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## Sunlight-assisted, biocatalytic formate synthesis from CO<sub>2</sub> and water using silicon-based photoelectrochemical cells†

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**We report on a silicon-based photoelectrochemical cell that integrates a formate dehydrogenase from *Thiobacillus* sp. (TsFDH) to convert CO<sub>2</sub> to formate using water as an electron donor under visible light irradiation and an applied bias. Our current study suggests that the deliberate integration of biocatalysis to a light-harvesting platform could provide an opportunity to synthesize valuable chemicals with the use of earth-abundant materials and sustainable resources.**

Solar energy is a clean and sustainable resource that is considered to be an alternative to fossil fuels. In nature, green plants possess a highly efficient solar energy harvesting system that exhibits nearly 100% quantum efficiency.<sup>1</sup> In natural photosynthesis, an anodic current generated in photosystem (PS) II is consumed by an oxygen-evolving complex to split water into electrons, protons, and oxygen. The protons are transferred and reduced at PS I to store solar-driven energy in a chemical form of nicotinamide cofactor [NAD(P)H].<sup>2</sup> Many researchers have attempted to design artificial photosynthetic systems for the conversion of solar energy to chemical fuels (*e.g.*, H<sub>2</sub>, hydrocarbons) using CO<sub>2</sub> as a carbon source and water as an electron donor. Biocatalysis is a promising route for environmentally friendly synthesis of chemicals because of a variety of natural (or engineered) enzymes capable of converting substrates with high specificity under mild reaction conditions.<sup>3</sup> Several efforts had been made to mimic natural photosynthesis by coupling redox biocatalysis with photocatalysis.<sup>4</sup> For example, formic acid was synthesized from CO<sub>2</sub> *via* formate dehydrogenase (FDH) by accepting electrons delivered from a photocathode (*e.g.*, p-type indium phosphide).<sup>5</sup> However, technological breakthroughs are still needed to implement biocatalyzed artificial photosynthesis; one of the major challenges is the use of water as the electron source instead of an organic sacrificial electron donor.<sup>3b,6</sup> In this

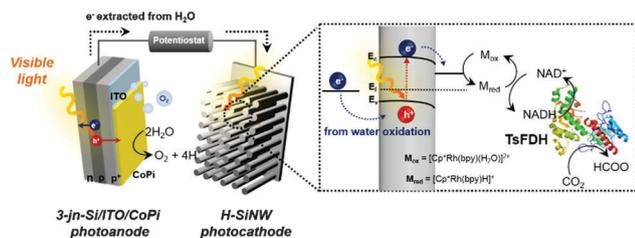
regard, a photoelectrochemical (PEC) cell composed of a semiconductor photoanode and a photocathode is an attractive option as a platform for biocatalytic artificial photosynthesis because it can effectively deliver the electrons extracted by water oxidation at the photoanode to the biocatalysts at the photocathode, minimizing back electron transfer.

Herein we report on the development of a silicon-based PEC cell for solar-assisted biocatalytic conversion of CO<sub>2</sub> to formate using water as an electron donor under natural sunlight and an applied bias. Formate is a valuable chemical that can participate in a series of reactions to make higher alcohols (*e.g.*, methanol),<sup>3f</sup> as well as it can be a source for animal feeds.<sup>7</sup> Silicon, one of the most abundant materials on the earth's crust, is an attractive photoelectrode material because it is an excellent light absorber with a long carrier lifetime.<sup>8</sup> As illustratively depicted in Scheme 1, we constructed a biocatalytic CO<sub>2</sub> fixation PEC cell through a direct connection of a photoanode (as a working electrode) to a photocathode (as a counter electrode) in a two-electrode configuration. We adapted cobalt phosphate (CoPi)-deposited, npp<sup>+</sup> triple-junction silicon on ITO (3-jn-Si/ITO/CoPi) as a photoanode for light-assisted water oxidation because of facile charge separation induced by internal bias.<sup>9</sup> We used hydrogen-terminated silicon nanowires (H-SiNWs) as a photocathode because H-SiNW is effective for delivering hydrides to an Rh-based organometallic electron mediator {M; [Cp\**Rh*(bpy)(H<sub>2</sub>O)]<sup>2+</sup>, Cp\* = C<sub>5</sub>Me<sub>5</sub>, bpy = 2,2'-bipyridine} in photobiocatalytic systems, which is a critical step for the regeneration of enzymatically active NADH. Note that H-SiNW shows superior performance on NADH regeneration to SiNW due to the role of hydrogen atom as an electron sink.<sup>6b,10</sup> The M reduces to M<sub>red</sub> by accepting two electrons from H-SiNWs and a proton from the aqueous solution, which subsequently returns to its initial oxidized state by providing a hydride ion to NAD<sup>+</sup> (Fig. S1, ESI†). The biocatalytic PEC system is completed by NADH-dependent FDH, which catalyzes the reduction of CO<sub>2</sub> to formate. Overall, electrons obtained from water by the 3-jn-Si/ITO/CoPi photoanode upon visible light irradiation ( $\lambda > 420$  nm) were transferred to the H-SiNW photocathode under an external applied bias, followed by the FDH-catalyzed CO<sub>2</sub> reduction with NADH regeneration.

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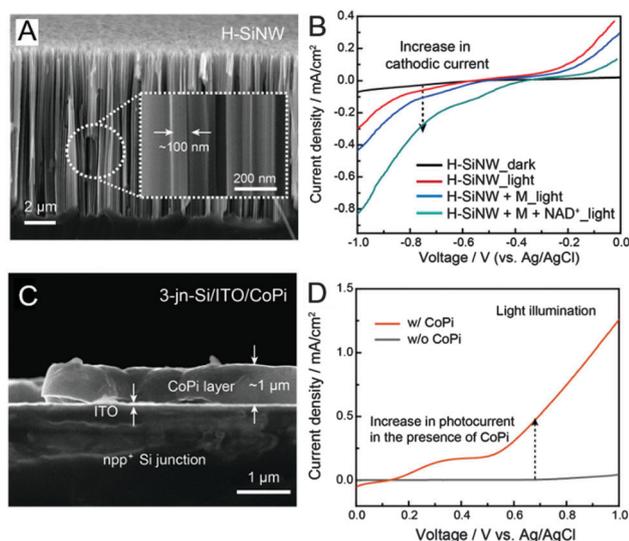
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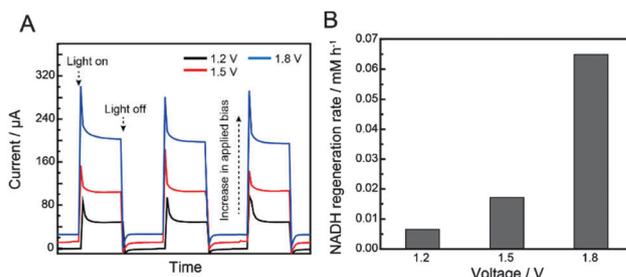


**Scheme 1** Schematic illustration of an all-silicon-based cell for solar-assisted biocatalytic CO<sub>2</sub> fixation in a two-electrode configuration. Electrons extracted by water oxidation at the 3-jn-Si/ITO/CoPi photoanode with an aid of external bias are supplied to the H-SiNW photocathode. The electrons are excited by visible light irradiation, followed by being transferred to NAD<sup>+</sup> via M, a Rh-based electron mediator. The reduced NAD<sup>+</sup> delivers two electrons and one proton used for converting CO<sub>2</sub> to formate by TsFDH.

For the photochemical regeneration of NADH, an essential step for sustainable reduction of CO<sub>2</sub> by FDH, we fabricated H-SiNWs of approximately 10 μm in length and 100 nm in diameter using a metal-assisted solution etching method (Fig. 1A). According to the *J*-*V* characteristic of the H-SiNW photocathode (Fig. 1B), the cathodic current density increased upon light irradiation and further increased by the addition of M and NAD<sup>+</sup>, which indicates that photo-excited electrons from H-SiNWs can effectively reduce NAD<sup>+</sup> with M as a mediator. To fabricate the 3-jn-Si/ITO/CoPi photoanode, we electrodeposited CoPi on 3-jn-Si/ITO at an applied bias of 0.9 V (vs. Ag/AgCl, Fig. S2A, ESI<sup>†</sup>). Using a scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy, we confirmed that CoPi was successfully deposited on 3-jn-Si/ITO (Fig. 1C and Fig. S2B, ESI<sup>†</sup>). As shown in Fig. 1D, the photocurrent density of the 3-jn-Si/ITO photoanode was significantly increased



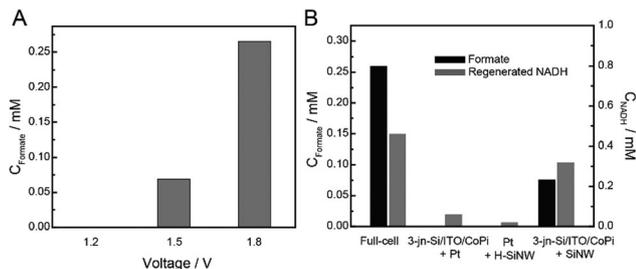
**Fig. 1** (A) SEM image of a H-SiNW photocathode and (B) Linear-sweep voltammogram of the H-SiNW under dark and light conditions with or without the addition of M and NAD<sup>+</sup>. The scan rate was 10 mV s<sup>-1</sup>. (C) SEM image of a 3-jn-Si/ITO/CoPi photoanode. CoPi was deposited on 3-jn-Si/ITO for 30 min at 0.9 V (vs. Ag/AgCl). (D) Linear-sweep voltammogram of the photoanode under light illumination with or without the CoPi catalyst. The scan rate was 50 mV s<sup>-1</sup>.



**Fig. 2** Characterization of the all-silicon-based full PEC cell that connects a 3-jn-Si/ITO/CoPi photoanode and a H-SiNW photocathode in a two-electrode configuration. (A) Photocurrent measurements for the all-silicon-based PEC cells at different applied biases. (B) Comparison of NADH regeneration rates at different applied biases.

with the deposition of water oxidation co-catalyst (*i.e.*, CoPi), under visible light irradiation. The prefeature observed between 0.2 and 0.5 V (vs. Ag/AgCl) is caused by the oxidation of residual Co<sup>2+</sup>. Light was illuminated to the n-side of npp<sup>+</sup> 3-jn-Si/ITO/CoPi (*i.e.*, the opposite side of the CoPi layer) throughout the experiments to achieve increased photocurrent density avoiding a light-blocking effect by the CoPi layer (Fig. S4, ESI<sup>†</sup>).

We constructed a silicon-based, full PEC cell by directly connecting the 3-jn-Si/ITO/CoPi photoanode with the H-SiNW photocathode in a two-electrode voltammetric configuration. When the *J*-*V* curves of each photoelectrode's half-cell were overlapped (Fig. S5, ESI<sup>†</sup>), no intersection was observed, which indicates that external bias should be applied for a current flow between the two photoelectrodes under visible light illumination. To investigate the characteristics of the full-cell in terms of external bias, we firstly monitored the photocurrent of the full-cell at neutral pH as shown in Fig. 2A; electrons could be effectively transferred from the photoanode at applied voltages of more than 1.2 V under light illumination. However, the photocurrent density generated by the 3-jn-Si/ITO/CoPi photoanode at the applied voltage less than 1.2 V was negligible regardless of illumination (data not shown), indicating the requirement of a minimum applied bias for efficient generation and transfer of photo-assisted charges. With this in mind, we performed NAD<sup>+</sup> reduction at different applied biases to find the threshold voltage for achieving an efficient NADH regeneration reaction rate. As shown in Fig. 2B, the NADH conversion rate increased significantly from 0.017 to 0.064 mM h<sup>-1</sup> with the increasing applied voltage from 1.5 to 1.8 V, while only 0.0066 mM h<sup>-1</sup> rate of NADH regeneration was shown at 1.2 V. When we coupled NADH photoregeneration with biocatalytic CO<sub>2</sub> reduction to formate by introducing FDH from *Thiobacillus* sp. (TsFDH, Fig. S6, ESI<sup>†</sup>) to the silicon-based cell, the amount of produced formate under different applied biases showed the same tendency as the NADH photoregeneration (Fig. 3A); the formate yield significantly increased from 0.069 to 0.26 mM at the applied bias of 1.5 and 1.8 V, respectively, while no formate was synthesized at 1.2 V. The above result suggests that silicon-based, TsFDH-catalyzed formate production can be effectively performed at the applied bias of more than 1.5 V. We utilized FDH from TsFDH, which exhibits prominent catalytic activity



**Fig. 3** (A) Biocatalytic CO<sub>2</sub> conversion to formate for 6 h with different applied biases by the full-cell in a two-electrode configuration. (B) Comparison of NADH and formate conversion yields for 6 h with different cell configurations (e.g., full-cell, cells comprised of a 3-jn-Si/ITO/CoPi (working electrode) and a Pt (counter electrode), a Pt (working electrode) and a H-SiNW (counter electrode), or a 3-jn-Si/ITO/CoPi (working electrode) and a SiNW (counter electrode)). The NADH yield was monitored by concurrent sampling during the CO<sub>2</sub> fixation reaction. The silicon-based, TsFDH-catalyzed formate production was performed at the applied bias of 1.8 V in a two-electrode configuration.

for CO<sub>2</sub> reduction in comparison with other conventional FDHs, such as CbFDH from *Candida boidinii*.<sup>11</sup> Our previous study suggested that TsFDH possesses a much higher CO<sub>2</sub>-reducing activity because it has a lower free energy barrier to CO<sub>2</sub> reduction than CbFDH, a conventional FDH, by approximately 10 kcal mol<sup>-1</sup> and exhibits a 21.2-fold higher turnover number for CO<sub>2</sub> reduction than CbFDH.<sup>11</sup> We further confirmed that hydride could not be transferred from the photoelectrodes to NAD<sup>+</sup> under dark conditions (Fig. S7, ESI<sup>†</sup>). While kinetic coupling of photocatalytic and biocatalytic cycles was found to be extremely difficult in one-pot systems with water as an electron donor,<sup>6a</sup> the physical separation of water oxidation and NAD<sup>+</sup> reduction by the PEC platform addressed the difficulties by reducing back electron transfer; for example, 0.19 mM of NADH was regenerated with the separate configuration, whereas 0.11 mM of regenerated NADH was detected when water oxidation and NAD<sup>+</sup> reduction occurred in the same pot.

Biocatalytic CO<sub>2</sub> reduction by the NADH-dependent TsFDH involves multiple components such as M, NAD<sup>+</sup>, and TsFDH, for which photo-induced electrons should be sequentially transferred from H-SiNWs to each component. While no formate was produced directly at the surface of H-SiNW alone at the applied bias of 1.8 V (data not shown), 0.26 mM of formate was synthesized in the presence of all biocatalytic components (i.e., M, NAD<sup>+</sup>, and TsFDH) for 6 h, with a faradaic efficiency of 16.18% (Fig. 3B and Fig. S8, ESI<sup>†</sup>). The redox potential of M (-0.54 V vs. NHE) is more positive than that for formate production (-0.6 V vs. NHE), which provides more driving force for the thermodynamic injection of photo-induced electrons from the conduction band of H-SiNW (-0.8 to -0.6 V vs. NHE) to M. In the presence of both M and NAD<sup>+</sup>, the electron injection rate from H-SiNW to M is increased by catalytic hydride transfer from M to NAD<sup>+</sup>, as we described earlier (Fig. 1B). Finally, the delivered hydride is used to reduce NAD<sup>+</sup> to NADH that activates NADH-dependent TsFDH to produce formate. As control experiments, we observed formate yields after replacing each photoelectrode (i.e., 3-jn-Si/ITO/CoPi photoanode and H-SiNW

photocathode) with a Pt electrode under an applied bias of 1.8 V (Fig. 3B). With the change of the H-SiNW photocathode to a Pt electrode, the regenerated NADH yield decreased drastically from 0.46 to 0.066 mM, and no formate was synthesized, which indicates that additional potential generated in H-SiNWs by light illumination enables thermodynamic electron injection to M from the H-SiNWs. When we replaced 3-jn-Si/ITO/CoPi by a Pt working electrode, no formate and only 0.002 mM of NADH was synthesized because there was an insufficient electron supply caused by the lack of a catalytic effect of the Pt electrode on water oxidation at the applied bias of 1.8 V. Moreover, when using the SiNW photoanode without hydrogen termination, the amount of synthesized formate and NADH was decreased to 0.076 and 0.32 mM, respectively, with a faradaic efficiency for formate production of 8.26% (Fig. 3B). The result supports that hydrogen atoms at the surface of SiNW, acting as an electron sink to promote electron transfer,<sup>6b,10</sup> can contribute to the enhanced biocatalytic production of formate.

We further compared formate conversion yields using regenerated NADH and fully reduced NAD<sup>+</sup> (i.e., NADH) to demonstrate the advantage of the cofactor regeneration system through our integrated all-silicon-based PEC cell for biocatalyzed CO<sub>2</sub> reduction. When TsFDH-catalyzed CO<sub>2</sub> fixation test was performed with 0.5 mM of fully reduced NAD<sup>+</sup> under continuous CO<sub>2</sub> purging, the equilibrium concentration of 0.13 mM formate was synthesized (Fig. S9, ESI<sup>†</sup>). Note that NADH was only oxidized to NAD<sup>+</sup> by TsFDH without the reduction to NADH in this case. Recognizing 0.26 mM of formate was produced with the 0.46 mM of regenerated NADH in our biocatalytic CO<sub>2</sub> fixation system, the difference in formate production with a similar amount of NADH suggests an apparent advantage in the TsFDH-catalyzed CO<sub>2</sub> fixation with our cofactor regeneration system; a continuous supply of NADH through the PEC platform, despite the simultaneous NADH oxidation to NAD<sup>+</sup> by TsFDH, can boost the CO<sub>2</sub> conversion with NADH-dependent TsFDH, resulting in the improvement of formate production yield.

For practical utility of the biocatalytic PEC cell as a sustainable solar energy harvesting system, the direct use of natural sunlight is highly desirable but has rarely been demonstrated in research on solar-to-chemical conversion thus far. We examined whether CO<sub>2</sub> could be reduced to formate under natural sunlight by using a solar-tracking module that consisted of a solar tracker (for sunlight harvesting) and optical fibers (for energy transfer) providing outdoor sunlight to the biocatalytic PEC cell (Fig. 4A). Note that in this experiment, we constructed a photoanode-driven, biocatalytic CO<sub>2</sub> fixation PEC cell that connected a photoanode (as a working electrode) and a photocathode (as a counter electrode) in a three-electrode configuration using Ag/AgCl as a reference electrode.<sup>12</sup> In this configuration, the external bias of 0.6 V was applied between the working (3-jn-Si/ITO/CoPi) and the reference electrode (Ag/AgCl) to drive the water oxidation reaction at the 3-jn-Si/ITO/CoPi photoanode and permitted electron flow from the photoanode to the H-SiNW photocathode of the PEC cell. We illuminated the 3-jn-Si/ITO/CoPi photoanode with natural sunlight (using the solar tracker in Fig. 4A) for supplying electrons, generated by the water oxidation reaction, to the H-SiNW

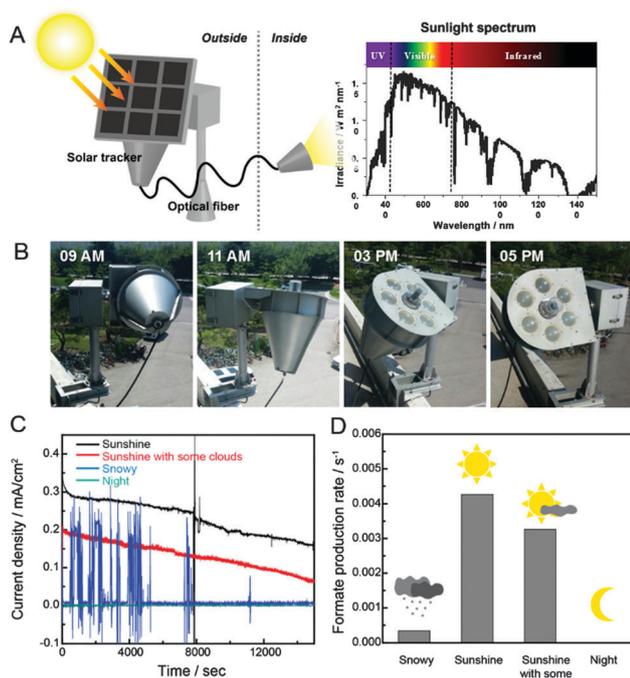


Fig. 4 (A) Schematic illustration of the solar-tracking module (installed at 36°21'54.3"N 127°21'40.6"E). The sun-tracking system consisted of a solar tracker and optical fibers provided outdoor sunlight to an indoor reactor. (B) As the sun moves from east to west, the solar tracker rotates for maximum harvesting of sunlight. (C) Comparison of photocurrent densities under irradiation of concentrated natural sunlight to the photoanode under different weather conditions. (D) CO<sub>2</sub> conversion to formate by the PEC cell using the solar-tracking module.

photocathode to produce formate *via* TsFDH. As shown in Fig. 4B, solar panels on the solar tracker automatically follow the movement of the sun by maintaining an optimum angle to collect most of the sunlight. We found that weather conditions significantly affected the photocurrent density, causing a differential rate in formate production by TsFDH (Fig. 4C); the rate was 0.004 s<sup>-1</sup> on a clear and sunny day and it slightly decreased to 0.003 s<sup>-1</sup> when the sunlight was partially covered with clouds. In the absence of sunlight, like on a snowy day or at night, a much reduced rate was observed (0.0003 s<sup>-1</sup> on a snowy day and no formate synthesis at night) (Fig. 4D). The above results demonstrate that a silicon-based biocatalytic PEC cell can use natural solar energy to produce a liquid fuel (*i.e.*, formate) using CO<sub>2</sub> as a carbon source and water as an electron donor.

In summary, we designed a new platform that integrates a silicon-based PEC cell with a biocatalyst (*i.e.*, TsFDH) for light-assisted electrochemical CO<sub>2</sub> reduction to formate. Our results revealed that sequential transfer of electrons, extracted *via* a water oxidation reaction at a 3-jn-Si/ITO/CoPi photoanode, to a H-SiNW photocathode, and further to TsFDH, leads to effective formate production with a faradaic efficiency of 16.18% under the applied bias of 1.8 V, while no formate was synthesized

directly at the H-SiNW photocathode alone. The formate yield increased significantly through the integrated PEC system, which continuously regenerated NADH for TsFDH-catalyzed CO<sub>2</sub> reduction. Moreover, we demonstrated that our silicon-based biocatalytic system could be operated under natural sunlight using a solar tracking module, which is a highly desirable result for the practical utility of the PEC as a sustainable solar energy harvesting system. The current study suggests that the deliberate integration of biocatalysis to a PEC platform can provide an opportunity to synthesize valuable chemicals with the use of earth-abundant materials and sustainable resources. With our biocatalysis-integrated PEC platform, further engineering of enzymes and photoelectrode materials would provide more opportunity to improve efficiency of the system.

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