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PERSPECTIVE

Wastewater treatment meets artificial photosynthesis: Solar to green fuel production, water remediation and carbon emission reduction

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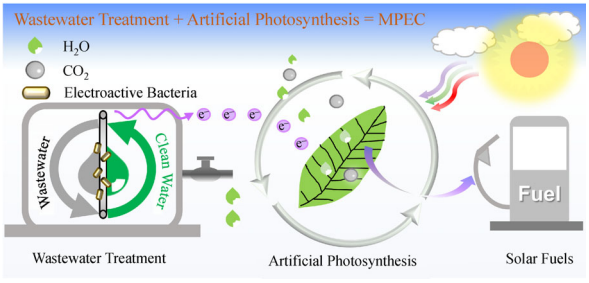
HIGHLIGHTS

- Mitigating energy utilization and carbon emission is urgent for wastewater treatment.
- MPEC integrates both solar energy storage and wastewater organics removal.
- Energy self-sustaining MPEC allows to mitigate the fossil carbon emission.
- MPEC is able to convert CO_2 into storable carbon fuel using renewable energy.
- MPEC would inspire photoelectrochemistry by employing a novel oxidation reaction.

GRAPHIC ABSTRACT



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ABSTRACT

Current wastewater treatment (WWT) is energy-intensive and leads to vast CO_2 emissions. Chinese pledge of "double carbon" target encourages a paradigm shift from fossil fuels use to renewable energy harvesting during WWT. In this context, hybrid microbial photoelectrochemical (MPEC) system integrating microbial electrochemical WWT with artificial photosynthesis (APS) emerges as a promising approach to tackle water-energy-carbon challenges simultaneously. Herein, we emphasized the significance to implement energy recovery during WWT for achieving the carbon neutrality goal. Then, we elucidated the working principle of MPEC and its advantages compared with conventional APS, and discussed its potential in fulfilling energy self-sustaining WWT, carbon capture and solar fuel production. Finally, we provided a strategy to judge the carbon profit by analysis of energy and carbon fluxes in a MPEC using several common organics in wastewater. Overall, MPEC provides an alternative of WWT approach to assist carbon-neutral goal, and simultaneously achieves solar harvesting, conversion and storage.

The nexus between greenhouse gas (GHG) emissions and global climate change stimulates worldwide interests in finding a sustainable development mode. Current wastewater treatment (WWT) is an energy-intensive and heavy carbon-emitting industry. Nearly 1000 km^3 of wastewater is produced around the world annually, which requires ~3% of global electricity to carry out purification and accordingly leads to significant GHG emissions including direct one due to degradation of pollutants and indirect one resulted from the use of fossil fuel (Lu et al., 2018). In this context, developing carbon-neutral WWT approaches is of great necessity. Note, wastewater is also a carrier of energy in its own right with the embedded chemical energy of waste organics exceeding several times of that required by its treatment (Qu et al., 2019; Qu et al., 2022). If energy recovery is conducted sufficiently, it hints that WWT can be an energy self-sustaining or even positive process to

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avoid indirect carbon emission or to even use reclaimed energy for GHG capture.

As the largest developing country, China accounts for ~28% of the world's total CO_2 emissions and pledged in 2020 that its carbon emissions will strive to peak by 2030 and become carbon-neutral by 2060. This was till then the largest climate commitment, and laid down a marker when many other countries were considering their climate commitments. To realize the "double carbon" goal, nearly all of Chinese industries associated with carbon emission are undergoing a paradigm shift in terms of policies and techniques. To the end of 2018, China has possessed over 5000 municipal WWT plants (WWTPs) with a daily treatment capacity of ~2×10^8 m^3 (Qu et al., 2019). Whereas, carbon-neutral WWT in China is still in its incubation stage but emerging as a hot topic. Searching for clean alternatives to fossil fuels while harvesting the energy stored in wastewater itself is one efficient pathway to enter WWT's carbon-neutral stage.

Solar is considered as one of the ultimate solutions to solve energy crisis and climate change, nevertheless, its intermittent nature makes it challenging to match human-kind's 24-hour energy demand. Converting solar energy as storable fuels, such as H_2 and hydrocarbons, by conventional artificial photosynthesis (APS) can potentially address above concern, but it suffers from inappropriate band positions of semiconductors (Figs. 1(A) and 1(B)) (Nguyen et al., 2017). Thus, most practical APS cases (e.g. photoelectrochemical systems, PEC) still need external voltage input.

Microbial photoelectrochemical (MPEC) system, a recently emerging hybrid APS, which combines microbial electrochemical oxidation with photoelectrochemical reduction is receiving increasing attention because of its potential in addressing both environmental and energy concerns (Fig. 1(C)) (Lu et al., 2017; Lu et al., 2019). Electroactive bacteria grown on the anode oxidize biodegradable organics in wastewater and release the electrons to an external circuit. The electricity is then used as a green energy supply to overcome the thermodynamic barrier and support an unassisted solar H_2 production or CO_2 reduction at a semiconductor cathode (Fig. 1(D)). Hence, the chemical energy embedded in wastewater, together with solar, is converted into clean hydrogen energy or energy of carbon fuels. Compared to conventional APS, MPEC reduces the energy required by oxidation reaction as much as 1.1 V through replacing sluggish water oxidation with more energetically favorable organics oxidation (Fig. 1(A)), corresponding to ~89% (H_2 production) and ~82% (CO_2 reduction to CO) reduction of overall energy demand. This allows most semiconductors' band gap to straddle the potentials of redox reactions to

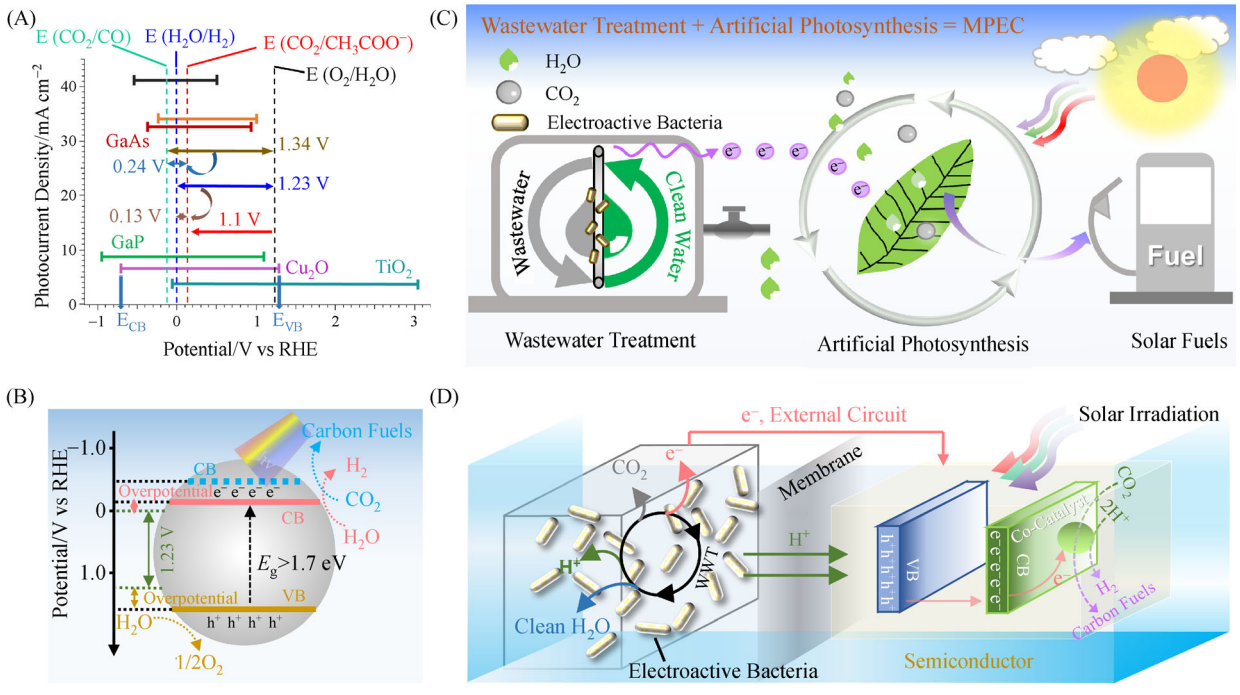

Fig. 1 Schematics of MPEC and conventional APS. (A) Band gap (horizontal line), conduction (E_{CB}) and valence band (E_{VB}) positions (vs. reversible hydrogen electrode, RHE), and photocurrent density of common semiconductors under conditions of pH = 7, T = 298.15K, P = 1 atm, and 1 sun illumination (100 mW/cm^2). The black, red, blue, and green dotted lines are the thermodynamic potentials for water oxidation, acetate (organic) oxidation, water reduction, and CO_2 reduction to CO, respectively. (B) APS water splitting and CO_2 reduction within single semiconductor (CB: conduction band; VB: valance band). (C) Integration of microbial electrochemical wastewater treatment and APS. (D) MPEC working principle. MPEC harvests the energy embedded in wastewater organics to power photoelectrochemical reduction, holding great promise to resolve water-energy-carbon problems simultaneously.

Table 1 The carbon profit of a MPEC using different types of organic substrates for CO_2 reduction to CO or H_2 production

Type of substrate	n_{CO_2}, (mol-CO_2 produced /mol-substrate)	n_{e^-} (mol-e^- produced /mol-substrate)	n_{CO} (mol-CO produced /mol-substrate)	Carbon profit of CO_2 reduction	n_{H_2} (mol-H_2 produced /mol-substrate)	Recovered hydrogen energy (kJ)	Energy required by CO_2 reduction to CO (kJ)	Carbon profit of H_2 production
Glucose	6	16.8	7.98	Negative (>1)	7.98	2234.4	1551.6	Negative (>1)
Ethanol	2	8.4	3.99	Negative (>1)	3.99	1117.2	517.2	Negative (>1)
Formate	1	1.4	0.665	Positive (< 1)	0.665	186.2	258.6	Positive (< 1)
Acetate	2	5.6	2.66	Negative (>1)	2.66	744.8	517.2	Negative (>1)
Lactate	3	8.4	3.99	Negative (>1)	3.99	1117.2	775.8	Negative (>1)
Proprionate	3	9.8	4.655	Negative (>1)	4.655	1303.4	775.8	Negative (>1)
Butyrate	4	14	6.65	Negative (>1)	6.65	1862	1034.4	Negative (>1)

Notes: For CO_2 reduction to CO in MPEC, the carbon profit is determined by a ratio of CO (mole) generated to CO_2 (mole) released due to substrate oxidation. For H_2 production in MPEC, the carbon profit is determined by a ratio of hydrogen energy (280 kJ/mol H_2) recovered to the energy required by CO_2 reduction to CO (258.6 kJ/mol in conventional APS). The electrons needed by CO_2 reduction to CO is 2 mol e^-/mol CO_2 to CO. A targeted Coulombic efficiency of 70% for substrate oxidation under anaerobic condition and a Faradaic efficiency of 95% for CO_2 reduction to CO or H_2 production were proposed here based on previously reported data. The ratio mentioned above >1, = 1, < 1 indicates that carbon profit is negative, neutral, positive, respectively.

generate self-sustaining current, and thus greatly expanding the category of semiconductors that are usable in unassisted APS, and also allows MPEC to choose semiconductors with narrow band gap for absorption of sunlight with broader spectrum. Our group has reported a record photocurrent up to 23 mA/cm^2 within MPEC, which for the first time exceeded the benchmark current of 10 mA/cm^2 for self-sustaining solar H_2 production by APS (Lu et al., 2019). However, most reported MPEC systems showed that solar-to-fuel reaction typically terminates at H_2 and the carbon-based fuels production is still challenging (Lu et al., 2017; Lu et al., 2019). This is due to that CO_2 reduction is more sluggish and energy-intensive than water reduction. One pioneering work conducted by our group realized self-sustaining transformation of CO_2 and H_2O to syngas (mixture of CO and H_2) (Lu et al., 2020), demonstrating the great potential of MPEC in direct CO_2 mitigation. Izadi and Yu commented that this work would bring studies on CO_2 reduction and MPEC to a new stage (Izadi and Yu, 2020). Besides the apparent energy-recovery merits, MPEC has showed a highly efficient removal of waste organics in real industrial wastewater with COD removal over 90%, indicating its potential application in water remediation (Lu et al., 2020).

Although MPEC eliminates the indirect GHG emissions associated with the fossil fuel and may also capture CO_2, it still releases GHG due to degradation of pollutants. The direct GHG emissions in conventional WWTPs accounts for ~1.57% of global value (Lu et al., 2018). Figuring out the carbon balance in MPEC is crucial to judge the carbon profit (carbon-positive, carbon-neutral or carbon-negative), which was preliminarily analyzed by employing several common organics in wastewater (Table 1). When using MPEC to drive CO_2 reduction, except formate, other substrates are shown to be carbon-negative because the generated electrons are more than that required to reduce the released CO_2 (2 mol e^-/mol CO_2 to CO). This is also the case for H_2 production. The theoretical energy embedded in H_2 exceeds that required by electrochemical reduction of CO_2 to CO, therefore all substrates but formate are calculated to be carbon-negative. Note here, a targeted Coulombic efficiency of 70% for organics oxidation under anaerobic condition, and a Faradaic efficiency of 95% for CO_2 reduction or H_2 production (water splitting) were employed for the calculation based on data in literatures (Li et al., 2020; Yang et al., 2021). In practical cases, the inevitable energy loss should also be taken into account before acquiring the final carbon profit. Overall, MPEC integrates spontaneous solar fuel production, wastewater treatment, and carbon emission reduction in one system, and offers potentials to realize carbon-neutral or even carbon-negative WWT. Although practical implementation will present challenges such as the slow electron transfer kinetics at the interface between microorganism and anode, the energy losses due to internal resistance, and the long-term stability of semiconductor that need further research efforts to overcome, we are optimistic that MPEC will play greater roles in tackling energy and environmental problems.

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