



Efficient solar-to-chemical conversion with chlorine photoanode



Zilong Liu^a, Zhenglei Yin^{a,b}, Zhaomin Wan^a, Li Xiao^a, Hualong Ma^a, Juntao Lu^a, Lin Zhuang^{a,b}

^a College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China

^b Institute for Advanced Studies, Wuhan University, Wuhan 430072, China

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ABSTRACT

The photoelectrochemical water splitting is an artificial photosynthetic approach that could provide a sustainable supply of clean energy, however, the sluggish kinetics of the oxygen evolution reaction (OER) has been a bottleneck to the solar-to-chemical conversion. Here we report an implementation of 8% efficient photoanode based on the photoelectrolysis of saturated NaCl solution. Replacing the OER with the chlorine evolution reaction (CER) has transformed both the thermodynamic basis and the kinetic process of the photoelectrolysis, more chemical energy can be produced with much less driving force. The RuO₂/TiO₂/n-Si photoanode exhibits a high rate of photoelectrochemical conversion (35 mA/cm² at equilibrium potential), which steadily and exclusively produces Cl₂ without detectable O₂.

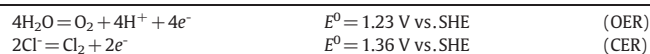
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1. Introduction

How to efficiently harvest the solar energy and convert it into chemical energy has been one of the most active research subjects in recent decades [1–3]. Once realized, this artificial photosynthetic approach would provide a sustainable supply of clean energy that could relieve the global energy and environmental crisis [4–6]. Among strategies for implementing the solar-to-chemical conversion, photoelectrochemical (PEC) water splitting has been of central interest and intensively studied [2,7], as the hydrogen cycling is thought to be more efficient than the carbon cycling [8]. A key challenge of PEC water splitting is the energy conversion efficiency [9–11], which is not only determined by the photoelectric conversion efficiency of the photoelectrode, but also by the electrochemical efficiency of the anodic oxidation of water [12,13].

To improve the photoelectric conversion efficiency, narrow-band semiconductors (such as GaAs, Si) are preferred in modern research [15–17] over the wide-band semiconductor TiO₂ originally applied by Fujishima and Honda [18]. Despite being able to harvest more solar energy, narrow-band semiconductors provide lower photovoltage and suffer from corrosion under electrochemical conditions [19]. These problems can be addressed by designing tandem-structured PEC cells (e.g. dual photosystem with photoanode and photocathode) [20,21] and by coating the semiconductor surface with a protective thin film [22–24]. Recent studies have demonstrated that protected Si photoanodes can stably supply a high rate of photoelectrochemical reaction (> 30 mA/cm² in saturated photocurrent density) [24,25]. Surprisingly,

however, the energy conversion efficiency of these advanced Si photoanodes was still lower than 0.5%. This is because of the large overpotential of the oxygen evolution reaction (OER), even with optimal catalysts.



In the present work, we demonstrate a new strategy for Si photoanode based on the chlorine evolution reaction (CER), which results in a peak efficiency of 8%. The advantages of using a CER photoanode instead of an OER photoanode are multiple (as illustrated in Fig. 1A): Thermodynamically, the electrolysis of chloride solution (saturated NaCl solution was used in this work) can generate more chemical energy ($\varepsilon_{\text{chem}}$) than does the electrolysis of water, since Cl₂ is a stronger oxidant than O₂. Kinetically, the CER is much faster than the OER, thus the activation energy needed for driving CER is less than that for OER. In photoelectrolysis, the activation energy is provided by an addition of the photoelectric energy (ε_{ph}) and the externally complemented energy (ε_{ext}). While the ε_{ph} is mostly determined by the nature of the semiconductor, the magnitude of ε_{ext} depends on the reaction kinetics. According to the concept of solar-to-chemical conversion efficiency (η_{STC}):

$$\eta_{\text{STC}} = \frac{\varepsilon_{\text{chem}} - \varepsilon_{\text{ext}}}{\varepsilon_{\text{solar}}} \quad (1)$$

(where $\varepsilon_{\text{solar}}$ is the input solar energy), both the increase in $\varepsilon_{\text{chem}}$ and the decrease in ε_{ext} (caused by replacing the oxygen photoanode with the chlorine photoanode) will boost the η_{STC} .

E-mail address: lzhuang@whu.edu.cn (L. Zhuang).

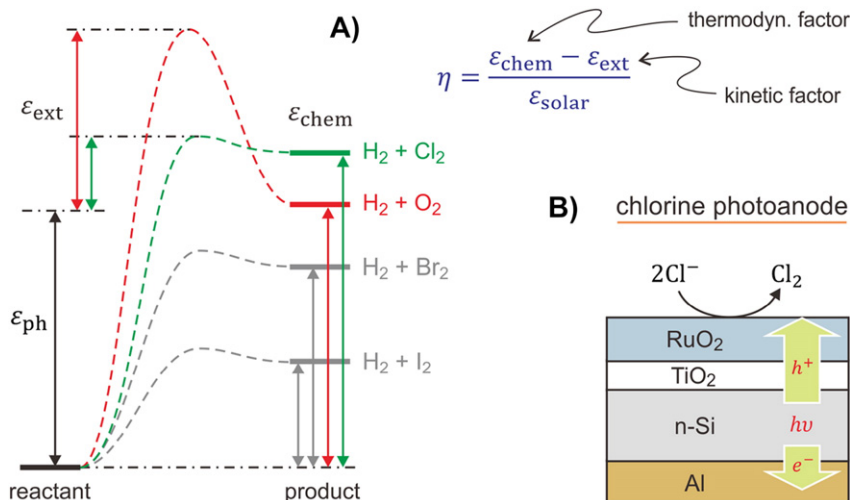
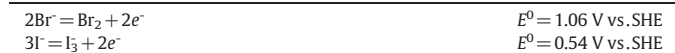


Fig. 1. Strategy for improving the solar-to-chemical conversion efficiency (η) via chlorine photoanode. (A) The superiority of chloride photoelectrolysis over water photoelectrolysis: Thermodynamically chloride electrolysis produces more chemical energy (ϵ_{chem}) than does water electrolysis; and kinetically the chlorine evolution reaction (CER) is much faster than the oxygen evolution reaction (OER), hence requiring less activation energy ($\epsilon_{\text{ph}} + \epsilon_{\text{ext}}$, photoelectric energy plus externally supplied energy). Both factors benefit the η . Note that bromide or iodide electrolysis is also superior in the kinetics of anode reaction, but produces less ϵ_{chem} than does water electrolysis. (B) The chlorine photoanode implemented in this work is composed of an n-type semiconductor (n-Si) covered with a TiO_2 protection layer and a RuO_2 catalyst layer, both prepared by sputtering.

The ϵ_{chem} stored in the product of chloride photoelectrolysis ($\text{H}_2 + \text{Cl}_2$) is actually more valuable than it appears. When converting this chemical energy to electricity, the efficiency of a H_2 - Cl_2 fuel cell (or flow battery) is greater than that of a H_2 - O_2 fuel cell, because, again, the kinetic loss of the chlorine reduction reaction (CRR) is much less than that of the oxygen reduction reaction (ORR) [26,27]. In other words, putting together the solar-to-chemical conversion and the following chemical-to-electrical conversion, the efficiency benefit of using a chlorine electrode will be doubled, in comparison to the strategy of using an oxygen electrode.



Note that the bromide and iodide photoelectrolysis have been reported before [28,29]. While both the bromine electrode and the iodine electrode are also superior in reaction kinetics over the oxygen electrode, the ϵ_{chem} stored in $\text{H}_2 + \text{Br}_2$ or $\text{H}_2 + \text{I}_2$ is less than in $\text{H}_2 + \text{O}_2$ (Fig. 1A). Hence the Cl_2 generation photoanode is favorable in both thermodynamics (compared with I_2 , Br_2 or O_2 generation) and kinetics (compared with O_2 generation).

2. Experimental

The structure of the chlorine photoanode implemented in this work is depicted in Fig. 1B. The electrode substrate was an n-type Si(100) sheet (400 μm thick, 3 ~ 5 $\Omega\cdot\text{cm}$, P-doped, doping density $\sim 10^{15} \text{ cm}^{-3}$) covered with a TiO_2 protection layer ($\sim 2 \text{ nm}$ thick) and a RuO_2 catalyst layer ($\sim 20 \text{ nm}$ thick), both overlayers were prepared subsequently by magnetron sputtering under O_2 containing atmosphere. The Si wafer was cleaned referring to the RCA-1 procedure, during which the Si wafer was soaked into a 3:1 (volume ratio) solution of H_2SO_4 (18.4 M) and H_2O_2 (1 M) for 10 min, then immersed into 10 vol% hydrofluoric acid for 10 s. Then the samples were etched using the RCA-2 procedure involving immersion into the 5:1:1 (volume ratio) solution of H_2O , concentrated hydrochloric acid (11 M) and H_2O_2 (1 M) for 10 min at 75 $^\circ\text{C}$. Then, the substrates were rinsed with DI water and dried by argon blow before use. Before sputtering, the native oxide layer was removed by 10 vol% hydrofluoric acid. The back of the Si substrate was sputtered with an Al layer so as to form an ohmic metal-semiconductor contact for electron extraction.

The PEC flow cell is as sketched in Fig. 2A. A Pt counter electrode was placed in an open cathode apartment (where the hydrogen evolution reaction took place), which was connected to the flow cell through a porous frit. A saturated calomel electrode (SCE) served as the reference electrode, and was connected to the flow cell through a capillary located close to the working electrode. The potential of the photoanode (E) is reported with respect to the reversible hydrogen electrode (RHE) in the same electrolyte, such that E can also be regarded as the externally applied bias voltage of a PEC cell (where a non-polarizable hydrogen

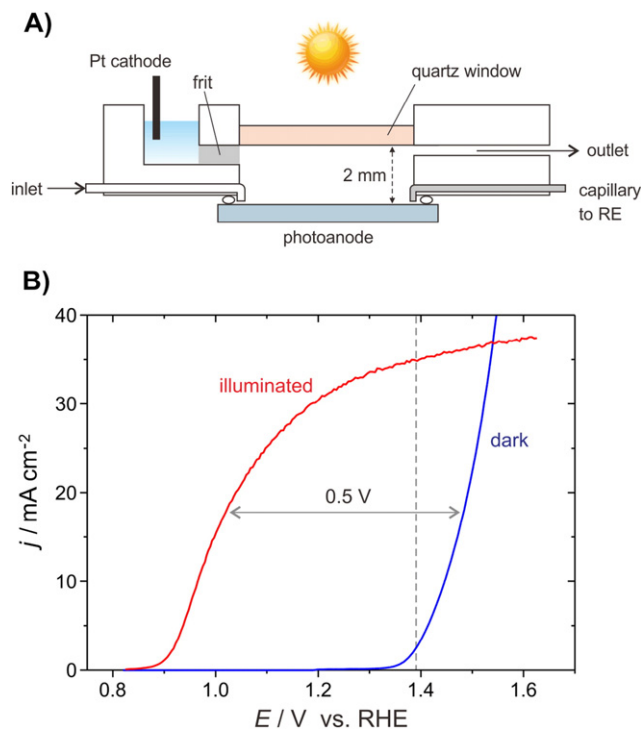


Fig. 2. Electrolysis and photoelectrolysis tests. (A) Schematic illustration of the structure of the PEC flow cell. The Pt counter electrode was placed in a frit-separated cathode apartment, so that the generated H_2 will not reach the photoanode. (B) Polarization curves recorded under illumination (red) and in dark (blue). The potential scan rate was 5 mV/s. For electrolysis in dark, the n-Si semiconductor was replaced with an electronically conductive p^+ -Si substrate.

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