

# Artificial photosynthesis: A two-electrode photoelectrochemical cell for light driven water oxidation with molecular components



Xin Ding<sup>a</sup>, Yan Gao<sup>a,\*</sup>, Linlin Zhang<sup>a</sup>, Ze Yu<sup>a</sup>, Jianhui Liu<sup>a</sup>, Licheng Sun<sup>a,b,\*\*</sup>

<sup>a</sup> State Key Laboratory of Fine Chemicals, Institute of Artificial Photosynthesis, DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology (DUT), Dalian 116024, China

<sup>b</sup> Department of Chemistry, School of Chemical Science and Engineering, KTH Royal Institute of Technology, 100 44 Stockholm, Sweden

## ARTICLE INFO

### Article history:

Received 15 August 2014

Received in revised form 14 October 2014

Accepted 22 October 2014

Available online 24 October 2014

### Keywords:

photoanode  
molecular device  
photoelectrochemical cell  
water splitting

## ABSTRACT

An efficient two-electrode molecular PEC was assembled, in which a photoanode was constructed using a co-adsorbed method with a molecular photosensitizer (PS) **1** and a molecular catalyst **2** on TiO<sub>2</sub>-sintered FTO electrode (TiO<sub>2</sub>(**1** + **2**)). Without applied bias against a reference electrode, the system achieves remarkable photocurrent densities and carries out light driven water oxidation as evidenced by Clark electrode measurements in solution. A photocurrent density of 70 μA/cm<sup>2</sup> has been obtained within 10 s illumination time, and a TON of about 220 was obtained with a maximum turnover frequency (TOF) of ca. 4 min<sup>-1</sup> within the initial 5 minutes illumination duration.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Utilizing solar energy to realize water splitting is one of the most important expectations in the field of energy conversion. Nature provides one efficient pathway: photosynthesis, in which photosystem II (PS II) utilizes solar energy to drive oxidation of water efficiently to release oxygen and protons without any additional energy input. Therefore, mimicking photosynthesis by using photoelectrochemical cells (PECs) to split water into hydrogen and oxygen is regarded as an ideal way to meet environmental problems and energy demands [1]. Various PECs have been assembled and most of them were composed of inorganic materials, only a few dye-sensitized PEC (DSPECs) were assembled with molecular photosensitizers (PS) and molecular catalysts [2–20]. In these PECs, an external bias must be imposed [9–18], which would potentially be a big obstacle for wide application of PEC devices in the future. Spiccia et al. reported the only two-electrode molecular PEC with a manganese cluster as a catalyst and polypyridyl ruthenium complex as a PS in the working electrode (WE). Without using any external bias, a photocurrent density of about 5 μA/cm<sup>2</sup> was obtained under light illumination of

100 mW/cm<sup>2</sup>, and small amount of generated oxygen was detected during the illumination period [21].

Recently, a highly efficient three-electrode molecular PEC was assembled in our group and a record photocurrent density of ca. 1.7 mA/cm<sup>2</sup> has been achieved in a phosphate buffer solution [18]. The *J*-*V* and controlled external bias studies of the PEC displayed a well photocurrent with small bias, which indicates that the PEC might also work without using any external bias. Herein, a two-electrode PEC, mimicking water oxidation process of PS II in nature, was assembled with the reported photoactive WE TiO<sub>2</sub>(**1** + **2**) [18] as a photoanode, a platinum (Pt) wire as a cathode and a copper line as a conducting wire, as shown in Scheme 1.

## 2. Experimental

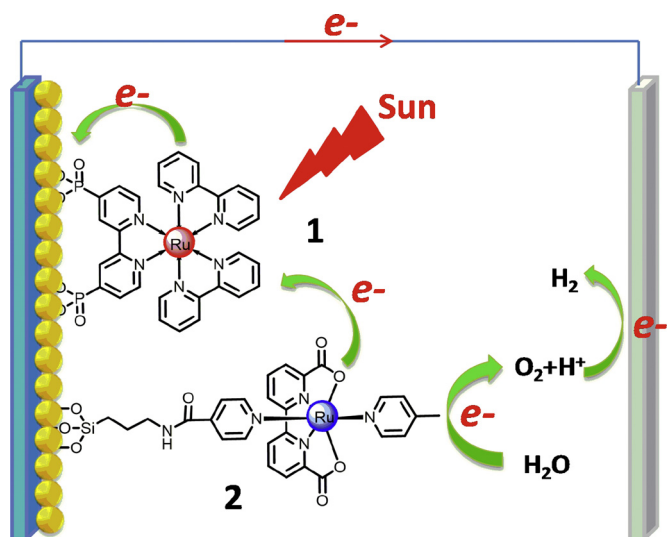
The photoanode was prepared as reported previously [18]. The nano-structured TiO<sub>2</sub> FTO electrode was immersed in a 20 mL methanol solution composed of the PS **1** (1 mg) and the catalyst **2** (5 mg) for 2 hours. Then the electrode was rinsed with methanol and water for several times and dried in dark to form WE TiO<sub>2</sub>(**1** + **2**). According to the method reported by Meyer et al [22], the surface loading of catalyst **2** on WE TiO<sub>2</sub>(**1** + **2**) was estimated by the area under cyclic voltammogram (CV) wave of the Ru<sup>II</sup>/Ru<sup>III</sup> at E<sub>1/2</sub> = 0.71 V to be 5.8 × 10<sup>-10</sup> mol/cm<sup>2</sup>.

A two-electrode system was built up in Clark-type oxygen electrode, with a prepared photoanode TiO<sub>2</sub>(**1** + **2**) as working electrode and a Pt wire as counter electrode connected with a copper wire, with pH = 6.4 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (total

\* Corresponding author. Tel.: +86 41184986249.

\*\* Corresponding author at: State Key Laboratory of Fine Chemicals, Institute of Artificial Photosynthesis, DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology (DUT), Dalian 116024, China.

E-mail addresses: [dr.gaoyan@dlut.edu.cn](mailto:dr.gaoyan@dlut.edu.cn) (Y. Gao), [lichengs@kth.se](mailto:lichengs@kth.se) (L. Sun).

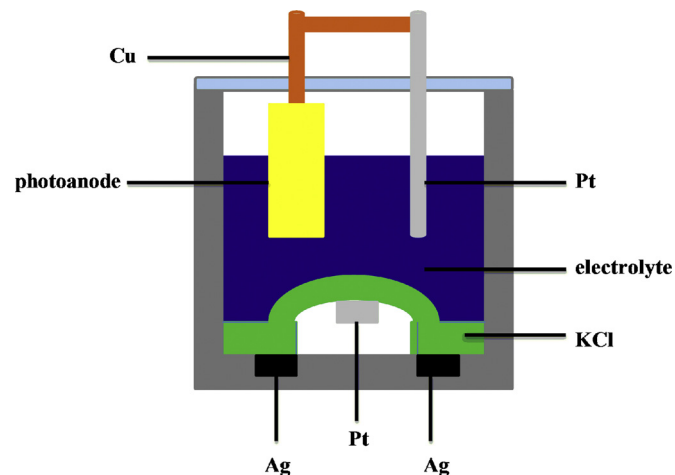


**Scheme 1.** Schematic illustration of the two-electrode PEC with a photoanode co-adsorbed with a PS **1** and a molecular catalyst **2** on nano-structured TiO<sub>2</sub> and a passive Pt cathode.

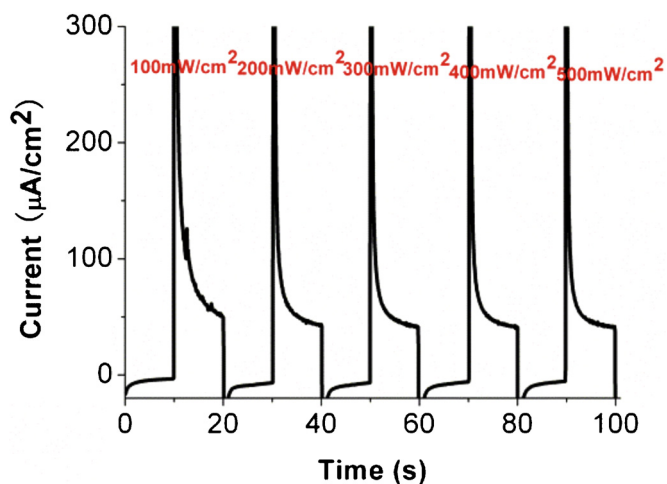
2 mL) as electrolyte, as shown in **Scheme 2**. After degassing, the above photoanode was irradiated by a 300 W xenon light source through a 400 nm cut off filter. The generated oxygen dissolved in water was measured directly by Clark-type oxygen electrode. The electrochemical measurements were recorded on a BAS-100W electrochemical potentiostat under argon atmosphere. The working electrode was a TiO<sub>2</sub>-sintered FTO electrode absorbing with catalyst and photosensitizer. The counter electrode and reference electrode was one platinum wire.

### 3. Results and discussion

Light intensities control measurement of the PEC was firstly carried out as shown in **Fig. 1**. Controlling the light intensity from 100 mW/cm<sup>2</sup> to 500 mW/cm<sup>2</sup>, no significant difference can be found from the photocurrent densities of the PEC. During the period of water splitting, the reduction of proton was quite slow on cathode, which may be caused by the absence of external bias. Therefore, during the water splitting period of the two-electrode PEC system, the reduction of proton becomes the rate-limiting step of water splitting. A light intensity of 100 mW/cm<sup>2</sup> was enough to



**Scheme 2.** Schematic illustration of the two-electrode DSPEC in Clark-type oxygen electrode.

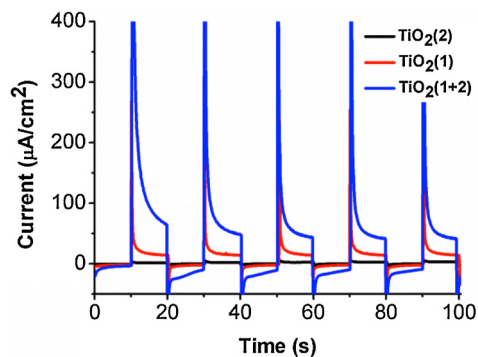


**Fig. 1.** Light intensities control measurements of two-electrode PEC with WE TiO<sub>2</sub>(**1+2**) as photoanode in 0.1 M Na<sub>2</sub>SO<sub>4</sub> with a 300 W xenon lamp white-light source coupled to a 400 nm long-pass filter.

excite the PS and drive water oxidation. Therefore, 100 mW/cm<sup>2</sup> is chosen as the light intensity in the following studies.

Light control photocurrent density measurements of the PECs with WEs TiO<sub>2</sub>(**1**) (red line), TiO<sub>2</sub>(**2**) (black line) and TiO<sub>2</sub>(**1+2**) (blue line) were performed in 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (pH=6.4) as shown in **Fig. 2**. With photoanode TiO<sub>2</sub>(**1**) as WE, the PEC displays low photocurrent densities in the initial and final illumination periods. When using photoanode TiO<sub>2</sub>(**2**) as a WE, the photocurrent densities are found nearly no change. In strong contrast, when using photoanode TiO<sub>2</sub>(**1+2**) as a WE, the initial photocurrent density is greatly improved, amounting to ca. 400 μA/cm<sup>2</sup>. This high initial photocurrent density is found to be unstable, which decays to ca. 70 μA/cm<sup>2</sup> after 10 seconds illumination. These results indicate that both the molecular PS **1** and the molecular catalyst **2** are indispensable to co-exist on TiO<sub>2</sub> surface of WEs in order to keep the device more efficiently.

Long-term illumination experiment was studied, under 800 seconds visible light illumination of the WE TiO<sub>2</sub>(**1+2**) in 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (pH=6.4), as shown in **Fig. 3**. During the testing period, the PEC shows a fairly stable photocurrent density, the average value of which is calculated to be ca. 40 μA/cm<sup>2</sup>. In the same time, water splitting of the PECs was confirmed by the formation of molecular oxygen with Clark oxygen electrode, as shown in **Fig. 4**. No oxygen is detected for PEC devices with photoanode TiO<sub>2</sub>(**1**) or TiO<sub>2</sub>(**2**) as WEs. With photoanode TiO<sub>2</sub>(**1+2**) as a WE, however, sustainable generated



**Fig. 2.** Light control photocurrent measurements of two-electrode PECs in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution (pH=6.4) upon illumination with a 300 W xenon lamp white-light source (light intensity ca. 100 mW/cm<sup>2</sup>) coupled to a 400 nm long-pass filter. WEs TiO<sub>2</sub>(**1**) (red line), TiO<sub>2</sub>(**2**) (black line) and TiO<sub>2</sub>(**1+2**) (blue line).

Download English Version:

<https://daneshyari.com/en/article/184971>

Download Persian Version:

<https://daneshyari.com/article/184971>

[Daneshyari.com](https://daneshyari.com)