

Enhanced Biophotocatalytic Performance via Photoinduced Interfacial Charge Transfer in MIP-208/E. coli Hybrids

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Abstract. Photosynthetic biohybrid systems (PBSs) represent a new paradigm combining the photon-capturing function of synthetic photodynamic sensitizers with the complex catalytic apparatus of living beings, and it is very promising for sustainable energy conversion. In order to avoid the dependence of intricate structural hybridization on interfacial electron transfer, we rationally designed a binary semi-artificial photosynthetic system that connects MIP-208 and Escherichia coli. This integrated platform has preserved the inherent metabolic ability of the biological chassis and significantly enhanced its capacity to utilise solar energy. Under the condition of 100 mW cm⁻² light irradiation, the MIP-208/E. coli system achieved a hydrogen production yield of 40.0 μmol per 10¹⁰ cells, which is 4.3 times that of the bacteria-only group. This work offers new ideas for the reasonable design of light-driven biohybrid systems to achieve hydrogen production.

Keywords: Biophotocatalytic, Metal-Organic Framework, E. coli, Charge Transfer

1. Introduction

As the most abundant and developable clean energy, solar energy is both cheap and promising in terms of development. However, natural photosynthesis is restricted by the relatively low solar-to-biomass conversion efficiency of only 1-2%, and its intervention capability is limited [1,2]. Artificial photosynthetic systems have problems with low conversion efficiency and unstable operation that do not meet people's requirements for green chemical production. At the same time, traditional artificial photosynthetic systems can no longer meet demands in terms of yield increase or quality improvement due to limitations caused by weather factors or time constraints [3]. Although progress has been made in light-driven green hydrogen production, the issue of low efficiency in photogenerated carrier separation and transport from photosensitisers to catalytic active centres is still present [4]. Biophotocatalytic systems based on photosensitiser/biohybrid assemblies, which are also known as semi-artificial photosynthetic systems, have become a new type of technological platform [5,6]. These systems integrate light-harvesting and charge transfer, using photosensitisers that can effectively absorb photons. They couple this with the selective biocatalytic activities of whole-cell microbial cells for a new type of mild condition for converting solar energy into chemical energy-cyclic regeneration of cofactors or reducing hydrogen [5,6]. Compared with traditional

porous materials, such as activated carbon, zeolite and mesoporous SiO₂, MOF exhibits a complex internal pore structure that can effectively guide photogenerated carriers. At the same time, due to its organic photosensitizer motif, MOF is easy to design structurally to enhance light collection capacity [7]. Photo-driven biological hydrogen production systems combine the high catalytic efficiency of biological systems with the light-harvesting and electron-transfer properties of photosensitisers, providing a potential approach to promoting solar-driven hydrogen production technologies [8,9].

A rational design of the Ti-based metal-organic framework (MIP-208)-*Escherichia coli* binary biohybrid semi-artificial photosynthetic system has been created to achieve high-efficiency biophotocatalytic hydrogen evolution. The composite structure has inherited basic catalytic function, at the same time improve photon utilizations rate by adding a photosensitizer part. Under the light irradiation condition at 100 mW/cm², MIP-208/*E. coli* system achieved a hydrogen production yield of 40.0 μmol per 10¹⁰ cells, which was approximately 4.3 times that of the bacteria-only control group. We have clarified the regulatory mechanism of photogenerated electrons on the central metabolic fluxes of *E. coli* and provided basic mechanistic insights into the interface electron transfer dynamics at the MIP-208-microbe interface.

2. Results

2.1. Synthesis and characterization of MIP-208

MIP-208 was synthesised by the solvothermal method, as described in a published report. Phase purity and morphology were determined by powder X-ray diffraction (PXRD) and Scanning Electron Microscopy (SEM), respectively. PXRD patterns are shown in Fig. 1a showed characteristic peaks at $2\theta = 8.1^\circ$, 12.1° and 14.6° , which matched the simulated pattern and confirmed that the crystalline phase had been successfully formed [10]. SEM images (Fig. 1b) showed that the uniform rod-shaped particles were about 3 μm long, with a rough surface and expected to help bacteria adhere during the assembly of this hybrid structure in the next step.

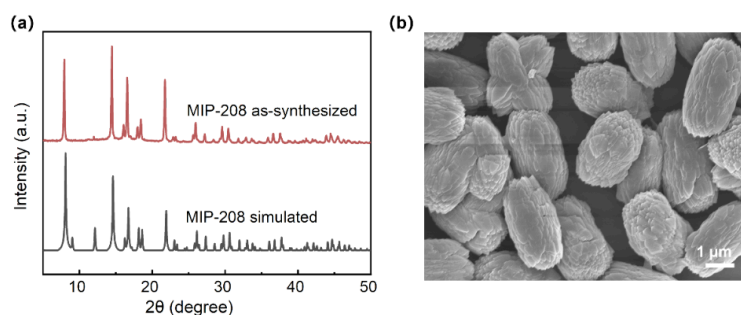


Figure 1. (A) PXRD pattern and (b) SEM image of MIP-208

2.2. Optoelectronic properties

The MIP-208 light-capturing ability was judged based on UV-vis diffuse reflectance spectroscopy (DRS). As illustrated in Fig. 2a, MIP-208 has strong absorption in the 200-600 nm range. Given that visible light (400–800 nm) constitutes ~43% of the solar spectrum, this broad absorption is advantageous for solar energy conversion. Assuming direct bandgap behaviors [11], the Tauc-plot analysis gives an optical bandgap (E_g) of 2.8 eV (Fig. 2a). Mott-Schottky tests at several frequencies (1000, 1500 and 2000 HZ) yielded a conduction-band (CB) position at -1.15 V vs. NHE (see Fig.

2b). The valence-band (VB) potential was then calculated as +1.65 V vs NHE by using the relation $E_{VB} = E_{CB} + E_g$. This type of band structure meets the thermodynamic criteria for photocatalytic hydrogen production (as shown in Fig. 2c).

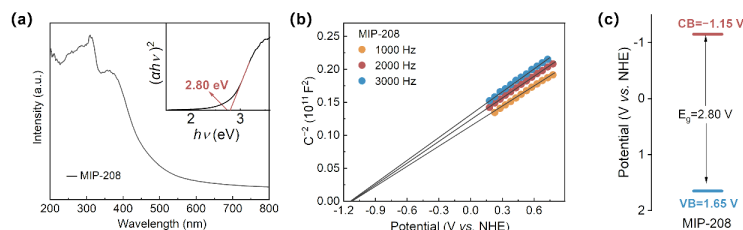


Figure 2. The figure illustrates the structure of this network. (a) UV-vis DRS and Tauc plot (inset), (b) Mott-Schottky plots at different frequencies, and (c) schematic band diagram of MIP-208

2.3. Biocompatibility of the hybrid system

Before evaluating photocatalytic performance, we need to evaluate the biocompatibility of MIP-208/*E.coli* interface, because only when the cell is alive and metabolically active can it efficiently and continuously carry out solar-to-chemical conversion [12,13]. In this experiment, to observe the impact of different combinations on bacterial physiology under a condition where $100 \text{ mW} \cdot \text{cm}^{-2}$ visible light irradiation is added along with MIP-208 at the same time. As shown in Fig. 3a illustrates this design, without light and without MIP-208 (all test concentrations), there was no substantial change in cell viability. Growth-curve analysis further showed that the hybrid system had a growth rate like that of *E. coli* alone (Fig. 3b-c). The hybrid exhibited an extended exponential stage, a delayed entry into the stationary phase, but the final cell density was comparable. The MIP-208/*E. coli* confirms this. The coli interfaces can still keep a high level of biocompatibility during actual applications so that the bacteria achieve their growth and Metabolism normally.

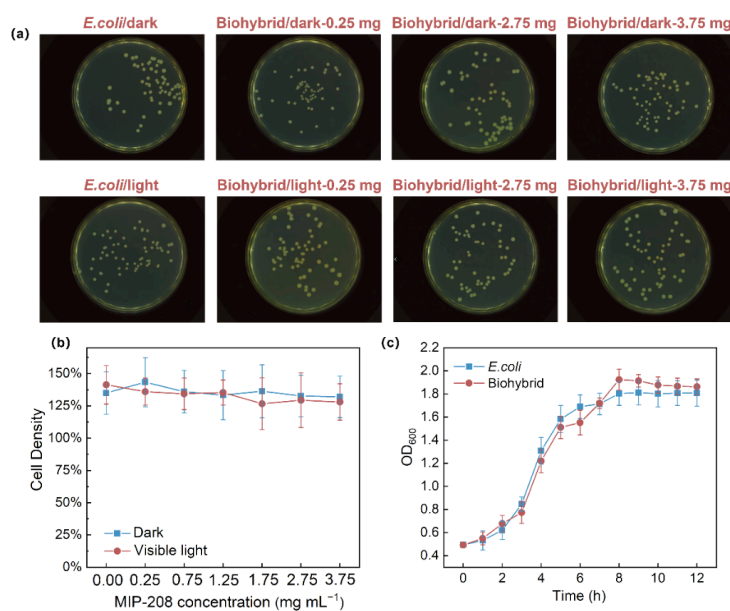


Figure 3. (A) Serial dilution plating images, (b) bacterial density after 3 hours of reaction, and (c) growth curves under photoradiation (corrected for the absorbance of MIP-208), comparing *E. coli* with MIP-208/*E. coli* systems

2.4. Optimization of hydrogen evolution performance

After confirming that there is no biocompatibility issue, we will proceed to systematically optimise the operating parameters of H₂ generation. Bacterial activity changes at different growth stages (lag, logarithmic and stationary), so we found the appropriate initial inoculum based on the *E. coli* growth curve shown in Fig. 4a. Subsequently, H₂ evolution was evaluated under the same illumination at initial optical densities (OD₆₀₀) of 0.25, 0.50 and 1.50. The MIP-208/*E. coli* system showed a significant improvement in H₂ production at OD₆₀₀ = 0.50 and 1.50, while the lower performance at OD₆₀₀ = 0.25 was attributed to the lag phase, during which cells adjust metabolically to the new environment [14,15].

We subsequently explored the effect of light intensity. As confirmed in the control experiment, MIP-208 itself cannot produce hydrogen (H₂). In Fig. 4b-d, comparable H₂ yields were obtained for both systems in the dark; therefore, MIP-208 does not affect bacterial metabolism under darkness. Under light, the intensity-dependent trend of H₂ yield was observed, peaking at 100 mW cm⁻² (1 sun). At the beginning, when OD₆₀₀ was 0.25, 0.50 and 1.50, the production rates were 11.7, 28.5 and 24.7 μmol·10¹⁰ cells⁻¹, respectively; all exceeded those of *E. coli* alone. At over 100 mW cm⁻², as irradiance increased, H₂ production decreased due to photoinduced cellular stress. Although some bacterial activities promote autorepair of the body, they divert a large amount of cell Energy is consumed to participate in microbial fuel production; Therefore, its yield decreases. Nevertheless, the hybrid system always performed better than the control in all illuminated conditions. In Fig. 4c, the primary source of photogenerated electrons is attributed to MIP-208. By adjusting the cell density and light intensity, it was found that the optimal performance was achieved when OD₆₀₀=0.50 under 100 mW/cm² (1 sun) illumination.

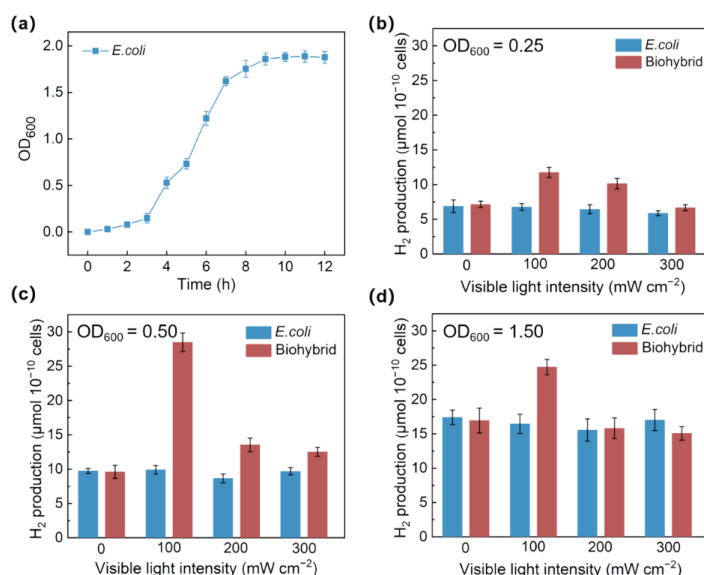


Figure 4. (A) The growth kinetics of *E. coli*; photobiocatalytic hydrogen evolution yield of MIP-208/*E. coli* hybrids at initial optical densities of (b) OD₆₀₀ = 0.25, (c) OD₆₀₀ = 0.50 and (d) OD₆₀₀ = 1.50 after 3 hours of visible light irradiation at various power densities

3. Conclusion

We have developed an efficient semi-artificial photosynthetic system for H₂ evolution by integrating the MOF photosensitizer MIP-208 with *E. coli*. The systems achieved an H₂ production yield of 40.0 μmol per 10¹⁰ cells, which is 4.3 times that of the bare bacteria. This paper provides a mechanism and regulations to effectively build an efficient construction of the solar-driven biohybrid system for exploring stable hydrogen production path. At this moment, it is promoting semi-artificial photosynthesis for sustainable H₂ production.

Acknowledgments

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