-Si photocathode exhibits outstanding catalytic performance for PEC dicarboxylation, achieving 77.7% FE toward phenylsuccinic acid at -2.4 V vs. Ag/AgCl. The system exhibits broad substrate scope under mild conditions without a sacrificial anode, establishing its practical applicability for the sustainable dicarboxylic acid production. This work not only advances the design of catalyst-integrated silicon photoelectrodes but also offers valuable mechanistic insights into PEC CO<sub>2</sub> fixation, contributing to the broader development of artificial photosynthetic systems for solar-to-chemical energy conversion and green organic synthesis.



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## Competing interests

The authors declare no competing interests.

## Data availability

The data supporting this article have been included as part of the Supplementary Information.

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## Data availability statements

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