



Photo-electrocatalytic hydrogen generation at dye-sensitised electrodes functionalised with a heterogeneous metal catalyst



Dijon A. Hoogeveen^a, Maxime Fournier^a, Shannon A. Bonke^a, Xi-Ya Fang^b, Attila J. Mozer^c, Amaresh Mishra^{d,1}, Peter Bäuerle^d, Alexandr N. Simonov^{a,*}, Leone Spiccia^{a,*}

^a School of Chemistry and the ARC Centre of Excellence for Electromaterials Science, Monash University, Victoria 3800, Australia

^b Monash Centre for Electron Microscopy, Monash University, Victoria, 3800, Australia

^c Intelligent Polymer Research Institute and the ARC Centre of Excellence for Electromaterials Science, University of Wollongong, Wollongong, 2522, Australia

^d Institute for Organic Chemistry II and Advanced Materials, University of Ulm, Albert-Einstein-Allee 11, 89081, Ulm, Germany

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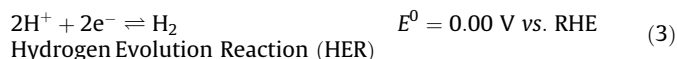
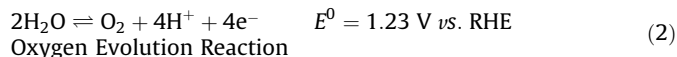
ABSTRACT

Dye-sensitised photocathodes promoting hydrogen evolution are usually coupled to a catalyst to improve the reaction rate. Herein, we report on the first successful integration of a heterogeneous metal particulate catalyst, viz., Pt aggregates electrodeposited from acidic solutions on the surface of a NiO-based photocathode sensitised with a *p*-type perylenemonoimid-sexithiophene-triphenylamine dye (PMI-6T-TPA). The platinised dye-NiO electrodes generate photocurrent density of ca -0.03 mA cm^{-2} (geom.) with 100% faradaic efficiency for the H_2 evolution at 0.059 V vs. reversible hydrogen electrode under 1 sun visible light irradiation (AM1.5G, 100 mW cm^{-2} , $\lambda > 400 \text{ nm}$) for more than 10 hours in 0.1 M H_2SO_4 (aq.). The Pt-free dye-NiO and dye-free Pt-modified NiO cathodes show no photo-electrocatalytic hydrogen evolution under these conditions. The performance of these Pt-modified PMI-6T-TPA-based photoelectrodes compares well to that of previously reported dye-sensitised photocathodes for H_2 evolution.

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1. Introduction

With 120 petawatts of electromagnetic irradiation reaching the surface of the Earth each year, sunlight is the largest sustainable and exploitable energy resource [1,2]. A great challenge exists, however, to take full advantage of this energy through conversion into a storable and transportable fuel [2–6]. Electrochemical water splitting (equation 1) has been widely investigated as a method for ‘solar fuel’ generation given its use of water as a cheap and abundant feedstock and its production of hydrogen as a carbon free fuel [4,7].



Tandem dye-sensitised (DS) photoelectrochemical cells (PECs) [8] are an emerging photocatalytic water splitting technology built upon foundations laid by research into dye-sensitised solar cells (DSCs) [9]. Both involve the sensitisation of a wide band-gap semiconductor with light harvesting dye molecules. Instead of reversible redox couples, materials catalysing water oxidation (photoanode, eq. 2) and hydrogen evolution (photocathode, eq. 3) are introduced to promote dye regeneration. Our pioneering work focussed on photoanodes [10]. Sun and co-workers subsequently reported transient water oxidation photocurrents above 0.5 mA cm^{-2} under 3 suns AM1.5G irradiation [11]. However, the photopotential of such anodes is not sufficient for complete water splitting and an adjuvant voltage is generally needed, e.g. 0.2 V vs.

* Corresponding authors.

E-mail addresses: alexandr.simonov@monash.edu (A.N. Simonov), leone.spiccia@monash.edu (L. Spiccia).

¹ Current address: School of Chemistry, Sambalpur University, Jyoti Vihar-768019, Sambalpur, India.

reversible hydrogen electrode (RHE) in the study by Sun and co-workers [11]. Alternatively, a photocathode can be introduced in a tandem configuration to give a fully light driven device. However, the efficiencies of the best DS photocathodes reported to date are much lower than those achieved thus far by photoanodes. On this basis, further progress in tandem DS-PEC water splitting technology relies on the development of photocathodes with much higher activity, and, equally importantly, long-term stability [12].

Till now, there have been few reports on DS photocathodes which satisfactorily promote hydrogen evolution in an aqueous medium [13–18]. They all consist of a mesoporous *p*-type NiO layer sensitised with a Ru^{II} or organic sensitizer, often functionalised with a molecular HER catalyst. The latter is needed to improve the rate of H₂ evolution, which is typically poor on dye surfaces. Promising catalysts include cobalt(II) difluoroboryl-diglyoximate (CodmgBF₂) and nickel(II) bis(1,5-*R'*-diphospha-3,7-*R''*-diazacyclooctane). These catalysts can be introduced by drop-casting on the DS surface [13], complexing to a co-adsorbed covalent linker [16], direct attachment to the dye [15], or ionic interactions [18]. To our knowledge, there is only one report on coupling a photocathode sensitised with an organic dye to an inorganic catalyst. This was achieved by introducing a molecular Mo₃S₄ cluster as a homogeneous HER catalyst into the solution [17]. This successful strategy, imitating to some extent the principle of a *p*-type photocathode in DSCs, resulted in reductive photocurrent densities of *ca.* –150 μA cm⁻². This performance was achieved over 16 hours continuous illumination (3.44 suns) and conditions favourable for hydrogen evolution, *viz.* in 1.0 M HCl at 0.0 V vs. RHE.

Notwithstanding the progress achieved, there are concerns over the stability of the HER photocathode systems while in operation, *viz.* rapid photocurrent loss and faradaic efficiencies well below 100% [13,15–18]. For example, molecular hydrogen measurements for the Mo₃S₄-based DS system in Ref. [17], undertaken at the negative potential (–0.30 V vs. RHE), indicated a faradaic efficiency of *ca.* 50%. This was attributed to the irreversibility of the Mo⁴⁺ reduction, and evidence for the catalyst decomposition was presented [17].

Overall, the molecular HER catalyst is typically the most fragile component of the photocathode system. Indeed, reductive degradation has been found elsewhere in the literature for cobalt and nickel complexes [19–23] with specific evidence provided in the case of cobaloximes [24], as well as with the cubane Mo₃S₄ cluster mentioned above [25]. Thus, both the activity and stability of molecular catalysts coupled so far with DS photocathodes are generally poorer than those of much simpler and, in some cases cheaper, heterogeneous inorganic catalysts, such as Pt-group metals [26] and transition metal sulphides, phosphides or carbides [27]. On top of reasonable activity and robustness, to sustain efficient electron transfer, it is desirable for the catalyst to be in intimate contact with the photoactive sites, as explicitly demonstrated in studies on water-splitting photoanodes [28–30]. However, achieving a favourable alignment of a purely inorganic catalyst on a monolayer of an organic dye is a challenging task. Moreover, the catalyst needs to be well dispersed to achieve optimum performance and efficient utilisation. The latter is very important particularly when using the best known hydrogen evolution electrocatalyst, *viz.* Pt metal [31–33]. Platinum has often been introduced onto non-sensitised narrow band gap photocathodes to promote hydrogen evolution [34–38], but has yet to be integrated to a DS photocathode.

In this study, we report the first successful functionalisation of a dye-sensitised photocathode with platinum particles that function as catalysts for the hydrogen evolution reaction. A *p*-type dye perylenemonoimid-sexithiophene-triphenylamine (PMI-6T-TPA) employed herein has been highly successful for application at *p*-type DSCs [39–42], and even more importantly, has been reported

to be capable of sustaining low levels of the light-driven HER without a catalyst [14]. The device assembly and dye structure are shown in Scheme 1.

2. Experimental

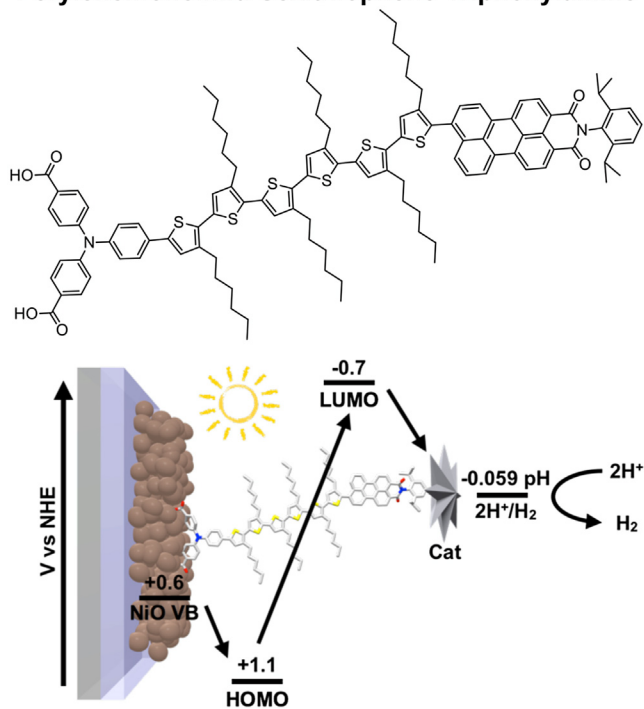
2.1. Materials

Reagent or analytical grade chemicals were used as received from commercial suppliers. Reverse osmosis purified water with a quoted resistivity of 1 MΩ cm at 25 °C was used in all experimental procedures and to prepare electrolyte solutions unless otherwise stated. Glass coated with fluorine-doped SnO₂ (FTO) (sheet resistance *ca.* 8 Ω sq⁻¹) was purchased from *Dyesol*. NiO nanoparticle powder (particle size ~20 nm; 73.22 wt.% Ni) was used as received from *Inframat*. The perylenemonoimid-sexithiophene-triphenylamine dye was synthesised following a published procedure [43].

2.2. Photocathode preparation

Procedures for the deposition of the NiO layer and its sensitisation with the PMI-6T-TPA dye were adopted from the literature [42,44]. A NiO paste was prepared by mixing NiO, ethyl cellulose solution (5 wt.% in ethanol) and terpineol in the ratio 4: 23: 23 (wt.) and ball milling this mixture at 400 rpm for 4 hours (Fritsch Pulverisette 7; 50 ml zirconia cylinder; zirconia balls of 11, 7, 5 and 3 mm diameter). A commercial semi-automatic screen-printer (*Keywell*) was used to print circular NiO films with a geometric area of 2 cm² on FTO. All current densities reported below are normalised to this area. Two successive printing cycles were performed resulting in a NiO film thickness of *ca.* 2.0 μm as

Perylenemonoimid-Sexithiophene-Triphenylamine



Scheme 1. Perylenemonoimid-sexithiophene-triphenylamine dye and schematic energy diagram of the catalyst/dye-NiO photocathode assembly. VB is the NiO valence band. HOMO and LUMO are the highest occupied and lowest unoccupied molecular orbitals of the dye. Cat is the HER catalyst.

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