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The electrochemical ion membrane system (EIMs) enhanced light reactions of photosynthesis with intermittent electrical stimulation†

Bicheng Deng,‡[ac] Yuyong Hou, ‡[bcde] Sihan Lu,[ac] Suihao Yan,[c] Zhile Guo,[ac] Zhiyong Liu,[ce] Xinqi Wang,[ac] Changhong Jia,[a] Weijie Wang,*[a] Longjiang Yu*[bd] and Lei Zhao *[cde]

Despite the widespread application of electrochemical systems in bioproduction, their detailed effects on photosynthetic organisms remain to be explored. In this study, a three-chamber electrochemical ion membrane system (EIMs) was optimized for minimizing carbon resource interference in the cathode chamber, thereby elucidating the role of EIMs in the light reactions of photosynthesis. By applying intermittent electrical stimulation, the photosynthetic activity of microalgae was enhanced, manifesting as the promoted accumulation of intracellular ATP and NADPH, while allowing the collection of hydrogen and oxygen as by-products. These findings suggest that EIMs not only facilitate photosynthesis by enhancing both light and dark reactions but also provide new avenues for improving the efficiency of photosynthetic production and advancing sustainable biotechnological processes.

Fossil fuels currently account for 81.5% of global energy consumption (https://www.energyinst.org/), contributing to the continuous rise in CO_2 levels in the atmosphere, which impacts both human life and the environment as the most significant greenhouse gas.[1,2] This has sparked increased interest in pollution-free CO_2 capture technologies.[3] Photosynthesis, which captures approximately 215 billion tons of carbon annually[4] as the most vital chemical process in nature, consists of two stages: the light reactions and the dark reactions. In the light reactions, electrons from water molecules are transferred to $NADP^+$ through an electron transport chain, generating NADPH and creating a proton gradient that drives ATP synthesis. The yielding products are then utilized for CO_2 assimilation in the dark reaction with RuBisCO as the key catalytic enzyme in the first step.[5] Enhancing the efficiency of both stages could significantly improve carbon sequestration, which would contribute to environmental protection and public health.

Among various photosynthetic organisms, microalgae exhibit a significantly higher photosynthetic CO_2 assimilation activity compared to higher plants.[6] Carbon-concentrating mechanisms (CCM) have evolved to increase the CO_2 concentration, which is beneficial for the carboxylation reaction in microalgae.[7] However, the slow mass transfer rates and low solubility of CO_2 in liquid medium still greatly limit the carbon fixation in microalgae. On the contrary, a high concentration of CO_2 in the culture medium not only results in a decreased pH value, which in turn inhibits carbon fixation of microalgae,[8] but also contributes to more than 90% of secondary CO_2 emissions to the atmosphere.[9] Remarkably, bicarbonate has been widely used as the effective solid carrier of CO_2 and alternative carbon resource for microalgae based on its solubility and alkalescence in liquid medium.[10] Nevertheless, microalgal cells maintain a much lower intracellular Na^+ level than that of the outside medium, and Na^+ from sodium bicarbonate is usually excluded from cells. Meanwhile, the high Na^+ levels in the medium always inhibit the carbon capture. Therefore, it is crucial to provide carbon resources for microalgae cultivation while preventing cation accumulation and CO_2 release to achieve efficient carbon fixation.

Recently, a water electrolysis-based microalgae cultivation system has been proposed to address the existing gaps.[11,12] Specifically, we previously developed and validated a novel three-chamber system integrating electrolysis and ionic membranes

[a] *College of Life Sciences, North China University of Science and Technology, No. 21 Bohai Avenue, Tangshan, Heibei 063210, P. R. China. E-mail: weijiewang@ncst.edu.cn*
[b] *Photosynthesis Research Center, Key Laboratory of Photobiology, Institute of Botany, Chinese Academy of Sciences, No. 20 Nanxincun, Xiangshan, Beijing, 100093, P. R. China. E-mail: longer@ibcas.ac.cn*
[c] *Key Laboratory of Engineering Biology for Low-carbon Manufacturing, Tianjin Institute of Industrial Biotechnology, Chinese Academy of Sciences, 32 West 7th Avenue, Tianjin Airport Economic Area, Tianjin 300308, P. R. China. E-mail: zhaol@tib.cas.cn*
[d] *University of Chinese Academy of Sciences, No. 1 Yanqihu East Rd, Huairou District, Beijing 101408, P. R. China*
[e] *National Center of Technology Innovation for Synthetic Biology, 32 West 7th Avenue, Tianjin Airport Economic Area, Tianjin 300308, P. R. China*

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‡ Bicheng Deng and Yuyong Hou contributed equally to this work.

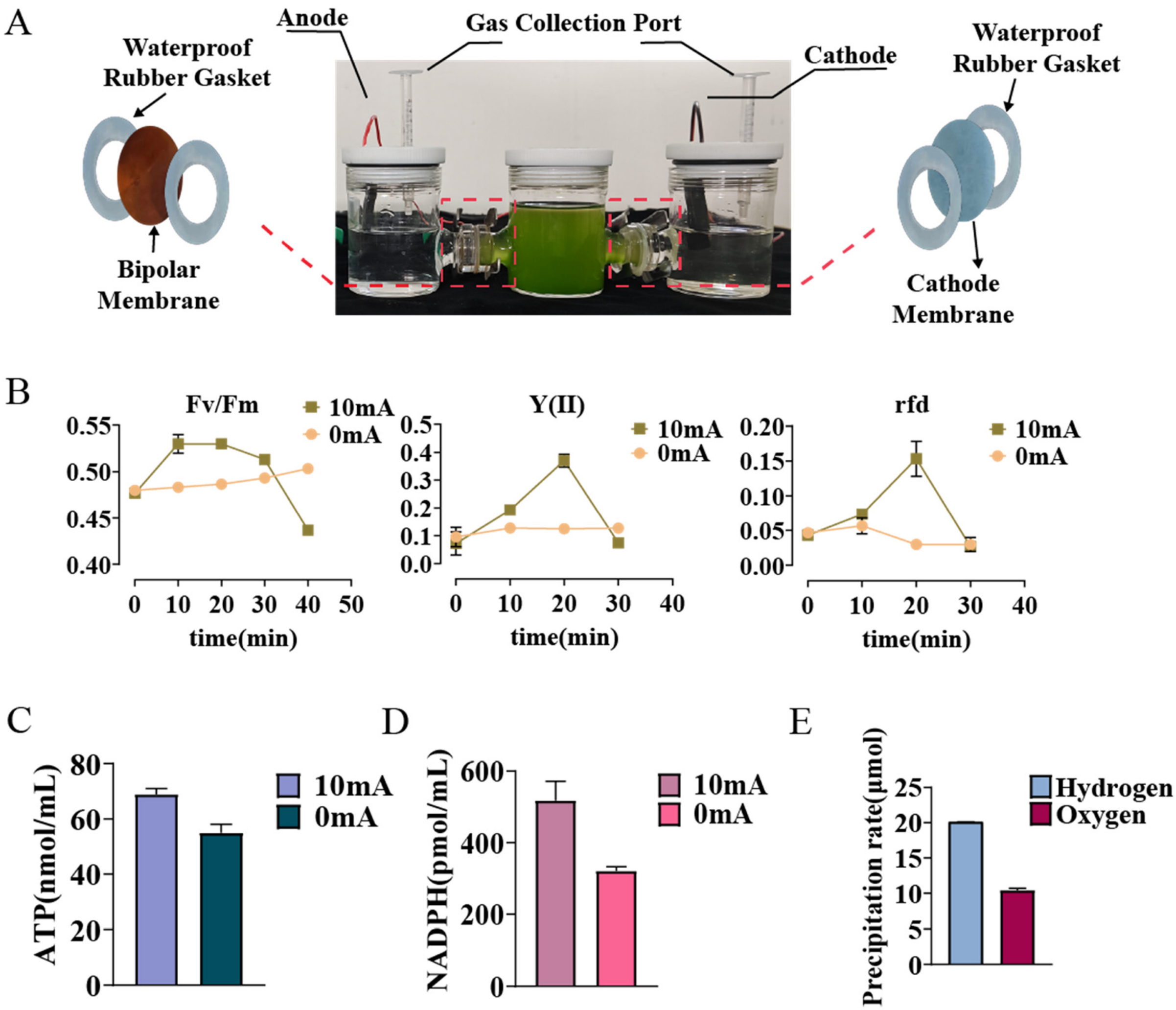

Fig. 1 Enhanced light reactions of photosynthesis with electrical stimulation enabled by electrochemical ion membrane systems. (A) Assembly and implementation of the designed EIMs in the experiment; (B) the chloroplast fluorescence parameters of cultured cells in the EIMs and control group (F_v/F_m, Y(II) and R_{fd}); (C) and (D) the intracellular contents of ATP and NADPH of cultured cells in the EIMs and control group; (E) the hydrogen and oxygen collected in EIMs at 30 min.

(EIMs) that enables the artificial recycling of CO_2 and alleviates metal cation stress during microalgae cultivation (Fig. 1A).[11] In the cathode chamber, a saturated bicarbonate solution is used, with HCO_3^- being transmembraneously driven into the middle microalgae chamber for carbon fixation. Hydroxide ions (OH^-) are produced through a reduction reaction at the cathode, which then directly absorb CO_2 from the air to replenish the consumed bicarbonate. Meanwhile, the anode chamber, equipped with bipolar membranes, facilitates the transfer of protons (H^+) to the culture medium, achieving ion equilibrium with the HCO_3^- from the cathode chamber. Although EIMs have been validated to significantly enhance the supply of carbon resources for dark reactions, its effects on light reactions of photosynthesis have not been examined. In contrast to photosynthetic organisms, cable bacteria, such as *Shewanella oneidensis*, are known to be an extracellular electron uptaking strain. Conductive materials typically exhibit high electrical conductivity and have the potential to mediate electron transfer between microorganisms.[13–15] In these studies, microorganisms are in direct contact with the electrodes, allowing for the direct absorption and utilization of generated electrons. In the EIM system, however, the membrane isolation means the electrodes do not come into direct contact with the photosynthetic organisms, leaving it unclear whether the EIM system can facilitate the transfer of energy synthesis to microalgal cells. This study aims to investigate the detailed effects of the EIM system on the light reactions of photosynthesis based on the chlorophyll fluorescence analysis in an effort to explore full potential of the microalgae-friendly system.

In this study, we replaced $NaHCO_3$ with ddH_2O to minimize interference from dissolved inorganic substances in the cathode chamber. During operation, hydrogen evolution occurs at the cathode, generating hydroxyl ions that are specifically transported across the anion-exchange membrane to the intermediate chamber, thereby balancing the protons produced at the anode. Consequently, an electrical signal and water are supplied with no additional nutrients affecting photosynthesis. This allows the system to elucidate the impact of EIMs on the light reactions. The photosynthetic parameters, along with intracellular ATP and NADPH contents, were measured to reveal the role of EIMs in the light reactions. Moreover, the byproducts H_2 and O_2 generated in cathode and anode chambers, respectively, were also analyzed to further evaluate its economics. Our findings demonstrate that intermittent electrical stimulation over a specified period positively influence the chlorophyll fluorescence parameters in microalgae, leading to increased production of ATP and NADPH, which in turn enhances carbon fixation.

The effects of electrical stimulation on the photosynthesis of microalgae were initially analyzed by monitoring the core parameters F_v/F_m and Y(II) of photosystem II. As shown in Fig. 1B, the values of F_v/F_m in the 10 mA treatment group were 9.73%, 9.05%, and 4.05% higher than those of the control without any treatment at 10, 20 and 30 min, respectively. The value of F_v/F_m was decreased after 40 minutes in the treatment group, which is consistent with our previous study.[11] Since F_v/F_m indicates the maximum photochemical efficiency of PSII after dark adaptation,[16] the increased value of F_v/F_m of microalgal cells in EIMs appears to benefit their photosynthetic capacity when cultured within 30 min, thereby promoting cell growth. Y(II), which represents the effective photochemical efficiency of photosystem II and reflects its capacity to convert light energy into chemical energy, manifested as a similar profile to that of F_v/F_m. Y(II) was measured to be a 198.49% higher value in the treatment group than that of the control cells at 20 min of electrolytic reaction. These results demonstrate that EIMs enhance the photosynthetic efficiency of the tested cells by increasing the activity of photosystem II to some extent, while excessive external electricity may bring in negative effects (Fig. 1B). Furthermore, the profiles of the chlorophyll fluorescence decline ratio (R_{fd}),[17] which depends on the overall electron transport chain and synthesis of ATP and NADPH, were measured with a higher value in the treatment group than the control group during the electrolytic period within 30 min. R_{fd} has been demonstrated to be highly correlated with CO_2 fixation, thus providing complementary evidence regarding PSII photochemistry. Similarly, the hybrid electrophototroph with PSII-deficient cells demonstrated that exogenous electrons can bypass Q_B and enter the photosynthetic electron transport chain downstream, with PQ acting as a key entry point for these electrons.[18] These findings suggest that EIMs may enhance PSII activity and promote ATP/NADPH generation, which is essential for the carboxylation reactions catalysed by RuBisCO.

To confirm the effects of EIMs on the light reactions, the generation of energy carriers and reductants, including both ATP (adenosine triphosphate) and NADPH (reduced nicotinamide adenine dinucleotide phosphate), was measured in tested cells. Considering that it takes time for the microalgal cells to accumulate ATP and NADPH, samples were collected at 30 min of treatment. As shown in Fig. 1C and D, the ATP and NADPH contents were increased by 13.98% and 38.08% with electrical stimulation compared to the control group, respectively. This indicates that EIMs indeed enhance the activity of light reactions, which boosts the generation of both NADPH and ATP, thus improving photosynthetic efficiency and carbon fixation.

As the primary byproducts of EIMs following electrification, hydrogen and oxygen have widespread applications in the energy sector, medical field, and chemical synthesis. The hydrogen and oxygen produced could be collected and utilized in the carbon fixation process, thereby reducing the overall cost. With the treatment of constant current of 10 mA for 30 minutes, which was proved to enhance the photosynthetic efficiency of microalgal cells in EIMs, approximately 20.09 μmol of hydrogen and 10.63 μmol of oxygen were produced from an ion-exchange area of 1.77 cm^2 with a 75 mL chamber (Fig. 1E). This result aligns with the theoretical principles of water electrolysis, where one molecule of water yields one molecule of hydrogen and half a molecule of oxygen. Notably, it is possible that further improvement could be made in these output values as a result of the effects of non-optimised electrodes and the relatively small volume of the reactor.

Since CO_2 is one of the greenhouse gases and a major contributor to climate change, bioelectrochemical systems are emerging as promising carbon capture devices in response to global warming with their energy potentially sourced from clean energy,[19] thus providing sustainable development advantages. Current research primarily focuses on the direct supply of current to cable bacteria (*e.g. Shewanella oneidensis* and *Desulfovibrio termitidis*),[20,21] while studies on non-cable bacteria, such as photosynthetic microalgae, are relatively scarce.[18] Specifically, under conditions where electrodes do not directly contact with the organisms, the effect of current on promoting the light reactions remains to be further investigated. This study elucidates the positive effects of EIMs on the light reactions of photosynthesis in microalgae. Measurements of photosynthetic parameters, such as F_v/F_m, Y(II), and R_{fd}, indicate that moderate electrical stimulation can enhance the photosynthetic capacity of microalgae even without direct contact with the electrode. Short-term electrical stimulation, *e.g.*, less than 30 minutes, does not induce negative effects on the cells and the carbon fixation could be accelerated with the increased generation of ATP and NADPH (Fig. 1C and D), which then leads to a higher cell density.[11] Excessive electrical stimulation resulted in the yellow coloration of the microalgae culture, suggesting that prolonged stimulation may lead to cell death (Fig. S1, ESI†).

In summary, although EIMs have been developed and demonstrated to enhance the carbon supply,[11] it remains unclear whether it affects the light reactions for achieving high biomass. To test the possibility, ddH_2O was used to replace bicarbonate as the catholyte. As a result, the transferred OH^- and H^+ from the cathode and anode chambers, respectively, formed only H_2O without introducing additional nutrient elements or causing pH changes, thus providing the conditions to examine the effect of electrical stimulation on photosynthesis. Furthermore, it is noteworthy to mention that the replacement of $NaHCO_3$ with NaOH could result in similar results. In the present study, the photosynthetic activity (F_v/F_m, Y(II), and R_{fd})

and energy carrier (ATP and NADPH) of cells cultured in EIMs were observed with an elevated profile to some extent, clearly demonstrating the potential of EIMs in promoting both the light and dark reactions for carbon fixation. Moreover, the yielding hydrogen and oxygen could be collected and used for the carbon fixation process by reducing the total cost in EIMs. In conclusion, the developed EIMs demonstrate significant potential for carbon capture, utilization, and storage, thereby paving the way for the application of green technology in carbon sequestration by photosynthetic organisms in the future.

Bicheng Deng: writing – review & editing, writing original draft, visualization, investigation. Yuyong Hou: writing – review & editing, writing original draft, validation, investigation, funding acquisition, conceptualization. Sihan Lu, Suihao Yan, Zhile Guo, Zhiyong Liu, Xinqi Wang and Changhong Jia: investigation. Weijie Wang, Longjiang Yu and Lei Zhao: writing – review & editing, writing – original draft, funding acquisition, conceptualization.

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Data availability

The experimental data are included in this article and its ESI.†

Conflicts of interest

There are no conflicts to declare.

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