Coordination Chemistry Reviews 357 (2018) 130–143

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Design of photoanode-based dye-sensitized photoelectrochemical cells assembling with transition metal complexes for visible light-induced water splitting

Xin Ding[a], Linlin Zhang[a,*], Yong Wang[c], Aihua Liu[a], Yan Gao[b,*]

[a] Institute for Biosensing, College of Chemical Science and Engineering, Qingdao University, Qingdao 266071, Shandong, PR China
[b] State Key Laboratory of Fine Chemicals, Dalian University of Technology (DUT), Dalian 116024, Liaoning, PR China
[c] Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China

ARTICLE INFO

Article history:
Received 1 September 2017
Accepted 27 October 2017

Keywords:
Dye-sensitized photoelectrochemical cell
Molecular catalyst
Water oxidation
Artificial photosynthesis
Solar fuels

ABSTRACT

Dye-sensitized photoelectrochemical cells (DS-PECs) are receiving increasing attention as a novel pathway for visible light-induced water splitting for hydrogen. As well-known, the whole water-splitting process consists of two parts, oxygen evolution reaction (OER) for water oxidation and hydrogen evolution reaction (HER) for proton reduction, occurring at (photo)anode and (photo)cathode, respectively. Water oxidation reaction is the key rate-determining step in water splitting for its four electrons transfer period. So the assembly of efficient and stable photoanode is an essential part of DS-PECs. Herein, we summarize the recent developments of photoanodes based dye-sensitized photoelectrochemical cells (PA-DS-PECs) with a focus on their design, assembly, and performance. Based on the results discussed, the current challenges are briefly presented and several future opportunities are proposed.

Contents

---

* Corresponding authors.
E-mail addresses: zll@qdu.edu.cn (L. Zhang), dr.gaoyan@dlut.edu.cn (Y. Gao).

https://doi.org/10.1016/j.ccr.2017.10.020
0010-8545/© 2017 Published by Elsevier B.V.

1. Introduction

The rising energy demands and environmental concerns have aroused an increasing public awareness of renewable and carbon–neutral energy sources to replace fossil fuels. In nature, the sun is the largest potential source of energy, providing approximately 3,850,000 exajoules (EJ) per year to our planet, which is approximately 10,000 times the current global rate of energy consumption [1]. If well managed, the sun's energy will be a precious resource for everyday life. Hydrogen, the smallest and simplest molecule, plays an increasingly important role in the global energy economy. Hydrogen is a zero-emission fuel when burned with oxygen or used in a contained cell, and reversal of the reaction is possible if needed. Therefore, transferring the sun energy to produce clean hydrogen to replace traditional fossil fuels is a possible pathway to develop a sustainable society in the future. Recently, dye-sensitized photoelectrochemical cells (DS-PECs) have been shown to provide a promising approach to solar fuels by splitting water into oxygen and energy-rich hydrogen and some exciting achievement have also been obtained.

While, to date, most existing review articles focus on the photoanode or photocathode for DS-PECs in a wide sense of working mechanism, photoactivity or stability [2–4]. Specific design principles and assembly methods had rarely been reported. As well-known, water oxidation reaction occurring at photoanode is the key rate-determining step in water splitting for its four electrons transfer period. So the assembly of efficient and stable photoanode is an essential part of DS-PECs. However, there are few review papers systematically investigating efficient synthetic strategies for assembling photoanodes for PA-DS-PECs. To the best our knowledge, the only complete and systematic review article was reported by Swierk and Mallouk in 2013 [5]. Herein, we summarize the recent developments and working experience in lab of PA-DS-PECs with a focus on their design, assembly, and performance. Based on the results discussed, the current challenges are briefly presented and several future opportunities are proposed. Normally, an integrated PA-DS-PEC is composed of a photosensitizer (PS), water oxidation catalyst (WOC), semiconductor, electrolyte and counter electrode (normally Pt) (Fig. 1). The PA-DS-PECs will be discussed from the above aspects.

2. Device composition

2.1. Photosensitizer

The photosensitizer is an important part of PA-DS-PECs. To be an effective choice, the photosensitizer should strongly absorb visible and even the near-infrared (NIR) light; the LUMO level of the photosensitizer should be more negative than the CB edge of the n-type semiconductor to facilitate efficient electron injection; and the HOMO level of the photosensitizer should be positive compared with the catalytic onset potential of the WOC for oxygen evolution. Additionally, the photochemical and electrochemical stabilities are two other important factors. As a model sensitizer, $[Ru(bpy)_3]^{2+}$ has many attractive features [6]: (i) it absorbs strongly between 400 and 500 nm ($\varepsilon_{450nm} = 14{,}400\ M^{-1}\ cm^{-1}$); (ii) it has a sufficiently long-lived excited state lifetime (*ca.* 600 ns) for a diffusional encounter with an electron donor or acceptor in solution; and (iii) the Ru(III)/Ru(II) reduction potential is sufficiently positive at 1.26 V versus NHE (Normal Hydrogen Electrode) to drive the water oxidation process, even in acidic solutions. As such, $[Ru(bpy)_3]^{2+}$ compounds have dominated PA-DS-PEC investigations to date (**PS1**–**PS4**) (Fig. 2) [7]. However, its instability in oxygen rich environments for water oxidation greatly limits its application. Meanwhile, high-charged but narrow absorption range porphyrins (**PS5**, **PS6**) [8,9] and high molar extinction coefficient organic dyes (**PS7**, **PS8**, **PS9**) [10–12] have also been investigated, although the risk of being oxidized is the biggest challenges for the use of organic dyes [13].

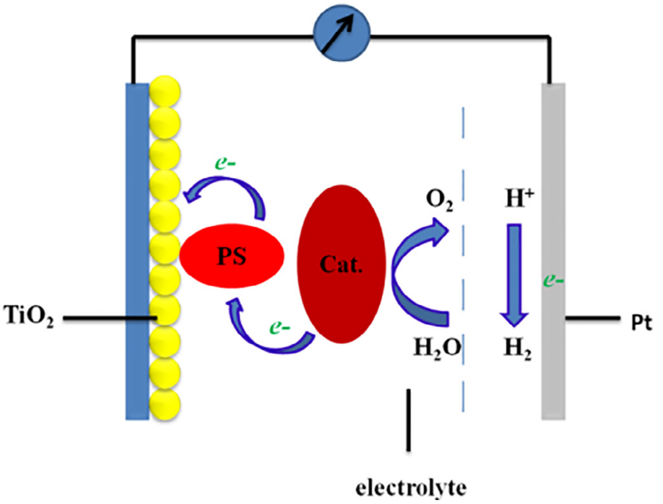

Fig. 1. Schematic illustration of PA-DS-PEC for water splitting.

2.2. Water oxidation catalyst (WOC)

Recently, great developments have been achieved in the design and synthesis of molecular WOCs based on Ru [14–31], Ir [32–35], Cu [36,37], and Co [38] complexes. To be an ideal choice for PA-DS-PECs, the WOC must collect four oxidizing equivalents per oxygen molecule generated, facilitate the formation of oxygen, and be chemically stable. For practical use, the catalyst should be very active or self-repairing. The onset potentials of the water oxidation catalyst should be lower so that it can be thermodynamically driven by photo-generated $[Ru\ (bpy)_3]^{3+}$ or other oxidized photosensitizers. The turnover number (TON), turnover frequency (TOF), and overpotential at the desired TOF are three quantitative criteria for the WOC. From these three criteria, **Cat. 2**–**Cat. 9** are commonly recognized as suitable choices for PA-DS-PECs (Fig. 3). Among the reported catalysts, $[Ru(bda)(isoq)_2]$(H_2bda = 2,2′-bipyridine-6,6′-dicarboxylic acid; isoq = isoquinoline) shows an unprecedentedly high reaction rate with a TOF of >300 s^{-1} with the Ce(IV) oxidant $Ce(NH_4)_2(NO_3)_6$ as electron acceptor, which is comparable with that of photosystem II in an homogeneous system [19]; [Ru(bda)(4-Br-pyridine)$_2$] displays a TON of 579 and a TOF of 20 (min^{-1}) for water oxidation in an homogeneous system with $[Ru(bpy)_3]^{2+}$ as photosensitizer and $Na_2S_2O_8$ as electron acceptor [30]; [Ru(tda)(L)$_2$[tda = 2,2′:6′,2″-terpyridine]-6,6″-dicarboxylato] exhibits a million TON determinations without any sign of degradation at pH = 7 with an E_{app} = 1.45 V versus NHE [39]; a TON of 498 and an average TOF of 1.0 s^{-1} for total water splitting were achieved with 500 seconds of light illumination in PA-DS-PEC with **Cat. 4** [40]. These discoveries established the foundation for the further development of PA-DS-PECs.

2.3. Adsorbing group

Adsorbing groups are key components to combine the semiconductor and PS or catalyst for assembling PA-DS-PECs. Generally, there are three main kinds of common adsorbing groups introduced in PA-DS-PECs, the carboxylic group [8,10], phosphonic group [21,41–45] and silicic group [40]. Hydroxamic group and dipicolinic acid group display a less number occurring in PA-DS-PECs [46,47]. From the published works [8,47–51] and previous