



Organic Photovoltaic Structures as Photo-active Electrodes



Matthew P. Gustafson^{a,*}, Noel Clark^b, Bjorn Winther-Jensen^c, Douglas R. MacFarlane^a

^a ARC Centre of Excellence for Electromaterials Science, Department of Chemistry, Monash University Clayton, Victoria, 3800, Australia

^b Materials Science and Engineering Division, CSIRO, Clayton South, Victoria, 3169, Australia

^c Department of Materials Engineering, Monash University Clayton, Victoria, 3800, Australia

ARTICLE INFO

Article history:

Received 6 January 2014

Received in revised form 21 March 2014

Accepted 23 March 2014

Available online 30 March 2014

Keywords:

P3HT:PCBM

Heterojunction

Water electrolysis

Photo-enhanced

ABSTRACT

This study demonstrated the novel use of a bulk heterojunction (BHJ), as present in modern organic solar cells, as a light-assisted electrocatalyst for water electrolysis reactions. Two separate organic photo-voltaic electrode structures were designed for targeting both the reduction, (ITO-PET/PEDOT:PSS/P3HT:PCBM)* and oxidation, (ITO-PET/ZnO/P3HT:PCBM)* reactions of water, denoted as OPE-R and OPE-O respectively. The OPE-R electrode supported both the proton reduction reaction (PRR) and oxygen reduction reaction (ORR) achieving photocurrents of -0.04 mAcm^{-2} (ORR) and -0.03 mAcm^{-2} (PRR) and a photovoltage of 0.50 V (ORR) and onset photovoltage at -0.59 V (PRR). By comparison, the OPE-O electrode achieved photocurrents of 0.15 mAcm^{-2} and photovoltages of 0.35 V for the water oxidation reaction (WOR). Both BHJ designs confirmed evidence of photo-enhanced Bulk Heterojunction Electrode (BHE) activity. The stability and sources of electrode degradation were also studied, with the OPE-O electrode proving to be more stable than the OPE-R electrode, most likely due to the PEDOT:PSS layer and PSS migration in the presence of water.

*Indium Tin Oxide (ITO), Polyethylene Terephthalate (PET), Poly(3,4-ethylenedioxythiophene) (PEDOT), Polystyrenesulfonate acid (PSS), Poly(3-hexylthiophene) (P3HT), Phenyl-C₆₁-Butyric acid Methyl ester (PCBM), Zinc Oxide (ZnO)

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

While photovoltaic solar cells can provide an alternative means of electrical energy production, it is important to note that approximately 56% of the world's energy consumption relies on fuels [1]. Alternatives to traditional carbon-based fuels include methanol, ethanol, diethyl ether, biofuels and hydrogen produced via water electrolysis [2]. While water electrolysis has been studied for over a hundred years, a cheap, commercially viable pathway has yet to be established [3,4]. Furthermore, these efforts are challenged by recent estimations of >70% energetic efficiency being required to reach commercial viability as a fuel [5]. Current industrial production techniques for hydrogen, such as steam reforming of hydrocarbons, range from 70% to 80% efficiency using nickel-based catalysts, providing hydrogen for ammonia production and hydrocracking processes [6,7]. Industrial water electrolysis however, has the advantage of producing high-purity hydrogen (99.99 vol.%) that is preferred for high-end applications such as rocket propellant, fuel cells and oxyhydrogen torches [6]. State-of-the-art high-purity

hydrogen via electrolysis requires expensive platinum based catalysts which are subject to degradation, emphasizing the need for an inexpensive and robust alternative catalyst [6].

Photo-enhanced electrolysis attempts to bypass the activation energy required by traditional catalysts by harnessing sunlight to aid, or ideally, drive the electrochemical reaction completely [8–10]. Historically, photocatalysis was realised by Fujishima and Honda using TiO₂ [11]. This sparked interest in the newly formed field, with modern studies continuing to build on the semiconductor heterojunction-based approach using materials such as carbon nitride:P3HT, Ti:PCBM, and PTCDA:PCBM [11–16].

Recently, Lanzarini *et al.* explored the much studied P3HT:PCBM junction by spin coating onto an indium tin oxide (ITO) coated glass substrate as a means of generating photocatalytic hydrogen [17]. They presented results pertaining to photocatalysis of the Proton Reduction Reaction (PRR) at the active polymer interface, using visible light in a NaCl electrolyte. However, the photocurrents reported were in the nanoamp range, or in arbitrary units, indicating that the processes involved were not efficient.

In the present work we have developed photovoltaic structures designed to optimise charge separation and electroactivity, in particular a hole conducting layer has been included to ensure good surface contact between the active layer and ITO.

* Corresponding author. Tel.: +613 9905 3698.

E-mail address: matthew.gustafson@monash.edu (M.P. Gustafson).

By tailoring a printed organic solar cell structure and applying it to electrolysis reactions, we utilise the existing BHJ concept behind the established P3HT:PCBM charge separation mechanism to create a photo-active electrode. Unsurprisingly, the shift between working environments, from solid-state photovoltaic to solution-based electrolysis, creates limitations [18,19] on the electrode performance, which we also investigate.

The Bulk Heterojunction (BHJ), formed by the energy level offset between the P3HT and PCBM materials, provides an avenue for photo-excitation, charge production and subsequent transport (Scheme 1 a & b.) [20]. For reduction reactions the organic photo-voltaic electrode structure developed here is denoted ITO-PET/PEDOT:PSS/P3HT:PCBM, which we refer to as OPE-R, and for oxidation ITO-PET/ZnO/P3HT:PCBM, which we refer to as OPE-O. Each geometry was designed to channel the electron or hole produced in the BHJ active layer to carry out a redox reaction at the electrolyte-electrode interface.

2. Experimental

2.1. Sample Preparation

The P3HT:PCBM combination was selected as a suitable platform for study, as is widely accepted as a successful BHJ in organic solar cells [20–22]. ITO-PET with a surface resistance of 15 ohms/square was supplied by Solutia Inc. (USA) and patterned to our specification by Mekoprint AB (Denmark). The materials poly-3,4-ethylenedioxy-thiophene:poly(styrene sulphonic acid) (PEDOT:PSS, Clevis FE T, Heraeus), poly(3-hexylthiophene) (P3HT, Merck), [6,6]-phenyl C61 butyric acid methyl ester (PCBM, technical grade, 99%, Solenne BV) were used as hole transport layer and active layer, respectively. The PEDOT:PSS aqueous dispersion was used as received, whereas the P3HT:PCBM solution (1:1 ratio by wt, 60 mg/mL total concentration) was prepared by separately

dissolving P3HT and PCBM in chlorobenzene:1,2-dichlorobenzene mixed solvent (CB:DCB = 3:1 by wt), with heating at 60 °C and stirring in air for 120 min, then cooling to room temperature before the two solutions were combined to make a printing ink. ZnO was synthesized as reported [23] by hydrolysis and condensation, where tetramethylammonium hydroxide (TMAH, $(\text{CH}_3)_4\text{NOH}$) dissolved in ethanol (0.55 M) was added into 30 mL of 0.1 M zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) dissolved in dimethyl sulfoxide (DMSO) by dropwise addition, followed by stirring for an hour at 60 °C. The ZnO nanoparticles were then washed and dispersed in ethanol to form a transparent printing ink.

The layers comprising the BHJ were applied to the 10-cm wide ITO-PET substrate by the reverse-gravure process using a Mini-Labo roll-to-roll printing system from Yasui Seiki (Japan) [24]. After annealing at 130 °C for 30 seconds under nitrogen, the electrodes were sputter-coated with platinum to facilitate the desired reduction and oxidation reactions at the electrolyte interface. To assess the role of the platinum, a series of control experiments were carried out to characterise electrocatalytic performance. Future development of this study will replace platinum with suitable alternative inorganic-based catalysts such as MoO_x [25,26]. After sputter-coating, the OPE was then laminated, leaving an exposed cut-out 0.2×0.2 mm window, with a titanium strip acting as a connector, to form the working electrode (See S1 in supporting information).

2.2. Electrochemical Setup

Cyclic voltammetry (CV) and chronoamperometry (CA) measurements were performed within a custom Teflon cell containing a three electrode setup to maintain consistent distances between electrodes and light source. A Ag/AgCl (3 M NaCl) reference and coiled platinum wire counter electrode were used while nitrogen and air were bubbled via a Pasteur pipette as required. Samples were illuminated through a quartz window by a KL 2500 LCD lamp (5E setting, equivalent to 3–4 suns) and monitored using a Princeton VMP potentiostat. CV and CA measurements were performed in 0.1 M phosphate buffers of pH 7, pH 4, or in 0.05 M borate buffer of pH 8.

2.3. Sample Preparation–Resistance Measurements

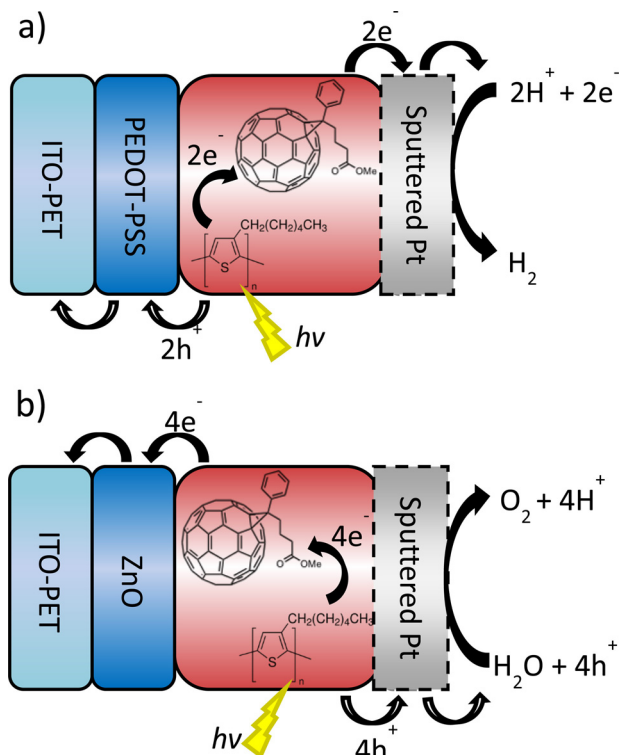
Samples for resistance measurements were prepared as described in section 2.1, however, the cut-out exposed a larger section of cell with two separate titanium strips to allow measurement across the film when immersed in deionised water (See S2 in supporting information). A CA scan was performed at several potentials to calculate average resistance via a two electrode setup.

3. Results and Discussion

3.1. Oxygen and Proton Reduction Reactions

Cyclic voltammetry (CV) was performed with and without illumination under nitrogen or oxygen enriched atmospheres when targeting the proton reduction (PRR) and oxygen reduction reactions (ORR) respectively (Fig. 1).

A clear photo-enhancement effect is seen for the both reduction reactions in Fig. 1. Under illumination, the ORR shows a photocurrent (ΔJ between dark and light) of -0.04 mA/cm^2 at -0.50 V . This can also be described as a photovoltage of 0.50 V at -0.02 mA/cm^2 which lowers the potential needed to drive the reaction. The proton reduction reaction shows a similar photocurrent effect, e.g. -0.03 mA/cm^2 at -0.80 V . While the initial onset seen at 0.30 V in



Scheme 1. Electron-hole pathways in the organic photovoltaic electrodes designed for (a) reduction (OPE-R), or (b) oxidation (OPE-O) reactions.

Download English Version:

<https://daneshyari.com/en/article/185224>

Download Persian Version:

<https://daneshyari.com/article/185224>

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