Functionalized Hematite Photoelectrode for Solar Water Splitting

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Abstract
We show how the enzymatic polymerization of tyrosine with tyrosinase can be exploited for the immobilization of the light harvesting protein C-phycocyanin on the surface of hematite. This results in the in situ formation of the organic semiconductor melanin which stabilizes the protein strains on the semiconductor surface and increases the photocurrent by a factor of two in environmentally benign conditions. The PC-melanin coating on the hematite exhibits a self-similar, comb-like fractal pattern, pointing to the possibility to control the orientation of the chromophore for optimal light harvesting. Operating this bio-hybrid photoelectrochemical cell in environmentally benign environment could extend its lifetime compared with those used in strongly alkaline electrolyte and enhance the acceptance of the PEC cells in the society.

Introduction
The use of solar energy to satisfy the increasing energy demand has been pointed out by Ciamician about 100 years ago [1]. Yet, 40 years after the pioneering photoelectrochemical water splitting on titanium oxide by Honda and Fujishima (1972), high conversion efficiencies in photoelectrochemical (PEC) cells are missing [2,3]. Hematite (α-Fe_2O_3) satisfies many requirements for a good photocatalyst and is thus a prospective photoanode material for PEC water splitting [4]. However, the conduction band of hematite is below the electrochemical water reduction potential and therefore needs a small bias voltage in a PEC cell. Its short hole diffusion length is believed to be the most probable cause for the low efficiency [5]. The performance of pristine hematite can be improved by increasing the semiconductor - electrolyte interface area via nanostructuring [6], cation doping [7], or by surface functionalization with proteins [11], which can enhance electron injection into the conduction band.
Artificial photosynthesis mimics the natural photosynthesis, a process that converts sunlight, water, and carbon dioxide into oxygen and carbohydrates. Various approaches [8-10] have been made to combine semiconductor electrodes with natural light harvesting motifs to mimic photosynthesis. The aim is to build a device for converting the energy from sunlight in the chemical bonds of a fuel. In the prokaryotic cyanobacteria and eukaryotic red algae, light

harvesting is performed by phycobiliproteins [11]. The phycobilisomes are the macromolecular complexes of these proteins [12] and act as light absorbing antennas. Their main components are phycoerythrin (PE), phycocyanin (PC) and allophycocyanin (APC), having different chromophores. The chromophore in PC is a linear tetrapyrrole called phycocyanobilin (PCB), absorbing between 590 - 610 nm [13]. 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 [14,15].

We present here a stable protein functionalized hematite photoanode assembly synthetized by enzymatic polymerization of melanin. The basic idea behind tyrosinase-catalyzed melanin formation in the context of PEC is on one hand, to integrate PC in a polymer structure of melanin, so as to have a mechanically and biologically stable protein coating on hematite. On the other hand, due to the semiconducting properties of melanin itself [16], to maintain or enhance the water splitting performance of the bio-functionalized hematite.

Experimental

Precursor synthesis and hematite film deposition. An FTO glass slide (12 x 30 x 2 mm, TEC-8 from Hartford Glass Inc.) was dip coated with the precursor [6] using DipMaster^{TM}-50 (Chemat Technology Inc., USA) and annealed for 30 min at 500°C. Dip coating and annealing were repeated three more times to obtain four layers of hematite with approximate 550 micrometer film thickness.

Electrochemical measurements. Linear voltammetry [17] in dark and under illumination was conducted using a photoelectrochemical cell and a potentiostat *(Voltalab80 PGZ 402).* The hematite film sample was connected as the working electrode in a three electrode configuration. A platinum plate was set as counter electrode and an Ag/AgCl (with sat. KCl) electrode was used as the reference electrode. The electrodes were immersed in 1 mol L^{-1} KOH (pH 14) or PBS, 0.05 mol L^{-1} sodium phosphate, 0.15 mol L^{-1} NaCl, pH 7.2), respectively. Simulated sunlight was provided by a *1 Sun Oriel Lamp* from *L.O.T. – Oriel AG*, corresponding to AM 1.5 global standard solar spectrum. The applied bias potential was 600 mV and 1000 mV in case of KOH and PBS electrolytes, respectively.

Gas chromatography. GC-2014 (Shimadzu) with TCD detector and Hayesep D 10' column was used to measure H_2 . Temperatures of the injector, column and detector were 60, 38 and 140 ˚C, respectively. The generated H_2 was recirculated with Ar carrier gas using a pump at 0.1 bar overpressure, enabling the online monitoring of H_2 evolution. 10 µL samples of the headspace were injected after selected reaction times. The evolved H_2 was quantified based on calibration with 50, 100 and 500 ppm standard H_2 in Ar.

Protein immobilization. For the cross-linking of proteins with the photoanode, the pristine hematite film was first conditioned with agarose and then activated with 1,1-carbonyldiimidazol (CDI) [8]. This conjugate [18] can react directly with primary amine groups on the surface of PC, or indirectly, involving enzymatic reactions such as with the subsequently formed melanin. These activated electrodes were then treated in two different ways to obtain melanin (A) and melanin-PC (B) coated surfaces.

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}) was added to 1 mL L-tyrosine solution. The activated hematite surface was covered with 200 µL of this solution for 1h.
B: Enzymatic cross linking of PC with tyrosinase in presence of L-tyrosine
0.1 mg mL^{-1} L-tyrosine solution in PBS was prepared. 1 mg PC was added to 5 mL of this L-tyrosine solution. 5 µL of the tyrosinase stock solution (10 mg mL^{-1}) was added to 1 mL L-tyrosine-PC solution. The activated hematite surface was covered with 200 µL of this solution and incubated for 1h at room temperature.

Results and discussion
Pristine hematite films are built from nanoparticles with average size of 50 nm and have a highly porous morphology. X-ray diffraction on the pristine film showed the typical Bragg reflections for hematite, the (104) and the (110). The photocurrent densities of the hematite electrodes for every level of processing in alkaline and neutral electrolytes are compared in Figure 1. The photocurrent density of the pristine hematite was 275 µA cm^{-2} at 500 mV in the standard 1 mol L^{-1} KOH electrolyte (Fig. 1, left panel), and 160 µA cm^{-2} at 900 mV in 0.05 mol L^{-1} phosphate buffer solution (PBS) (Fig. 1, right panel). Coating the pristine hematite with melanin only yields a slightly increased photocurrent of 300 µA cm^{-2} in KOH, whereas in PBS the photocurrent is slightly decreased to 140 µA cm^{-2}. In alkaline electrolyte the photocurrent density of the hematite further functionalized with both melanin and PC differs not significantly from the only melanin coated and pristine hematite. However, in PBS, the melanin-PC functionalized hematite yields a photocurrent density of 450 µA cm^{-2}. This is more than double enhancement compared to the pristine electrode in PBS, and still a 50% enhancement when compared to the electrode measured in strongly alkaline standard electrolyte.

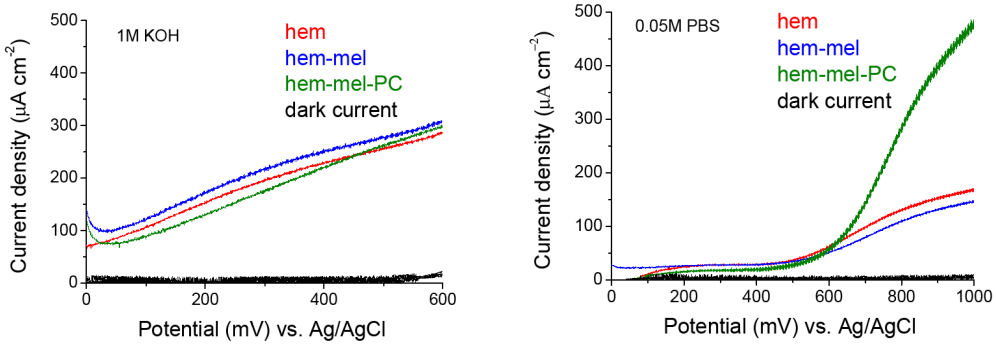

Figure 1. Current density of the pristine hematite (—), melanin coated hematite (—) and melanin-PC coated hematite films (—) recorded in 1 mol L^{-1} KOH (left panel) and 0.05 mol L^{-1} PBS (right panel). The black curves show the dark current density.

The striking difference in the photocurrent density for the differently functionalized films is paralleled by the evolution of H_2 as monitored with gas chromatography (GC). After 20 min of chronoamperometry the calculated H_2 concentration produced by the PC-melanin coated hematite was about tree times more than produced on the pristine hematite. This corresponded to the aforementioned photocurrent density enhancement.

Note that the photoanode in fact evolves O_2 from water splitting, whereas the H_2 is evolved at the counter electrode.

We have shown recently that the combination of adsorption and cross linking of PC to hematite photoanodes results in a doubling of the photocurrent density in 1 mol L^{-1} KOH electrolyte [8]. There, the chromophores remain active even in strongly alkaline conditions as high as pH ~ 14, when attached to a hematite support. This situation cannot be the case in the present work because melanin can be dissolved in KOH [10], hence it could likely cause disintegration of the protein network. Even when the chromophores remain intact in the alkaline electrolyte, the dissolution of the melanin disrupts the attachment of the PC to the hematite. Consequently, charge transfer between PC and hematite is not warranted anymore. However, when we chose PBS as electrolyte, enzymatic melanin-PC coating allowed for an enhancement in photocurrent density by a factor of almost 3. Equal important to the increase of the photocurrent density is that this hybrid photoanode works in pH neutral electrolyte. This shows that water splitting devices can be fabricated and used also in a protein friendly, and thus in a generally more benign environment [19]. For the acceptance of a solar energy conversion system in public areas, environmentally benign components, i.e. phosphate buffer rather than concentrated KOH, are more likely to be accepted.

The electron micrographs in Figure 2 provide a visual impression of the morphology of the melanin-PC coated (right panel) and melanin coated (left panel) hematite surface. Most interesting, the organic layer from melanin and PC has arranged in a regular, self-similar pattern with a comb-like architecture on the hematite. The comb branches are aggregates from globular primary particles of around 200 nm diameter. The aggregate branches range from 500 nm to 5 µm in length. The reason behind the high structural organization could be due to the PC-melanin polymer assembly.

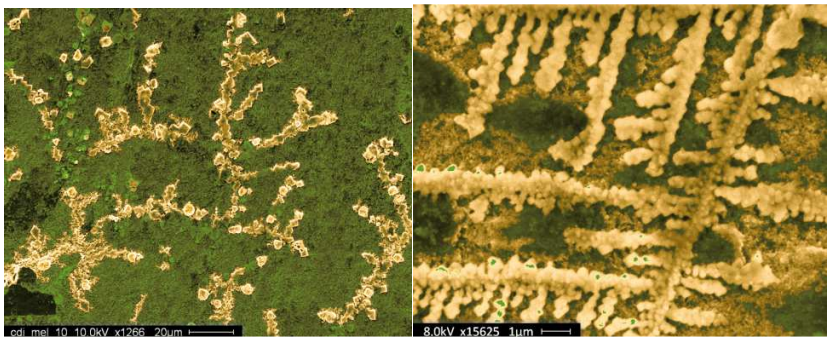

Figure 2. SEM micrographs of PC-melanin (left panel) and melanin-only (right panel) coated hematite films surfaces with 2 different magnifications.

Hematite films functionalized with only melanin are shown in left panel of Figure 2. Melanin chain organizes in a different pattern when PC is not present, in contrast to hematite co-functionalized with melanin and PC. In particular, melanin arranges in more random bow-like branches, where the branches consist of chain of nanoparticles similar in morphology obtained by earlier study [20]. Highly organized structures formed only in the presence of PC, and may

potentially be responsible for the high increase of the photocurrent due to optimized orientation of the chromophores [21,22].

Conclusion

In this work we show how enzymatic formation of melanin can immobilize the cyanobacterial light harvesting protein PC on the surface of hematite and in this way enhance the efficiency of the photoanode. Upon addition of tyrosinase to a PC-L-tyrosine mixture on hematite surfaces, a melanin-PC network is formed which is cross-linked to the hematite, causing an increase in photoelectrochemical performance by a factor of two. Melanin-PC coating shows a fractal structure which might contribute to the observed photoelectrochemical efficiency. At this point it remains open whether this fractal structure is functional or coincidental. Enhanced H_2 production rates were observed for lab-scale PEC cell with melanin-PC coated hematite photoanode. A technological and societal benefit of the demonstrated system is its operability under benign conditions at neutral pH.

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