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Coupling of One-Dimensional TiO2 with Hydrogenase: Simultaneous Visible-Light Driven H2 Production and Treatment of an Organic Pollutant

Reporting

Project Information

1DH2OP

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Final Report Summary - 1DH2OP (Coupling of One-Dimensional TiO2 with Hydrogenase: Simultaneous Visible-Light Driven H2 Production and Treatment of an Organic Pollutant)

Overview of Results

We have applied semi-biological approach, integrating enzymes onto the electrodes for investigation in the strategies to split water into oxygen and hydrogen using sunlight. The first aim of the project is to achieve advances in enzyme-electrode materials integration based on two benchmark enzymes, Photosystem II for water oxidation and hydrogenase for proton reduction. Further to this, we assembled all enzymes based photoelectrochemical cell for water splitting, hence examine a pathway inaccessible to biology and develop in-vitro platform for the controlled coupling of enzymatic redox processes for photocatalytic reactions. In the second objective of the project, we developed strategy to immobilise hydrogenase on a p-Si photocathode for hydrogen production. This is motivated by such strategy will allow the development of all enzymes based tandem photoelectrochemical cell. This could also allow the achieved of unassisted photocatalytic system for solar water splitting. Within the third objective of the project, we investigated two simultaneous processes, with respect to H2 production and CO2 reduction via bacterial formate hydrogenlyase complex. This work has leads to the design of novel artificial biomimetic systems for bioenergy application.

In the first research objective, the work has been carried out in collaboration with a PhD student of Reisner group, Dirk Mersch who has developed a new inverse opal mesoporous ITO electrode. Using this novel electrode as a platform for enzymes immobilization, I have investigated the detailed electrochemistry of hydrogenase. The significant advantage of this electrode was the enabling of a very high loading of the hydrogenase, hence allowing the achieving of the highest proton reduction catalytic current of NiFeSe hydrogenase to date that was in a range of several mAcm-2. A significant extended stability was also shown with insignificant dropped in performance over the first 3 hours. Dirk Mersch on the other hand has studied the photoelectrochemisty of PSII on this electrode and found equally impressive results. We have then developed an electrochemical setup to investigate the wiring of PSII to hydrogenase for full photoelectrochemical (PEC) water splitting. The reported enzymes based hybrid cell shows red-light-driven water splitting at an electrochemical bias below its thermodynamic potential and H2 and O2

production separated in two compartments in the expected stoichiometric two-to-one ratio, yielding a light-to-hydrogen conversion efficiency of up to 5.4%. The result has been recently published in ‘D. Mersch, C.-Y. Lee, J. Z. Zhang, K. Brinkert, J.C. Fontecilla-Camps, A. W. Rutherford, E. Reisner, Wiring of Photosystem II to Hydrogenase for Photoelectrochemical Water-splitting. J. Am. Chem. Soc. 2015, 137, 8541-8549.’

In the second research objective, we have developed photoelectrochemical based system with the incorporation of hydrogenase as a proton reduction catalyst on a p-Si for H2 production. This involved the development of strategy to effectively immobilise hydrogenase on p-Si. Initial work performed by the used of polymyxin as a co-adsorbent but it did not show a significant improvement with a rather poor stability. Taking advantage of high hydrophilicity of TiO2 for hydrogenase, we employed it as a support material to immobilize hydrogenase. Improvement in both photocurrent and stability were achieved. We show that TiO2 can act as an efficient interfacial layer for hydrogenase immobilization. This proof-of-concept study shows excellent interaction of TiO2 with the hydrogenase that provides a viable platform for the linking of enzyme to a p-type semiconductor to perform light driven proton reduction catalytic reaction. This synergetic effect resulting for the first time the assembly of hydrogenase on a photocathode that exhibited relatively stable performance over 1 h, and allowing quantitative detection of H2 with a faradaic efficiency of 95 % is achieved. This strategy with enhanced interfacial engineering of an enzyme with a semiconductor potentially could realize all-enzymes based tandem photoelectrochemical bio-hybrid water splitting cell.

In the third research objective, the kinetic and thermodynamic properties of membrane bound Formate Hydrogenlyase (FHL) vesicles, expressed from a strain of E. coli for H2 production and CO2 reduction processes has been investigated. This E. coli strain was engineered for high H2 production with formate as an electron source. Since it contains both hydrogenase and formate dehydrogenase, hence allowing backward reaction of H2-driven CO2 reduction, which is a great interest from bioenergy perspective. Our results show that the understudied bacterial formate hydrogenlyase (FHL) complex was capable of operating in both forward and reverse directions, namely formate oxidation to produce H2, and H2-driven CO2 reduction to formate. Nevertheless, the reaction rate for the H2 production was occurred at a much faster rate than the case of CO2 reduction. The optimal pH range for H2 production for FHL was in agreed with the optimal pH for H2 reduction by hydrogenases, and was also in a range where isolated formate dehydrogenase has a good formate oxidation activity. Similarly, H2 driven CO2 reduction falls at the optimal pH for H2 oxidation by hydrogenase and isolated formate dehydrogenase for CO2 reduction activity. Thermodynamic studies revealed a very small potential difference (a few mV) between those processes, allowing the reaction to occur spontaneously. This leads to the design of biomimetic system by immobilize hydrogenase and formate dehydrogenase on graphite particles, and we further developed the bioelectrochemical fuel cell based on this system.

Conclusions

We have successfully achieved all the three research objectives of this project, which are the assembly of all enzymes based bio-hybrid photoelectrochemical cell, enzyme based photocathodes and enzymatic processes with simultaneous H2 production and CO2 reduction. The outcome from this project essentially demonstrated the versatility of biological enzymes when coupled with inorganic and semiconductor materials. Specifically, the direct coupling of PSII to H2ase has revealed to be an efficient route for photo-

biological H2 production, and further improvements in the light-to-product conversion efficiencies are expected to accompany with advances in the PSII-photoanode interface. The strategy with the used of TiO2 as bi-functional material as protective layer and as an efficient interfacial layer for hydrogenase immobilization provides a viable platform for the linking of enzyme to a p-type semiconductor to perform light driven proton reduction catalytic reaction. Further improvement can be made to achieve better interfacial layer such as the use of a conformal coating of a thin TiO2 layer via atomic layer deposition method. The work on formate hydrogenlyase demonstrated an exemplary system where the enzymes can react to perform H2 production and CO2 reduction within a single complex. The developed biomimetic system is a novel concept for biofuel H2 production.

The usefulness and socio-economic impact of the project
The strategy of bio-production of solar fuel as demonstrated in this proposal that mimics natural photosynthesis is one of the main areas of global interest. Innovations in advancing the concept and design of more efficient and cost effective biomimetic artificial photosynthesis systems as shown in this project would definitely generate new knowledge and increase the competitiveness of the European Research Area in renewable energy research. Specifically, knowledge of the reactions of enzymes could provide a benchmark for the desirable properties of future H2-cycling catalysts, which could assist in the development of synthetic clusters to catalyze H2 oxidation and proton reduction. In a wider context, the idea of capture and deliberately store solar energy in the chemical bonds of a fuel provides sustainable forms of alternative energies that would transform our future energy options, which indirectly address climate change issue and provide a long-term wealth creation.

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