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Hematite photoanode co-functionalized with self-assembling melanin and C-phycocyanin for solar water splitting at neutral pH

Krisztina Schrantz[a,b], Pradeep P. Wyss[a,c], Julian Ihssen[d], Rita Toth[a], Debajeet K. Bora[a,e], Elina A. Vitol[f,g], Elena A. Rozhkova[g], Uwe Pieles[c], Linda Thöny-Meyer[d], Artur Braun[a,h,*]

[a] *Empa, Swiss Federal Laboratories for Materials Science and Technology Laboratory for High Performance Ceramics, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland*
[b] *University of Szeged, Department of Inorganic and Analytical Chemistry, Dóm tér 7, H-6720 Szeged, Hungary*
[c] *FHNW – University of Applied Sciences Northwestern Switzerland, School of Life Sciences and Institute for Chemistry and Bioanalytics, Grüdenstrasse 40, CH-4132 Muttenz, Switzerland*
[d] *Empa – Swiss Federal Laboratories for Materials Science and Technology Laboratory for Biomaterials, Lerchenfeldstrasse 5, CH-9014, St. Gallen, Switzerland*
[e] *Laboratory of Energy Science and Engineering, ETH Zürich, Leonhardstrasse 21, CH-8092 Zürich, Switzerland*
[f] *Materials Science Division, Argonne National Laboratory, 9700 South Cass Ave, Argonne, IL 60439, USA*
[g] *Nanophotonics and Biofunctional Structures, Center for Nanoscale Materials, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL, 60439, USA*
[h] *Hawaii Natural Energy Institute, School of Ocean and Earth Science and Technology University of Hawaii at Manoa, 1680 East-West Rd, Honolulu, HI 96822, USA*

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ABSTRACT

Nature provides functional units which can be integrated in inorganic solar cell materials, such as light harvesting antenna proteins and photosynthetic molecular machineries, and thus help in advancing artificial photosynthesis. Their integration needs to address mechanical adhesion, light capture, charge transfer and corrosion resistance. We showed recently how enzymatic polymerization of melanin can immobilize the cyanobacterial light harvesting protein C-phycocyanin on the surface of hematite, a prospective metal oxide photoanode for solar hydrogen production by water splitting in photoelectrochemical cells. After the optimization of the functionalization procedure, in this work we show reproducible hydrogen production, measured parallel to the photocurrent on this bio-hybrid electrode in benign neutral pH phosphate. Over 90% increase compared to the photocurrent of the pristine hematite could be achieved. The hydrogen evolution was monitored during the photoelectrochemical measurement in an improved photoelectrochemical cell. The C-phycocyanin-melanin coating on the hematite was shown to exhibit a comb-like fractal pattern. Raman spectroscopy supported the presence of the protein on the hematite anode surface. The stability of the protein coating is demonstrated during the 2 h GC measurement and the 24 h *operando* current density measurement.

1. Introduction

The use of solar energy to satisfy the increasing energy demand has been pointed out by Ciamician more than 100 years ago [14]. About 4 decades after the pioneering photoelectrochemical water splitting on titanium oxide by Honda and Fujishima [24], photoelectrochemistry for solar hydrogen production in photoelectrochemical (PEC) cells is a resurging field [24,45,46]. Hematite (α-Fe_2O_3) satisfies many requirements for a good photocatalyst and is thus a prospective photoanode material for PEC water splitting [6,32]. Interestingly, the actual conversion efficiencies for hematite are lower than predicted by theory. The conduction band

* Corresponding author at: Empa – Swiss Federal Laboratories for Materials Science and Technology Laboratory for High Performance Ceramics, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland.
E-mail addresses: sranc@chem.u-szeged.hu (K. Schrantz), pradeep.wyss@makro.uni-freiburg.de (P.P. Wyss), Julian.ihssen@gmx.net (J. Ihssen), rita.toth@empa.ch (R. Toth), bora.debajeet@mavt.ethz.ch (D.K. Bora), evitol@anl.gov (E.A. Vitol), rozhkova@anl.gov (E.A. Rozhkova), uwe.pieles@fhnw.ch (U. Pieles), Linda.Thoeny@sg.ch (L. Thöny-Meyer), artur.braun@alumni.ethz.ch (A. Braun).

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of hematite is below the electrochemical water reduction potential and therefore needs a small bias voltage in a PEC cell. A high rate of electron-hole recombination due to its short hole diffusion length is believed to be the most probable cause for the low efficiency [38]. Most of the solar photons between 450 and 570 nm are absorbed in hematite via an indirect band transition. These photons have deep penetration and therefore can generate holes beyond the depletion layer; hence they recombine fast with the electrons before they arrive to the surface. The performance of pristine hematite can be improved by increasing the semiconductor – electrolyte interface area via nanostructuring [7,39,46], cation doping [43], or by surface functionalization with proteins [8,9,21,28,39,40] which can enhance electron injection into the conduction band.

Artificial photosynthesis mimics natural photosynthesis, a process that converts sunlight, water, and carbon dioxide into oxygen and carbohydrates. Various approaches [1,3,8,30,34,39,40] have been made to combine semiconductor electrodes with natural light harvesting structures to mimic photosynthesis. The aim is to build a device for converting the energy from sunlight into the chemical bonds of a fuel. In the prokaryotic cyanobacteria and eukaryotic red algae, light harvesting is performed by phycobilisomes [26]. Phycobilisome is a light harvesting complex, consisting of a supramolecular complex of phycobiliproteins, which are macromolecular protein complexes like phycoerythrin (PE), phycocyanin (PC) and allophycocyanin (APC), having different chromophores [10,33]. The chromophore in PC is a linear tetrapyrrole molecule called phycocyanobilin (PCB), absorbing between 590–640 nm, when assembled in proteins [5]. An absorbed photon can initiate electron excitation and transfer. The energy is funneled to the reaction center and converted into chemical energy in photosystem II [17,25,47].

We have recently optimized a method using enzymatic polymerization of melanin to functionalize the hematite photoanode with a stable protein layer [21]. Tyrosinase oxidizes L-tyrosine and other mono-phenols to a reactive quinone species at the expense of molecular oxygen [22]. In the case of L-tyrosine the reaction product L-DOPA quinone spontaneously polymerizes and forms melanin [23]. This black pigment is a light-excitable organic semiconductor [11] that absorbs over the entire visible solar spectrum. The basic idea of using tyrosinase-catalyzed melanin formation in presence of PC, is to integrate PC in the polymer structure of melanin, to have a mechanically and biologically stable protein coating on the hematite. Beside the light harvesting properties of PC, the water splitting performance of the bio-functionalized hematite could be maintained or even be enhanced due to the semiconducting properties of melanin itself [11].

Energy generating hybrid systems were already described in the literature. The Bacteriorhodopsin/TiO_2 nanotube arrays hybrid system shows 50% enhancement in the photocurrent density compared to the bare TiO_2 [1,48,49]. A Chlorosome assisted TiO_2 columnar film-based biomimetic light harvesting device has also been developed. 30 fold enhancement in the photocurrent density was observed in the wavelength region from 640 nm to the near infra-red [37], however the reported photocurrent does not reach 40 μA.

The hybrid system discussed in the present work shows substantially better photoelectrochemical performance than the pristine hematite film and additionally does not depend on the extra Nernst potential from a strongly alkaline electrolyte. This novel method allows for operation of the PEC photoanode at neutral pH while at the same time increasing the photocurrent to even higher values than with direct non-enzymatic C-phycocyanine functionalization [8]. The improved PEC cell allowed stable and reproducible photoelectrochemical hydrogen generation.

2. Materials and methods

2.1. Materials

Iron nitrate nonahydrate (≥98%), tetrahydrofuran (THF, ≥99.9%), 1,4-dioxane (99.8%), 1,1′-carbonyldiimidazol (CDI, ≥97%), NaCl (5 mol L^{-1}), H_2KPO_4 (1 mol L^{-1}), HK_2PO_4 (1 mol L^{-1}), KOH (95%), 2,2′-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS, ≥98%) and C-phycocyanin (PC, 99.9%) isolated from *Spirulina* sp. were purchased from Sigma-Aldrich and were used without further purification. Oleic acid (≥60%) and L(+)-tartaric acid (≥ 99.5%) were Fluka products. Tyrosinase was produced with recombinant *E. coli*. [22,41].

2.2. Precursor synthesis and hematite film deposition

Hematite films were prepared as described previously [7]. FTO glass slides (12 × 30 × 2 mm, TEC-8 from Hartford Glass Inc.) were dip coated in the precursor solution (DipMaster™-50, Chemat Technology Inc., USA). The precursor solution was removed from the back of the glass with THF-soaked wipe and dried at 75 °C for 5 min on a hot plate. The samples were then further annealed for 30 min at 500 °C. Dip coating and annealing were repeated three more times to obtain four layers of hematite with 510 ± 65 nm film thickness.

2.3. Protein immobilization

For the covalent attachment of proteins to the photoanode, the pristine hematite film was first conditioned with agarose and then activated with CDI, as described previously [8]. This conjugate [4] can either react directly with the primary amine groups of PC, or indirectly, by the enzymatic polymerization of L-tyrosine with tyrosinase, subsequently forming melanin. These activated electrodes were then treated in two different ways to obtain a melanin (A) and a melanin-PC (B) coated surface. We have used an optimized procedure described previously [21]. The reaction steps are illustrated in Fig. 1.

A: Melanin synthesis with tyrosinase from L-tyrosine

0.1 mg mL^{-1} L-tyrosine solution in PBS was prepared. 5 μL of the tyrosinase stock solution (10 mg mL^{-1} in 10 mM Tris HCl pH 8.0) was added to 1 mL L-tyrosine. The activated hematite surface was covered with 200 μL of this mixture for 3 h. The electrodes were then rinsed with phosphate buffer saline (PBS) and with distilled water to remove any potentially unbound polymer and excess reactants.

B: Enzymatic cross linking of PC with tyrosinase in presence of L-tyrosine

1 mg PC was added to 5 mL 0.1 mg mL^{-1} L-tyrosine PBS solution. 5 μL of the tyrosinase stock solution (10 mg mL^{-1}) was then added to 1 mL tyrosine-PC solution. The *activated* hematite surface was covered with 200 μL of this mixture and incubated for 3 h at room temperature. The electrodes were then washed as described above.

2.4. Photoelectrochemical measurements

For the photoelectrochemical assessment of the photoanode, we followed the recommendations provided in [12], when not otherwise stated. Linear voltammetry was conducted in dark and under illumination using a specifically designed photoelectrochemical cell made of polyether ether ketone (PEEK) and Plexiglas (Fig. 2), and a potentiostat (*Voltalab80 PGZ 402*). The hematite photoanode was connected in a three electrode configuration as the working electrode. A platinum plate was set as counter electrode and an Ag/AgCl (with sat. KCl) electrode was used as a reference electrode. The electrodes were immersed in 1 mol L^{-1} KOH (pH 14)

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