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Noble metal-free hydrogen-evolving photocathodes based on small molecule organic semiconductors

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Abstract

Organic semiconductors have great potential for producing hydrogen in a sustainable and economically viable manner because they rely on readily available materials with highly tunable properties. We demonstrate here the relevance of heterojunctions to the construction of H₂-evolving photocathodes, exclusively based on earth-abundant elements. Boron subnaphthalocyanine chloride proved a very promising acceptor in that perspective. It absorbs a part of the solar spectrum complementary to α -sexithiophene as donor, thus generating large photocurrents and provides a record onset potential for light driven H₂ evolution under acidic aqueous conditions using nanoparticulate amorphous molybdenum sulfide catalyst.

Keywords

planar heterojunction; small organic molecule semiconductors; organic photovoltaic; hydrogen evolution reaction (HER); photocathode; amorphous molybdenum sulfide

1 Introduction

Conversion of sunlight in a form of a useable and storable fuel remains a great challenge. In that prospect, the splitting of water in a photoelectrochemical cell (PEC) is a sustainable way to produce hydrogen [1, 2]. Such a process, mimicking photosynthesis in plants and micro-algae, also allows for the storage of large amounts of solar energy in a chemical form (the H-H bond) that can be used on-demand, for example to power fuel cells [3]. To be economically viable, PEC technology needs to respond to four main characteristics: sustainability, cost-effectiveness, stability and safety. Fulfilling these requirements raise important scientific questions regarding mainly the elaboration and the combination of the best possible materials able to harvest light and catalyze H₂ and O₂ evolution. A number of inorganic solid-state semiconductors have been intensively investigated as photocathodes [2,

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4–8] or photoanode materials [9], however with poor process efficiencies and generally low quantum yields when considering the cheapest metal oxide-based materials [10]. On the other hand, molecular-based dye-sensitized photoelectrodes for H₂ or O₂ evolution have been recently developed, inspired by the design of dye-sensitized solar cells (DSSCs) [2, 11]. Despite still low efficiencies, this field is highly promising due to the high tunability of the molecular constructs. Between these two approaches, an additional option is to exploit the unique properties of organic photovoltaic (OPV) materials, combining chemical versatility, processability and tunability of optical and electronic properties. [12]. OPV cells have reached power conversion efficiencies exceeding 10 % [13] but have been only rarely used in the context of water splitting. However, a triple-junction polymer OPV cell-configuration powering a water electrolyzer has been reported with a solar-to-hydrogen (STH) conversion efficiency up to 4.9 % [14, 15]. O₂-evolving photoanodes [16–18] and H₂-evolving photocathodes [2] have also been described. The use of organic junctions in the context of direct PEC water splitting sets various constraints: (i) the organic layer in contact with a liquid electrolyte should maintain the capacity of light absorption, charge separation and transport to the interface with the electrolyte; (ii) an appropriate photovoltage must be reached to allow for water oxidation or reduction to occur (iii) the electrochemical reaction at the interface must be facilitated by an appropriate catalyst [2]. Platinum is widely used in that context [19–23], but is not a sustainable solution, owing to the scarcity and limited stocks of this metal [24].

Our groups recently described efficient H₂-evolving OPV-based photocathodes [25, 26] using amorphous molybdenum sulfide (a-MoS_x) [27], a coordination polymer based on {Mo₃S₁₁} clusters catalyzing H₂ evolution under acidic conditions [28]. For that work, we exploited bulk heterojunctions of phenyl-C61-butyric-acid methyl ester (PCBM) and p-type poly(3-hexylthiophene) (P3HT) conjugated polymer. We investigate here another approach based on the planar p/n heterojunctions of small molecules and oligomers, a technology holding promises in the OPV field [12, 29, 30]. Compared to the polymer-based technology, this approach specifically allows for the use of a wider variety of donor and acceptor molecules. Significantly higher open circuit voltages (V_{OC}) could specifically be obtained for a boron subphthalocyanine chloride (SubPc)/C₆₀ thin film OPV cell [31]. We demonstrate below that such a property can be used to increase both the onset potential and the solar-to-hydrogen power saved [25, 32] for H₂ evolution of OPV-based photocathodes.

2 Experimental details

2.1 Materials and reagents

Indium tin oxide (ITO)-coated glass substrates (XY20S) were purchased from Xinyan Technology. The ITO film had a film thickness of 90 nm, and sheet resistance of about 20 Ω/sq. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, Al 4083) was purchased from Ossila. Alpha-sexithiophene (α-6T), boron subphthalocyanine chloride (SubPc) and fullerene (C₆₀) were purchased from Sigma-Aldrich and purified in a home-built thermal gradient sublimator before use. Boron subnaphthalocyanine chloride (SubNc) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) were purchased from Luminescence Technology Corp and used as received. The a-MoS_x nanoparticles were

prepared according to literature [26, 33]. A detailed procedure is given in the Supporting Information. H₂SO₄ (Sigma-Aldrich, 98 %) and ultrapure water (18.2 MΩ·cm resistivity at 25 °C) were used for the preparation of the electrolytic solution. Manipulations were carried out under an inert argon atmosphere in a glove box, if not otherwise mentioned.

2.2 OPV solar cell fabrication and testing

ITO-coated glass substrates were placed in a sample holder and cleaned through (i) sonication in detergent solution, (ii) rinsing twice in deionized water, (iii) sonication for 15 min in acetone, (iv) sonication for 15 min in isopropanol and (v) 15 min treatment in a UV-ozone cleaner. A 30 nm thick PEDOT:PSS hole-transport layer was spin-coated (speed: 5000 rpm/ramp: 5s/dwelling time: 30 s) and followed by a thermal treatment in the air for 5 min at 130 °C. The substrates were then placed into the vacuum chamber of an evaporator located in the glove box. Small organic molecules were deposited by high vacuum ($< 10^{-6}$ mbar) thermal vapor evaporation. The deposition rates of the organic molecules were controlled by two quartz crystal sensors. The system allows simultaneous deposition of two distinct molecular species. LiF (1.2 nm) followed by Al (100 nm) layers were finally evaporated ($0.4 \text{ Å} \cdot \text{s}^{-1}$ for LiF, $1.5 \text{ Å} \cdot \text{s}^{-1}$ for Al) through a shadow mask (0.28 cm^2).

The current-voltage (j -V) characteristics of OPV cells were recorded in the glove box both in the dark and under simulated solar illumination, using a Keithley 2635 measurement unit and an Atlas Solar Constant 575PV simulator under AM 1.5 G spectrum at $100 \text{ mW} \cdot \text{cm}^{-2}$ (1 sun).

Absorption spectra were recorded with a JENWAY 6800 UV/vis spectrophotometer.

2.3 Photocathode fabrication

Electrodes architectures were constructed similarly as for the above-described OPV solar cells, but without LiF/Al layers. The electrodes were then transferred out of the glove box and heated on a hot plate (80 °C) while the a-MoS_x suspension was sprayed as previously described [25]. The electrodes were then quickly transferred back in the glove box.

2.4 Photoelectrochemical characterization

Photoelectrochemical measurements were carried out in acidic aqueous electrolyte (0.5 M H₂SO₄) using a Bio-Logic model VSP potentiostat and a three-electrode configuration (figure S1). A glassy carbon plate and an Ag/AgCl electrode (3.5 M KCl, $E^\circ_{\text{Ag/AgCl}} = 0.205 \text{ V vs. NHE}$) were used as the auxiliary and reference electrodes, respectively. All potentials reported in this paper have been referred to the RHE electrode: $E(\text{V vs. RHE}) = E(\text{V vs. Ref.}) + E(\text{V of Ref. vs. NHE}) + 0.059 \times \text{pH}$. Only the MoS₃ side of the photocathodes was interfaced with the electrolyte using a rubber seal mask with a hole corresponding to the electrochemical area (0.06 cm^2). The glass/ITO side of the photocathodes was illuminated with a 200 W Hg-Xe lamp operated at 106 W coupled with a Spectra-Physics 59472 UV cutoff filter ($\lambda > 440 \text{ nm}$) and a circular mask. Irradiance at the substrate surface was measured to $\sim 100 \text{ mW cm}^{-2}$ thanks to a Coherent PowerMax-USB PM150-50C power sensor.

Linear scan voltammograms (LSV) of ITO/a-MoS_x electrodes have been recorded on 0.196 cm² area.

3 Results and Discussion

We fabricated bilayer and three-layer planar heterojunction (2-PHJ and 3-PHJ) as well as hybrid heterojunction (HHJ) architectures combining bulk and planar heterojunction with boron subphthalocyanine (SubPc) and subnaphthalocyanine (SubNc) chloride as acceptor and alpha-sexithiophene (α -6T) as donor. Such configurations yielded highly efficient solar cells [30] and we first reproduced the fabrication of operational OPV cells. Figure 1 (a, b) shows the chemical structures of the active small organic molecules used in this study as well as the architecture of prepared OPV cells. Phthalocyanines are well-known donor materials for OPV cells and they have been employed to construct several OPV-based photoelectrodes [19, 21, 22]. Sub(na)phthalocyanine derivatives are a class of phthalocyanine-related molecules made of three instead of four diiminoisindoline units arranged around a boron atom. They are characterized by rather unique spectral and electronic features such as nonplanar aromaticity [34, 35]. They have been used as both donor and acceptor materials in OPV devices [35, 36] but not involved in the design of H₂-evolving photocathodes so far. Specifically, OPV cells based on subphthalocyanine or subnaphthalocyanine derivatives as acceptor and α -6T small molecule as donor have been previously described by Cnops et al. [30]. The main reason for their superior performance compared to fullerenes has been assigned to their efficiency to generate and collect charges under 1 sun illumination [30, 37]. Fullerenes indeed display high electron mobility and large exciton diffusion length [38] but their relatively low band gaps and reduced light absorption within the solar spectrum limit the maximum obtainable V_{OC} in devices [39].

Bilayer OPV cell architectures are ITO/PEDOT:PSS/**D**/A/BCP/C₆₀/LiF/Al, where **D** is the electron donor (e. g. α -6T) and **A** is the electron acceptor (e. g. SubPc or SubNc). Three-layer heterojunction and hybrid heterojunction OPV cells include an additional layer between **D** and **A**: SubNc or a blend of α -6T and SubNc was introduced between α -6T and SubPc or α -6T and SubNc, respectively. BCP was used as an exciton-blocking layer, the thickness of which was set to 5 nm. The final layer of the OPV core consists in an interfacial thin layer of C₆₀ fullerene (100 nm). Finally a LiF/Al-based cathode was deposited on the top of the structures. The multilayer cascade energy level diagrams are shown in figure 1c and figure S2, based on data reported in the literature [31, 40, 41].

Figure 2 displays the UV-visible absorption spectra of some OPV cells architectures. Clearly, the inclusion of SubPc and SubNc results in the absorption of a wider part of the solar spectrum as compared to cells only based on α -6T and C₆₀ (figure S3), which only absorb radiations with wavelengths below 550 nm.

Figure 3 shows the current density-voltage (*j*-V) curves measured under solar AM 1.5 G illumination (1 sun) of the prepared OPV cells. Table 1 summarizes the values of open circuit voltage (V_{OC}), short circuit current (J_{SC}), fill factor (FF) and power conversion efficiency (PCE) extracted from the *j*-V curves. The thicknesses of the donor and acceptor layers were optimized to increase PCE for each architecture. PHJ cells are characterized by

high V_{OC} and J_{SC} values, resulting in PCE ranging from 1.38 % to 2.24 %. The HHJ device exhibits a lower PCE of 1.08 % with $V_{OC} = 0.71$ V. These efficiencies are lower than those reported in the literature for similar architectures (PCE ranging from 4 to 8.40 %) [30, 36]. We attributed this effect to the presence of a thicker C_{60} extraction layer. Nevertheless, it was required in the perspective of the construction of a H_2 -evolving photoelectrode directly contacted with aqueous electrolyte, both for stability issues and because it enhances charge transfer towards the electrolyte [25].

We next adapted these cell architectures to transform them into photoelectrodes that can be integrated into a water-splitting cell. To that aim, we did not deposit the LiF/Al anode and deposited a nanoparticulate a-MoS_x material, known to catalyze H_2 evolution from acidic aqueous solutions with onset overpotential as low as 150 mV [27, 28, 33]. Importantly, this noble-metal free H_2 -evolving catalyst can be solution-processed directly onto the OPV-based photoelectrode by spray casting. A schematic representation of the ITO/PEDOT:PSS/D/A/BCP/C₆₀/MoS₃ photocathodes developed in this work and interfaced with a 0.5 M H₂SO₄ aqueous electrolyte is shown in figure 4.

The LSV recorded for the most promising photocathode architecture, ITO/PEDOT:PSS/ α -6T/SubNc/BCP/C₆₀/a-MoS_x, in 0.5 M H₂SO₄ electrolyte under chopped illumination is presented in figure 5. The photocurrent value measured at 0 V vs RHE is 3.6 mA cm⁻² close to the 3.8 mA cm⁻² plateau current and improved compared to maximum current output of the corresponding OPV cell (figure 5a, Table 1). The onset of light-driven H_2 evolution (values were taken at 0.2 mA·cm⁻²) was observed at +0.69 V vs RHE. Dark H_2 evolution (figure 5, purple line) onset determined on a-MoS_x catalyst deposited directly on an ITO electrode was measured at -0.15 V vs RHE, as expected for a-MoS_x under these conditions. We therefore calculate a 0.84 V value for the light-driven anodic shift of the onset potential for hydrogen evolution reaction (HER), or photovoltage V_{photo} . This value is very close to the open-circuit voltage (V_{OC}) of the organic solar cell (0.83 V, Table 1, figure 5b). Other electrode architectures led to the same conclusions as shown in Table 2, which gathers values of current density at 0 V vs RHE and plateau together with onset potential measured for the different electrodes.

To illustrate the role of the C_{60} interfacial layer, figure S4 shows the initial photocurrent obtained for the best photocathode architecture, ITO/PEDOT:PSS/ α -6T/SubNc/BCP/C₆₀/a-MoS_x when the thickness of this layer is varied. Very low photocurrents are observed in the absence of C_{60} or for a 50 nm thickness. Best performances were obtained for 100 nm thick C_{60} layer. A 200 nm thick layer results in lower performances, maybe due to additional electronic resistance of such a thick layer. We note that the thickness of this layer do not significantly alter the performance of the corresponding OPV cell. We therefore conclude that the C_{60} layer both allows optimal electronic transfer between the light-absorbing organic core and the H_2 -evolution catalyst. It also protects the OPV core from the aqueous electrolyte, maintaining its structural and functional properties [25].

Compared to previously reported bilayer PHJ photoelectrodes [19, 22], the constructions reported here display photovoltages approximatively twice higher and plateau photocurrent values almost one order of magnitude higher. The improvement of onset potential for HER is

also significant when compared with the previously reported photoelectrodes based on a polymer P3HT/PCBM core. Table 2 gathers ratiometric power-saved metrics as figure-of-merit adapted to benchmark the performances of photoelectrodes characterized in three electrode configurations (see the Supporting Information for details). The power-saved measurement relative to the RHE, i.e. an ideally non-polarizable dark electrode for the same reaction, $\Phi_{\text{saved,ideal}}$ provides information on the solar energy stored through hydrogen production when the photocathode is operated at its maximum efficiency [32]. Clearly the SubNc-based bilayer PHJ provides a 20 fold improvement of $\Phi_{\text{saved,ideal}}$ as compared to P3HT:PCBM bulk heterojunction, in photocathodes containing the same a-MoS_x catalyst. Besides, the use of oxides (reduced graphene oxide, nickel oxide or molybdenum oxide) as hole-extracting layer alternative to PEDOT:PSS recently proved very efficient to enhance both photocurrent and stability of BHJ-based photocathodes [23, 42]. However, this strategy has not been successful in the case of the PHJ and HHJ architectures investigated in this work.

Figures 6 and figure S5 show the time profile of the photocurrent measured at an applied potential of 0 V vs. RHE for all four photocathodes developed in this work. As expected for the voltammograms (figure 5a), the ITO/PEDOT:PSS/ α -6T/SubNc/BCP/C₆₀/a-MoS_x photocathode develops a significantly higher photocurrent (around 3.5 mA·cm⁻²) comparing to *ca* 2.5 mA·cm⁻² for ITO/PEDOT:PSS/ α -6T/ α -6T:SubNc/SubNc/BCP/C₆₀/a-MoS_x or *ca* 1 mA·cm⁻² for ITO/PEDOT:PSS/ α -6T/SubPc/BCP/C₆₀/a-MoS_x and ITO/PEDOT:PSS/ α -6T/SubNc/SubPc/BCP/C₆₀/a-MoS_x. The best performing photoelectrode also proves the most stable as shown in figure 7. In this case, a loss of 30 % of the photocurrent is observed after 5 min, while the other photocathodes lose up to 90 % (α -6T/ α -6T:SubNc/SubNc/-based photocathode) of their performance under similar conditions. Such results highlight the potential of SubNc for promoting efficient photoelectrocatalysis in small molecule OPV-based photocathode architectures. The photocurrent value of the α -6T/SubNc-based photocathode over 30 min is indeed still noteworthy (*ca* 0.5 mA·cm⁻²). We note that the decrease in photocurrent value is not accompanied with a decrease in the onset potential for light-driven H₂ evolution (figure 5b). We therefore conclude that the light-active core is left intact. As a-MoS_x is also stable under such conditions, we assign the decrease in photocurrent to a degradation of the charge extracting C₆₀ layer, possibly due to water diffusion in this interfacial layer or C₆₀ degradation following reduction to the dianion state [19]. Future work will address the long term stability of such OPV-based photoelectrodes.

4 Conclusions

We have demonstrated the relevance of bilayer planar heterojunction for the construction of H₂-evolving photoelectrodes containing noble metal-free catalyst. SubNc proved a very promising component in that perspective. It absorbs a part of the solar spectrum complementary to α -6T, thus generating large photocurrents and provides a record onset potential for light driven H₂ evolution. The latter reaction was mediated in acidic aqueous solution by a-MoS_x. Importantly, all components of this photocathode can be potentially solution processed, which is another asset for large scale deployment of such a technology. The thickness of the fullerene C₆₀ layer plays a critical role on the efficiency of the photocathode. The stability nevertheless needs to be improved before envisaging practical

applications. Further research will aim at finding novel formulations allowing more durable activity.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

OPV cell architectures: (a) Molecular structures of the active components; (b) Schematic representation of the device architectures; (c) Schematic energy level diagram of 2-PHJ cell based on α -6T/SubNc or α -6T/SubPc active layers (see figure S2 for the energy diagrams of other cell architectures).

Figure 2. UV-Vis absorption spectra of the active units in OPV cells: α -6T/SubNc, α -6T/SubPc, α -6T/SubNc/SubPc.

Figure 3. Current density vs. voltage (j -V) characteristics of OPV cells under 1 sun AM 1.5 G simulated illumination.

Figure 4. Schematic representation of the ITO/PEDOT:PSS/D/A/BCP/C₆₀/a-MoS_x photocathode architecture.

Figure 5.

LSVs recorded at 50 mV·s⁻¹ in H₂SO₄ 0.5 M electrolyte with chopped visible light for ITO/PEDOT:PSS/ α -6T/SubNc/BCP/C₆₀/a-MoS_x: (a) 1st measure, (b) following sweeps. The polarization curve of a-MoS_x recorded at 5 mV·s⁻¹ is shown for comparison (purple curve)).

Figure 6.

Chronoamperometry measurements for the ITO/PEDOT:PSS/ α -6T/SubNc/BCP/C₆₀/a-MoS_x photocathode at 0 V vs. RHE in 0.5 M H₂SO₄ electrolyte with chopped visible light.

Figure 7. Photoelectrocatalytic performances of ITO/PEDOT:PSS/**D/A**/BCP/C₆₀/a-MoS_x photocathodes measured initially and after 300 s.

Table 1

Parameters and performance characteristics for the reported OPV cells architectures

Architecture	Structure	Donor (nm)	Acceptor (nm)	V _{OC} (V)	J _{SC} (mA·cm ⁻²)	FF (%)	PCE (%)
2-PHJ	α-6T/SubPc	60	15	0.93	3.06	57.6	1.64
2-PHJ	α-6T/SubNc	50	20	0.83	3.19	52.2	1.38
3-PHJ	α-6T/SubNc/SubPc	50	20/10	0.91	4.35	56.7	2.24
HHJ	α-6T/α-6T:SubNc/SubNc	20	10	0.71	3.36	45.0	1.08

Table 2Efficiencies in a three-electrode configuration for the different photocathodes ^{*}

Architecture	OPV-core structure	$V_{\text{onset HER}}$ (V)	$J_{0V \text{ vs RHE}}$ (mA·cm ⁻²)	J_{plateau} (mA·cm ⁻²)	$\Phi_{\text{saved, ideal}}$ (%)
2-PHJ	α -6T/SubNc	0.69	3.6	3.8	0.118
3-PHJ	α -6T/SubNc/SubPc	0.70	1.4	1.5	0.027
HHJ	α -6T/ α -6T:SubNc/SubNc	0.68	2.4	2.6	0.087

* see details in Supporting Information