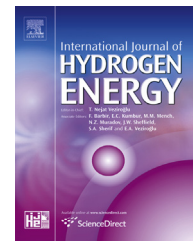




ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

Efficient p-zinc phthalocyanine/n-fullerene organic bilayer electrode for molecular hydrogen evolution induced by the full visible-light energy

Toshiyuki Abe^{a,*}, Yudai Hiyama^a, Katsuma Fukui^a, Kana Sahashi^a,
Keiji Nagai^b

^a Department of Frontier Materials Chemistry, Graduate School of Science and Technology, Hirosaki University,
3 Bunkyo-cho, Hirosaki 036-8561, Japan

^b Chemical Resources Laboratory, Tokyo Institute of Technology, Suzukake-dai, Midori-ku, Yokohama 226-8503,
Japan

ARTICLE INFO

Article history:

Received 7 November 2014

Received in revised form

14 May 2015

Accepted 22 May 2015

Available online 16 June 2015

Keywords:

Hydrogen evolution

Organic semiconductor

p–n Bilayer

Visible-light energy

Fullerene

Phthalocyanine

ABSTRACT

A photoelectrode featuring an organic p/n bilayer was used to generate H₂ from H⁺, where n-type fullerene (C₆₀) was used in combination with p-type zinc phthalocyanine (ZnPc). When a Pt catalyst was loaded on the surface of C₆₀ in the organo-photoelectrode, a photocathodic current was successfully generated via H₂ evolution at the Pt-coated C₆₀ surface. On the basis of the results of action spectral measurements for photocurrent, the H₂ evolution appeared to be induced over the entire visible-light wavelength range of <750 nm. In particular, the visible-light absorption of ZnPc/C₆₀ bilayer efficiently contributed to carrier generation, consequently leading to the H₂ evolution at the C₆₀ surface via reducing power generated through a series of photophysical events within the bilayer.

Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Solar hydrogen has attracted attention for its possible use as a clean energy source alternative to fossil fuels to facilitate the establishment of a sustainable society. The production of molecular hydrogen (H₂) has been actively investigated through both photocatalytic [1–5] and photoelectrochemical [6–11] approaches, which are the most reasonable and promising methods. From this viewpoint, the development of

active photocatalyst materials, particularly those that make the efficient use of the solar spectrum to bring about a high output, is the vital issue. However, as shown in numerous previous studies, the use of inorganic semiconductors as visible-light-responsive photocatalysts usually involves lowering their activities with decreasing the magnitude of the band-gap energy between their valence and conduction bands; i.e., inducing the formation of H₂ under irradiation by visible light of longer wavelengths has proven difficult [12–14].

* Corresponding author. Fax: +81 172 39 3580.

E-mail address: tabe@hirosaki-u.ac.jp (T. Abe).
<http://dx.doi.org/10.1016/j.ijhydene.2015.05.155>

0360-3199/Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

We have focused on the application of organic semiconductors to photocatalyst materials in the water phase. We have previously evaluated the photoelectrochemical performance of organic p/n bilayers [15–18] and its application to photocatalysis systems [19–23]. When the organic bilayer was irradiated with visible light, a series of photophysical events (i.e., light absorption, formation of an exciton, its transfer to the p/n interface, carrier generation at the heterojunction, and the conduction of electrons and holes in each layer) within the bilayer occurred, which allowed the oxidizing and reducing powers to be separately produced at the p-type and n-type surfaces, respectively. Distinct from the sole use of a semiconductor as a photocatalyst material, the aforementioned organo-photocatalyst material has advantages in terms of the uptake of solar energy and its derivative generation of the oxidizing and reducing powers, which originate from the two types of semiconductors employed (i.e., p-type and n-type semiconductors). As previously mentioned, this approach to H₂ production via an organic p/n bilayer is novel and may lead to an innovative breakthrough for the production of solar hydrogen.

In the present study, an organic p/n bilayer composed of zinc phthalocyanine (ZnPc, p-type) and fullerene (C₆₀, n-type) was prepared and used to reduce H⁺ into H₂. The results of its photoelectrochemical evaluation for H₂ production are described herein.

Experimental

Chemicals

Pure C₆₀ (>99.5%, Tokyo Chemical Industry Co., Ltd. (TCI)) was used as received. Commercially available ZnPc (TCI) was purified by sublimation prior to use, as described elsewhere [16]. The other reagents were of the extra-pure grade and were used as received. The indium–tin oxide (ITO)-coated glass plates (sheet resistance, 8 Ω cm⁻²; transmittance, >85%; ITO thickness, 174 nm) were obtained from Asahi Glass Co., Ltd.

Film preparation

The organic p/n bilayer was fabricated by vapor deposition at room temperature (pressure, <1.0 × 10⁻³ Pa; deposition speed, ca. 0.03 nm s⁻¹). ZnPc was first coated on ITO, followed by a coating of C₆₀ on the top of the ZnPc layer (denoted as ITO/ZnPc/C₆₀).

Measurements

Absorption spectral measurements were performed using a Hitachi U-2010 spectrophotometer. The resulting absorption spectra of ZnPc (α-phase) [24] and C₆₀ [25] were identical to those reported previously, and their absorption coefficients were used to determine the thickness of the prepared film.

Photoelectrochemical measurements were performed in a single-compartment glass cell (Fig. 1). The measurements were performed using a potentiostat (Hokuto Denko, HA-301) equipped with a function generator (Hokuto Denko, HB-104), a coulomb meter (Hokuto Denko, HF-201), and an X–Y recorder

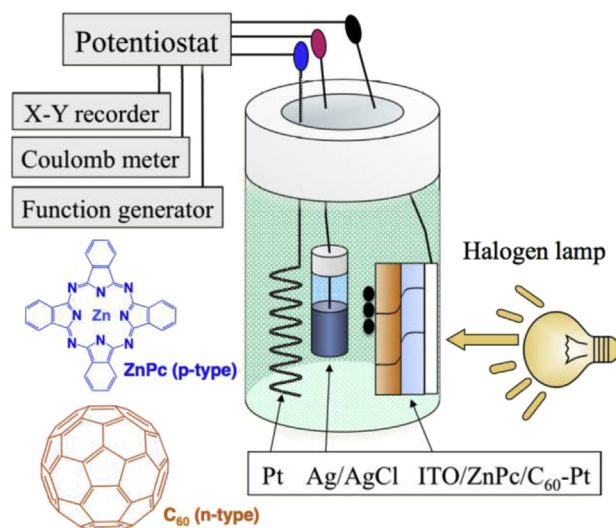


Fig. 1 – Schematic of the photoelectrochemical cell employed in the present study and of the chemical structures of organic semiconductors.

(GRAPHTEC, WX-4000). In particular, the deposition of Pt on ITO/ZnPc/C₆₀ was performed under photocathodic conditions where the photoelectrode was polarized from +0.4 V (vs. Ag/AgCl (sat.)) to -0.2 V in an acidic solution (pH = 2) containing 5.0 × 10⁻⁴ mol dm⁻³ H₂PtCl₆·6H₂O under anaerobic condition. The amount of Pt deposited was controlled by controlling the amount of charge passed (typically, 2.0 × 10⁻² C). The resulting device is abbreviated as ITO/ZnPc/C₆₀-Pt.

Other photoelectrochemical measurements (e.g., voltamogrammic measurements, potentiostatic electrolysis, and photocurrent measurements (under potentiostatic condition) for measuring action spectra) were performed under Ar atmosphere and in an aqueous solution of phosphoric acid (pH = 2). A halogen lamp (light intensity: 100 mW cm⁻²) was usually used as the light source; irradiation was usually performed from the back side of the ITO-coated face. For the measurements of the action spectra for photocurrents, a monochromatic light generated by the combination of a monochromator (Soma Optics, Ltd., S-10) and a light source was used to irradiate the samples. The light intensity was measured using a power meter (Ophir Japan, Ltd., type 3A).

The H₂ produced was analyzed using a gas chromatograph (Shimadzu, GC-8A) equipped with a thermal conductivity detector and a molecular sieve 5-Å column; Ar was used as the carrier gas. The quantification of H₂ was performed using a chromatogram analyzer (Shimadzu, C-R8A) equipped with the chromatograph.

Calculation methods

The Faradaic efficiency (F.E.) of H₂ evolution was calculated according to the procedure as follows:

- i) During photoelectrochemical H₂ evolution, the amount of charge passed was measured using a coulomb meter. The

Download English Version:

<https://daneshyari.com/en/article/7715097>

Download Persian Version:

<https://daneshyari.com/article/7715097>

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