COMMENTARY

A new frontier in artificial photosynthesis: Silicon nanowire biophotochemical diode for light-driven CO_2 reduction and glycerol valorization

Shijie Yu,[1,*] Yameng Ren,[2] and Yu Peng[3]

[1]Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117585, Singapore

[2]School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

[3]East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China

*Correspondence: yusj@nus.edu.sg

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The intensifying global climate change and the energy crisis have created an urgent need for sustainable energy technologies. Current renewable energy technologies, particularly those harnessing solar power through photovoltaic, are facing significant challenges. The intermittent nature of sunlight makes it difficult to integrate solar-generated power into the grid alongside existing energy sources, thereby necessitating large-scale energy storage solutions. Natural photosynthesis is the process by which plants, algae, and certain bacteria convert carbon dioxide and water into organic matter and oxygen by means of light energy, utilizing light-trapping molecules, such as chlorophyll, to absorb the sun's energy and drive the electron transport chain for energy storage and the construction of chemical bonds. Artificial photosynthesis mimics the mechanism of natural photosynthesis, using man-made systems to convert light energy into chemical energy. The direct one-step conversion and storage of solar energy in chemical bonds can be realized via photoelectrochemical (PEC) reactions, such as through photochemical diodes where a p/n PEC configuration drives redox reactions.[1,2] For instance, the reduction of CO_2 through PEC reactions not only stores energy, but also converts the greenhouse gas CO_2 into chemicals, thus contributing to carbon-neutrality goals.

While the hydrogen evolution reaction (HER) is relatively easier to achieve thermodynamically and kinetically, the CO_2 reduction reaction (CO_2RR) is more challenging due to its higher catalytic overpotential.[3] Existing bias-free abiotic PEC systems have yet to produce more reduced products beyond CO. However, about a decade ago, Yang and coworkers successfully created a biological PEC (BPEC) system realizing bias-free CO_2 to acetate, which serves as a biosynthetic precursor to various fine and commodity chemicals via acetyl coenzyme A (acetyl-CoA) including functionalized aliphatics, aromatics, lipids, alkanes, and complex natural products, by incorporating microbial catalysts, such as bacteria, into traditional abiotic PEC systems (Figure 1A).[4] This BPEC system is based on a Si/TiO_2 nanowire biophotochemical diode that can operate near the standard potential of the reaction, achieving a photocurrent density (J_{op}) of ~0.3 mA cm^{-2}. However, to enable widespread application, further enhancement of the system's bias-free J_{op} is required. Two primary limitations have been identified: the high oxidative potential of the oxygen evolution reaction (OER) and the slow kinetics of CO_2 reduction caused by the low turnover rate of the wild-type *S. ovata*.

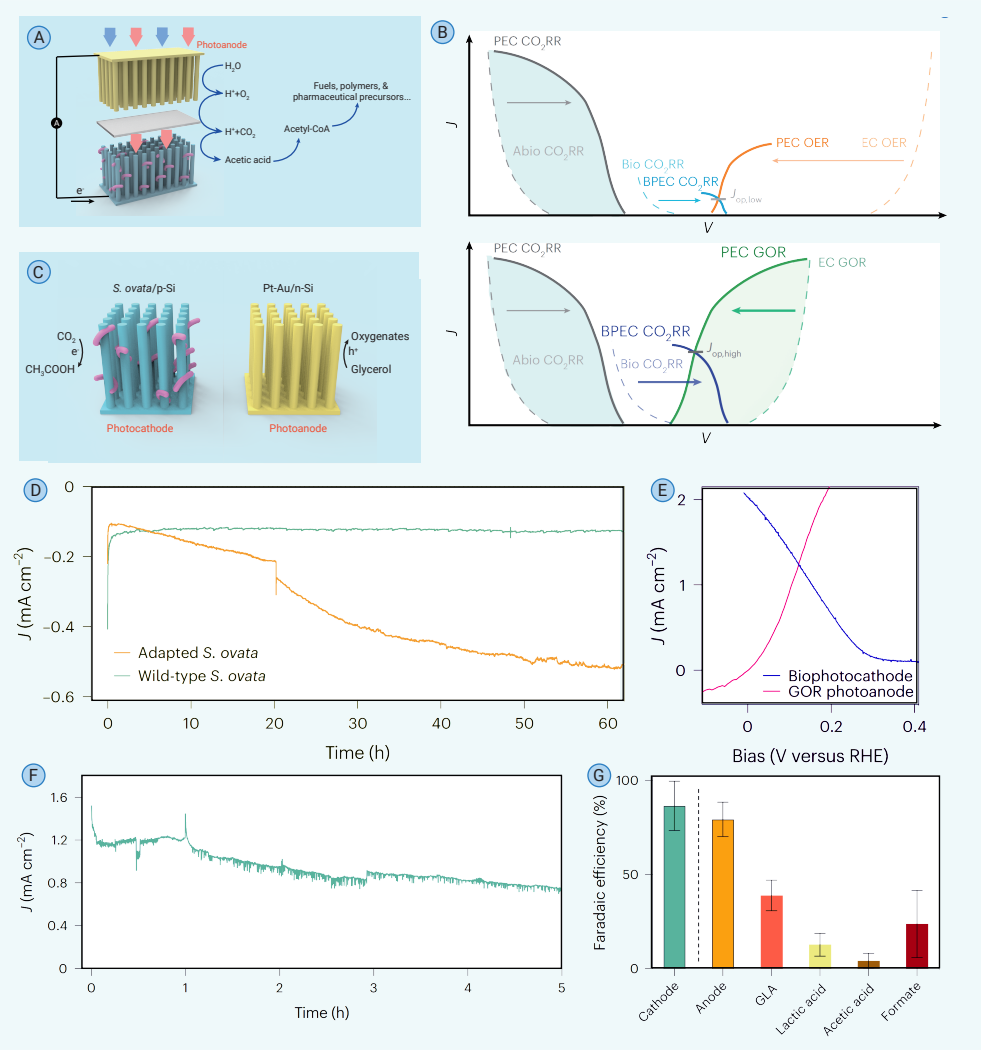

Figure 1. Design and performance of SiNW biophotochemical diode systems for solar-driven CO_2 reduction. (A) The first biophotochemical diode system based on SiNW achieving bias-free CO_2-to-acetate synthesis. (B) A comparison of current density–voltage curves for abiotic CO_2RR, biotic CO_2RR, OER, and GOR under both electrochemical (EC) and PEC conditions. (C) A SiNW-based biophotochemical diode system integrated with GOR to enable bias-free CO_2-to-acetate synthesis and glycerol valorization. (D) Stability of photocurrent density in SiNW biophotocathodes with wild-type and methanol-adapted *S. ovata*. (E) Intersection of the current density–voltage curves for the biophotocathode and the photoanode. (F) Stability of the photocurrent density of bias-free biophotochemical diode under continuous red light irradiation. (G) Faradaic efficiencies of the cathodic product and the anodic products of the biophotochemical diode under bias-free operation. Adapted from ref. 4 and 5.

To address the aforementioned challenges, Yang and coworkers recently further enhanced the J_{op} of the BPEC system by implementing two new strategies.[5] First, they improved the current density by replacing the thermodynamically high-potential OER with the lower-potential glycerol oxidation reaction (GOR). This change increased the intersection point of the current density curves of the photocathode and photoanode, subsequently raising the J_{op} of the BPEC system (Figure. 1B). Second, they increased the turnover rate of the biocatalyst, *S. ovata*, through metabolic engineering based on methanol, further boosting the reaction process's current density and conversion efficiency. Utilizing these two strategies, the system achieved a maximum bias-free J_{op} of ~1.2 mA cm^{-2} for PEC CO_2-to-C_2 reduction with high Faradaic efficiency (FE) of ~80% for both the cathodic and anodic reactions.

The researchers first assessed the photoelectrochemical performance of silicon nanowire (SiNW) photocathodes in a neutral pH environment. These photocathodes were structured with a p-type silicon core and an n^+ silicon shell (n^+p-SiNW) coated with a protective layer of TiO_2 and a 3 nm platinum deposit as a co-catalyst to facilitate the charge transfer and enhance photocatalytic performance (Figure. 1C). Under red light (740 nm) irradiation, the SiNW photocathode demonstrated efficient electron-hole pair separation and maintained stability throughout 12 hours of experimental operation, sustaining a consistent J_{op} under neutral pH conditions.

Furthermore, they integrated the SiNW photocathode with a microbial catalyst to test the performance of the bioCO_2RR half-reaction. Compared to the wild-type *S. ovata* strain, the methanol-adapted *S. ovata* showed enhanced autotrophic metabolism and a faster uptake of electrons and hydrogen, thereby increasing the charge transfer rate at the bio-nanowire interface (Figure. 1D). Combining this with the SiNW photocathode improved bioCO_2RR performances, achieving over 80% FE for acetic acid generation under bias-free conditions and a five-fold increase in J_{op} over 60 hours of operation. On the anodic side, the GOR was driven by a Pt-Au co-sputtered SiNW photoanode, producing oxidation products like glyceric acid, which further enhanced the system's economic efficiency. These two half-reactions overlapped with a high bias-free J_{op} of ~1.2 mA cm^{-2} (Figure. 1E).

Finally, the researchers integrated the two half-reactions by placing the photocathode and photoanode in two separate chambers, divided by a bipolar membrane, to measure the performance of the entire SiNW photochemical diode. In this configuration, the BPEC system achieved a bias-free J_{op} of ~1.20 mA cm^{-2} with a starting potential of −0.8 V, indicating that the system is capable of operating without an applied voltage. Additionally, the system maintained a stable J_{op} of 1.2 mA cm^{-2} during a prolonged operation of 1 h, showcasing its stability over extended periods of time without performance degradation (Figure. 1F). The primary product at the cathode was acetate, with an FE of 86.8% (Figure. 1G). The anodic products mainly consisted of glyceric acid, with an FE of 38.8%, and the FE for all the anodic products was 79.3%. Overall, this system exhibited high product selectivity and conversion efficiency under bias-free conditions.

In summary, the biophotochemical diode approach, based on a synergistic combination of highly efficient carbon-sequestering microorganisms and nanomaterials constructed from the earth-abundant, inexpensive silicon, offers a promising platform for harnessing solar energy while converting CO_2 and glycerol into high-value-added chemicals. This method also provides a novel reaction pathway for artificial photosynthesis and offers a good paradigm for interdisciplinary solutions to critical scientific problems. Despite the exciting progress that has been made, challenges remain including poor interfacial compatibility between the photoelectrode and the biological system, stability issues in long-term operation, efficiency limitations of the biocatalysts, insufficient energy efficiency of the photoelectrode system, inadequate selectivity of the target product, and challenges in scaling up applications. To further address the energy crisis and climate change through artificial photosynthesis, collaboration across chemistry, materials science, biology, and engineering is necessary to advance the development of related technologies.

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DECLARATION OF INTERESTS

The authors declare no competing interests.