Photoelectrocatalytic reduction of CO2 to methanol over a photosystem II-enhanced Cu foam/Si-nanowire system

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ABSTRACT

A solar-light double illumination photoelectrocatalytic cell (SLDIEPC) was fabricated for autonomous CO2 reduction and O2 evolution with the aid of photosystem II (PS-II, an efficient light-driven water-oxidized enzyme from nature) and utilized in a photoanode solution. The proposed SLDIEPC system was composed of Cu foam as the photoanode and p-Si nanowires (Si-NW) as the photocathode. Under solar irradiation, it exhibited a super-photoelectrocatalytic performance for CO2 conversion to methanol, with a high evolution rate (41.94 mmol/hr), owing to fast electron transfer from PS-II to Cu foam. Electrons were subsequently trapped by Si-NW through an external circuit via bias voltage (0.5 V), and a suitable conduction band potential of Si (−0.6 eV) allowed CO2 to be easily reduced to CH3OH at the photocathode. The constructed Z-scheme between Cu foam and Si-NW can allow the SLDIEPC system to reduce CO2 (8.03 mmol/hr) in the absence of bias voltage. This approach makes full use of the energy band mismatch of the photoanode and photocathode to design a highly efficient device for solving environmental issues and producing clean energy.

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Introduction

Utilization of solar light and its storage in the form of chemical fuels is a promising strategy to deal with current and future energy supply demands (Habisreutinger et al., 2013). With the consumption of fossil fuel and increase in CO2 house gas, it is desirable to design a suitable route to address these problems. Alternatively, utilizing abundant and clean solar energy to convert CO2 into fuels, such as methane or methanol, could dispose of both problems as well as provide a simple form of energy storage (Ma et al., 2014). However, the conversion of CO2 into a single substance using solar light is challenging. Recently, CO2 conversion to methanol—which can be stored, transported, and used easily—has received a great deal of attention (Rezayee et al., 2015; Haunschild, 2015; Behrens, 2014; Graciani et al., 2014). Thus, it is urgent to improve the selectivity of methanol production.

Photoelectrocatalysis (Barton et al., 2008; Kaneco et al., 2006) is one of the most promising techniques for CO2 conversion. This method is seen as an artificial model for photosynthesis owing to its direct and effective use of solar energy. More importantly, highly effective catalytic materials and reaction systems for CO2 reduction must be improved and developed (Cheng et al., 2014; LaTempa et al., 2012). Photosynthesis has inspired us to use its unique characteristics to achieve our goal of sustainable energy utilization (Georgianna and Mayfield, 2012). Generally, the overall water splitting for O2 evolution is not feasible in thermodynamics.
and is difficult to achieve through photocatalytic reactions using inorganic photocatalysis (Xu et al., 2015). Nevertheless, nature offers an efficient light-driven water oxidizing enzyme, photosystem II (PS-II), which can capture a relatively wide range in the sunlight spectrum (Efrati et al., 2013; Yehezkeli et al., 2012, 2013; Oppelt et al., 2013). Additionally, it is generally recognized that water oxidation for O₂ evolution is a challenging task in catalysis. Thus, it is highly desirable to choose a suitable catalyst to achieve this goal. Furthermore, PS-II is an ideal substance because of its easy access, low cost, non-toxicity and high efficiency. Meanwhile, Cu foam is often used as a current collector electrode due to its 3D structure and high adsorption (Mazouzi et al., 2014). Additionally, silicon nanowires have demonstrated excellent performance for CO₂ reduction. Nevertheless, it is unfavourable for high selectivity during synthesis of liquid fuels (Habisreutinger et al., 2013; Hinogami et al., 1994; Huang and Tan, 2014). Thus, it is highly desirable to design a suitable photoelectrocatalytic device to improve both the conversion rate and selectivity of CO₂ reduction.

Here, Cu foam as a current collector soaking in a chlorophyll solution (providing PS-II) and p-type silicon nanowires (p-Si NW) in a CO₂-saturated NaHCO₃ solution were combined as the photoanode and photocathode, respectively, with the formation of a PEC reactor via double-sided illumination with simulated solar light. O₂ evolution in the anode chamber and CO₂ reduction to methanol in the cathode chamber were achieved via externally biased voltage. Moreover, the proposed reactor also allowed the construction of a Z-scheme system to reduce the combination rate of photo-induced electrons and holes arising from the mismatched Fermi levels between Cu and Si NW. With the aid of the PS-II, this solar-light double illumination photoelectrocatalytic cell exhibited an excellent CO₂ reduction performance, with high selectivity for methanol evolution. It can also be used to drive O₂ evolution under solar light irradiation.

1. Experimental section

1.1. Synthesis of Si NW

In a typical synthesis of Si NW, metal-catalysed electrolysis etching of bulk Si was used (Oh et al., 2012). Single-crystal B-doped silicon (100) wafers (10 mm × 20 mm, thickness 0.5 mm, resistivity 0.01–1 Ω m, p-type) were degreased by rinsing with acetone, ethanol and deionized water and ultrasonic cleaning for 15 min in sequence. The degreased Si surface was treated with a standard RCA cleaning step (Edwards et al., 2000). For metal-catalysed electrolysis etching, the Si sample was immersed in an AgNO₃ aqueous solution (20 mmol/L) and a 20.0 wt.% aqueous HF solution in a 100-mL Teflon-lined autoclave for various time periods. The treated Si films were further immersed in diluted 20.0 wt.% HNO₃ for 24 hr to remove residual Ag seeds.

1.2. Synthesis of chlorophyll (PS-II)

Fresh spinach leaves (0.5 g) were placed in the mortar and 90% ethanol was added. The filtered extract was centrifuged at 9000 r/min for 10 min, and the supernatant was centrifuged for another 10 min at 9000 r/min. A green pellet of chlorophyll was obtained and suspended in a 90% ethanol solution (Yehezkeli et al., 2012).

1.3. Characterization

X-ray diffraction measurements were recorded in a Rigaku Dmax-3C Advance X-ray diffractometer (Cu Kα radiation, λ = 1.5406 Å). The morphologies of the products were observed using a field emission scanning electron microscope (FESEM, S-4800Hitachi, Japan). Transmission electronic microscopy (TEM) images were collected on a JEM-2010. The surface electronic states were analysed by X-ray photoelectron spectroscopy (XPS, PHI 5000, Perkin-Elmer, Waltham, MA, USA). All binding energy values were calibrated using C1s = 284.8 eV as a reference. The liquid optical absorption was determined by UV–vis spectroscopy (UV-7504/PC, Xinnao instrument Company, Shanghai, China). The optical property was analysed by UV–vis diffuse reflectance spectra (DRS, MC-2530, Shinadzu, Japan).

1.4. Photoelectrocatalytic reaction

A double-chamber simulated solar-light double irradiated photoelectrocatalytic cell (SLDIPEC, 120 mL) was used for the simultaneous photoelectrocatalytic reaction. Both anode chamber and cathode chamber were made of quartz glass, and the two chambers were separated by a Nafion membrane (cation exchange membrane). The anode chamber was filled with 60 mL buffer solution (50 mmol/L sodium phosphate, 15 mmol/L NaCl, pH 6.0), and 2 mL of the as-prepared chlorophyll solution (23.33 mg/L calculated based on the reported route (see Supplementary Data) (Lichtenthaler, 1987)), sealed in a flask, degassed thoroughly under vacuum and filled with N₂ gas. The cathode chamber was filled with 60 mL 1 mol/L NaHCO₃ solution and further bubbled with CO₂ for approximately 60 min to saturate the solution with CO₂. A different bias voltage was applied to the three-electrode systems. The Cu foam (1 cm × 3 cm) and Si NW were used as anode and cathode electrode, respectively. The saturated calomel electrode (SCE) was considered a reference electrode inserted in the anode chamber. A 300 W Xenon lamp (AM 1.5 filter) was used as simulated solar light.

The methanol in the liquid products was detected using a gas chromatograph (GC2002, Shanghai Kechuang, China) equipped with a flame ionization detector (FID) and an Rx-5 column (30 m × 0.25 mm × 0.25 μm, USA) and was injected with a DK-2010A headspace auto-sampler (Shanghai Kechuang, China). The standard curve of methanol was described in Fig. S1a. The amount of evolved O₂ was determined using a gas chromatograph (Shanghai Kechuang, China GC-9800, thermal conductivity detector (TCD), N₂ carrier and 5 Å molecular sieve columns). The standard curve of O₂ is shown in Fig. S1b.

1.5. Photoelectrochemical measurement

Photoelectrochemical measurements were carried out in a conventional three-electrode two-chamber SLDIPEC reactor on an electrochemical station (CHI 660D, Chenhua Instrument Co., China). Impedance measurements were performed under
simulated solar-light illumination (300 W Xe lamp, AM 1.5 filter) under open circuit voltage over a frequency range from $10^0$ to $10^{-1}$ Hz with an AC voltage of 5 mV. To measure the response of current to potential under illumination or dark, a much high scan rate of 100 mV/sec was adopted to obtain the CV profiles.

2. Results and discussion

2.1. Working mechanism for the PS-II participated SLDIPEC system

To clarify the working mechanism of the proposed PS-II-participating SLDIPEC system, a schematic illustration including charge separation, electron flow, O$_2$ evolution and CO$_2$ reduction is shown in Fig. 1. The process includes the following three steps: (1) in the PS-II process, photo-induced electrons were transferred through several intermediate processes to finally reach the $Q_b$ site (electron acceptor) in the chlorophyll matrix (Yehezkeli et al., 2012, 2013). (2) Cu foam was considered to be the electron collector at the $Q_b$ site. The potential of $Q_b/Q_b^-$ was approximately 0 V, and the copper work function was approximately 4.65 eV vs. vacuum energy. Its Fermi level approached 0.15 eV, and thus, electrons from $Q_b$ could transfer to Cu foam to allow the following reaction to occur. In addition, the light-driven oxidizing enzyme in the PS-II could oxidize water to O$_2$. (3) As a photocathode, Si nanowires could be excited by simulated solar-light to produce electrons and holes. The holes in the valence band (VB) of Si could be recombined with electrons from photoanode electrons in the Cu foam, which was composed of the Z-scheme (Tada et al., 2006). The electrons in the conduction band (CB) of Si could reduce CO$_2$ to fuel products and H$^+$ to produce H$_2$.

However, the CB of p-Si NW was approximately $-0.6$ eV (Walter et al., 2010; Bae et al., 2015), which could process six electrons to reduce CO$_2$ to liquid-phase methanol rather than formic acid (a four-electron process), according to the potential fundamental. The two-electron process for H$_2$ evolution occurred easily and usually competed with the CO$_2$ reduction to methanol. Nevertheless, the gap in the CB potential of Si vs. that of the reduction potential of CO$_2$/CH$_3$OH was higher than that of H$^+$/H$_2$. Thus, more electrons were generated in the p-Si NW and could be quickly transported to reduce CO$_2$ to methanol. Thus, the process as constructed through a Z scheme in the SLDIPEC system can serve as an excellent tool to convert CO$_2$ to methanol with high selectivity through a photoelectrocatalytic process under solar-light irradiation.

2.2. Characterization of the proposed PS-II participated SLDIPEC system

In Fig. 2a, it can be seen that the proposed SLDIPEC system includes two chambers separated with a Nafion membrane for cation exchange. In the anode chamber, Cu foam with chlorophyll served as the photoanode. As shown in Fig. 2b, the Cu foam exhibited perfect macroporous structures, providing a large specific surface area to trap chlorophyll in the reaction solution. The p-Si NW, acting as the photocathode, had an average length of 35 $\mu$m as shown in Fig. 2c. In the case of the chlorophyll solution and Si-NW film, both were evaluated through UV–vis absorption to evaluate the light adsorbing capability. As shown in Fig. 2d and e, both exhibited a wide range of solar-light absorption, suggesting excellent light absorbing capability to efficiently drive the autonomous reaction in the photoanode and photocathode under solar-light irradiation.

The photo-electronic properties of electrodes always play an important role in photoelectrocatalytic performance. Here, electrochemical impedance spectroscopy (EIS) was carried out to explore the performance between the electrode and electrolyte in the SLDIPEC reactor. A semicircle in the Nyquist plot at high frequency represented the charge-transfer process, while the diameter of the semicircle reflected charge-transfer resistance (Fig. 3a). It was clear that the arch under solar light illumination was much smaller than in the dark, implying that low

![Fig. 1 – Schematic illustration of O$_2$ evolution and CO$_2$ reduction of methanol through charge separation and electron flow in the proposed SLDIPEC system with PS II. NHE: normal hydrogen electrode.](image-url)
conductivity could accelerate electron transfer under light irradiation to enhance its photoelectrocatalytic activities in the entire reaction. Furthermore, to evaluate the photoelectronic response of the SLDIPEC system, photocurrent was used to verify the separation of photo-induced electrons and holes. As shown in Fig. 3b, a much higher photocurrent density was obtained under solar light irradiation. This indicated that many electrons can be generated for CO₂ reduction, with enhanced photoelectrocatalytic performance.

2.3. Photoelectrocatalytic performance of the proposed PS-II participated SLDIPEC system

To evaluate the photoelectrocatalytic performance of the proposed SLDIPEC system, simultaneous O₂ evolution and CO₂ reduction was chosen as a probe reaction. As shown in Fig. 4, a high methanol evolution rate (41.94 mmol/hr) and O₂ evolution rate (3.43 mmol/(gchl·hr)) were obtained under solar light irradiation with a bias voltage of 0.5 V. It is interesting that only methanol was detected in the liquid-phase reaction system in the cathode chamber, according to the LC results shown in Fig. S2. This high evolution of methanol revealed that the proposed hybrid photoelectrocatalytic system exhibited high selectivity for CO₂ conversion to methanol. To clarify the factors affecting photoelectrocatalytic performance in both methanol and oxygen evolution, various reaction conditions were selected for better evaluation. No methanol or O₂ was detected in the absence of chlorophyll or light irradiation. The Z-scheme cannot work without chlorophyll because no photogenerated electrons are generated at the photoanode in the absence of chlorophyll.

Fig. 2 – (a) Schematic diagram of the SLDIPEC setup, FESEM images of (b) photoanode Cu foam and (c) photocathode Si nanowires, (d) liquid UV–visible absorption spectrum of chlorophyll, (e) solid UV–vis diffuse reflectance spectra (DRS) of Si nanowires.

Fig. 3 – Electrochemical impedance spectroscopy (a) and cyclic voltammetry (b) curves of the proposed SLDIPEC system in dark and under simulated solar light irradiation (300 W Xenon lamp, Air mass 1.5 filter).
Meanwhile, it should be acknowledged that such a simultaneous reaction cannot be triggered in the absence of light illumination, even using a 0.5 V external voltage. It was also noted that the evolution rates of methanol and O₂ can reach 8.03 mmol/hr and 2.01 mmol/(gchl·hr), respectively, when the bias voltage was decreased to zero. Such high photoelectrocatalytic activity in the absence of external voltage was ascribed to the self-built voltage between the Cu foam and Si NW, which may well accelerate electron transfer from Cu to Si. These results prove that the proposed SLDIPEC system possessed excellent photoelectrocatalytic performance for both CO₂ reduction and oxygen evolution owing to high charge separation efficiency resulting from the Z-scheme.

To validate the electron transfer process in the SLDIPEC system, various reactive species were introduced into the reaction shown in Fig. 5. Upon introducing 3-(3,4-dichlorophenyl)-1,1-dimethylurea (DCMU) into the photoanode chamber, only a trace amount of O₂ was detected and a much lower methanol evolution rate (15.6 mmol/hr) was achieved. This is because DCMU can act as an inhibitor to terminate the electron transfer of PS-II by occupying Q₈ sites, resulting in recombination of the excited PS-II state. This suggested that the electrons that transferred from the Q₈ sites in chlorophyll to the Cu foam play an important role in O₂ evolution for increasing the charge separation rate. To exclude the effect of oxidative enzymes on water-splitting for O₂ evolution, Mn-depleted PS-II (Yamamoto et al., 1981; Wang et al., 2014) was also introduced. O₂ evolution was effectively prohibited, and a 50% decrease in methanol evolution rate was obtained. This indicated that oxidative enzymes are the key to O₂ evolution. Nevertheless, it should be acknowledged that nearly 50% of the methanol evolution capability from reducing CO₂ in the photocathode chamber was maintained, even in the presence of DCMU or Mn-depleted PS-II. This strong photoelectrocatalysis-induced CO₂ reduction performance may be attributed to the special SLDIPEC system based on the Z-scheme. This system could allow photo-generated electrons in chlorophyll to transfer from the Q₈ site to the Cu foam and then transfer through the external circuit to recombine with holes in the VB of p-Si NW, with the formation of an accelerated charger separation efficiency.

3. Conclusions

In conclusion, we have developed a large-scale method to simultaneously produce methanol and O₂ through CO₂ reduction and water oxidation with the help of PS-II using a self-driven double illumination photoelectrocatalytic system under solar light irradiation. The proposed Z-scheme based SLDIPEC system serves as a blueprint for the design of other photoelectrocatalytic reaction types to accelerate charge separation, light harvesting, and catalytic efficiency for practical applications, including biomass production and solar overall splitting.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2016.12.018.

REFERENCES


