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Hematite-based photoelectrode for solar water splitting with very high photovoltage

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ABSTRACT

Hematite photoelectrode is a promising candidate for photoelectrochemical (PEC) water splitting. However, the high density of surface defects and slow kinetics for oxygen evolution have restricted the PEC performance of hematite photoelectrodes, mainly their low photovoltage. This study provides the hematite surface modification combining two strategies, annealing at high temperatures (800 °C) and coating with RuO_2 and IrO_2/RuO_2 co-catalysts. IrO_2/RuO_2-coated hematite thin film exhibited a low turn-on potential of 0.48 V_{RHE} and a final photovoltage of 1.20 V, which is the highest photovoltage reported for hematite-based photoelectrodes. A photocurrent density of *ca.* 1.52 mA cm^{-2} was obtained at 1.23 V_{RHE}, corresponding to *ca.* 140% increase compared to bare hematite; the photocurrent obtained at 0.60 V_{RHE} was 0.34 mA cm^{-2}, the highest value ever reported. The IrO_2/RuO_2-coated hematite photoelectrode showed a quite stable performance at 0.80 V_{RHE} for over 72 h. The water oxidation efficiency was therefore enhanced with values above 90% for potentials higher than 1.00 V_{RHE} due to faster charge transfer and reduced electron-hole recombination at its surface.
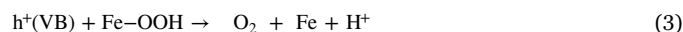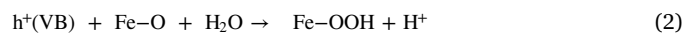
1. Introduction

Hematite presents several favorable characteristics that turn this material very attractive for solar-driven water splitting, namely a 2.1 eV bandgap, appropriate valence band position towards water oxidation, excellent chemical stability, abundance and low-cost [1,2]. However, hematite conduction band is more positive than hydrogen evolution reaction and so its integration in a tandem PEC device with a photocathode or a photovoltaic cell can solve this mismatch [3]. Despite these encouraging characteristics, the highest solar-to-hydrogen (STH) efficiency achieved so far is 3.1% [4], though STH efficiencies lower than 1% are more typically reported using hematite photoanodes [3].

The overall STH efficiency is mainly controlled by the efficiency of three general processes: i) light harvesting/charge separation − η_{light}; ii) charge transport/recombination within the semiconductor − η_{ct}, *i.e.* fraction of valence band holes that reach the semiconductor/electrolyte interface and conduction band electrons reaching the back contact; and iii) hole collection at electrode surface − η_{hc}, *i.e.* fraction of surface holes that oxidize water subtracted from the ones that recombine at the surface [5]. In an ideal hematite photoanode, the plateau photocurrent is the maximum photocurrent in the optical limit (J_{max} = 12 mA cm^{-2}) and the onset potential (E_{onset}) equals the flatband potential (E_{fb} is normally between 0.40 and 0.60 V_{RHE}); the photocurrent should reach

J_{max} within 0.10 V from E_{onset} [6]. State-of-the-art nanostructured hematite photoanodes show J_{max} = 5.70 mA cm^{-2} at 1.23 V_{RHE} and E_{onset} of *ca.* 0.70 V_{RHE} [7]; however, the potential for reaching the maximum photocurrent density is very high for practical PEC devices. The photovoltage of hematite photoelectrodes is usually much lower than the theoretical maximum (typically smaller than 0.40 eV) [6], which is, therefore, one of the main performance-limiting factors.

The photoelectrochemical activity of hematite is limited by its small light absorption (light absorption depth of hundred nanometers) and a very short minority carrier lifetime and mobility; both combined hinder efficient carrier separation and transport (decrease of η_{light} and η_{ct}) [3]. Bulk modifications, *e.g.* by doping [8], nanostructuring [9] or surface modification [10], have shown to be effective in alleviating this problem. In addition, the oxygen evolution reaction (OER) kinetics is reported to be sluggish, increasing the recombination of the surface holes with conduction band electrons that competes with the forward water oxidation efficiency (low η_{hc}) [11]. The water oxidation mechanism on hematite surface is currently subject of intense investigation; Young et al. [12] proposed the following reaction scheme:

$$h^+(VB) + Fe−OH → Fe−O + H^+ \tag{1}$$

$$h^+(VB) + Fe−O + H_2O → Fe−OOH + H^+ \tag{2}$$

$$h^+(VB) + Fe−OOH → O_2 + Fe + H^+ \tag{3}$$

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$$h^+(VB) + Fe + H_2O \rightarrow Fe-OH + H^+ \tag{4}$$
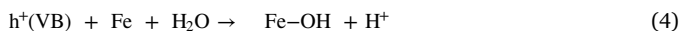
The OER involves four holes for each O_2 molecule produced and the formation of reaction intermediates, such as Fe-O and Fe-OOH. This is consistent with the hypothesis that the OER occurs *via* the holes trapping at Fe species on the electrode surface and then the transport of these holes to the electrolyte (rate limiting step) [6,12]. These states are often referred as surface states; the recombination at surface states of hematite is the process mostly contributing to the large potential necessary to oxidize water [5]. When a high anodic potential is applied to hematite, the holes are transferred to electrolyte with an efficiency, η_{hc}, close to unity [6]. Understanding the loss mechanisms at the hematite surface is critical to solve the highly anodic electrochemical potential required to initiate the OER and then the improvement of photovoltage and photocurrent.

The recent advances using hematite photoanodes for PEC water splitting are then focused on lowering the high onset potential for the OER by hematite surface treatment, since the semiconductor/electrolyte interface has proven to strongly influence the charge separation/recombination, the catalytic activity and also the stability of the photoelectrode [6]. Several strategies have been investigated in the field, such as: introducing underlayers and/or overlayers [13], using semiconducting heterojunctions [14], using co-catalysts [10], optimizing the post-fabrication annealing conditions [15], *etc*.

In the present study, high-temperature annealing of the hematite film combined with an efficient and stable OER co-catalyst coating was envisaged to decrease the turn-on potential for water oxidation, aiming at improving charge transfer and minimizing the surface state recombination. The shift of the onset potential towards negative potentials upon surface modification has been attributed to the mitigation of Fermi level pinning at the hematite/electrolyte interface [16]. The annealing of hematite thin films at 800 °C was found to minimize the recombination phenomena at hematite surface, but it also promotes the diffusion of Sn atoms from the FTO (fluorine-doped tin oxide) layer into the hematite lattice, enhancing the PEC properties of the hematite [17]. On the other hand, an ideal co-catalyst would minimize the unfavorable energetic relation between intermediate species of the water oxidation mechanism [18]. To date, many co-catalysts were studied for hematite photoelectrodes such as CoO_x [19], Co-Pi [20], IrO_2 [21], $NiFeO_x$ [22] and $Ni(OH)_2$ [23]. RuO_2 is an exceptional co-catalyst to accelerate the OER kinetics, since it has proved to be the material presenting the highest catalytic activity among the single-transition metal oxides, followed by RhO_2, IrO_2 and PtO_2 [18,24]. While RuO_2 has already been used as an OER co-catalyst for overall water splitting on $Ga_{1-x}Zn_xN_{1-x}O_x$ [25] and for the HER on Cu_2O [26,27] displaying high performances, its performance as co-catalyst on hematite photoelectrodes for the OER was not yet thoroughly investigated [6]. Majumder and khan [28] reported an onset potential shift of *ca.* 120 mV using hematite coated with RuO_2 co-catalyst; more recently, the integration of hematite with molecular Ru catalyst were tested by Chen et al. [29] showing an onset potential shift of *ca.* 300 mV and by Fan et al. [30] showing an improved photocurrent though with a rather poor stability – *ca.* 3 h in a KOH solution. RuO_2 stability of in alkaline solutions, however, is an issue for OER on hematite films. Mixed oxide layers of ruthenium and iridium are state-of-the-art catalyst materials for the chlorine evolution in chlor-alkali and chlorate processes [31] and for OER in polymer electrolyte membrane fuel cells (PEMFC) [32]; these systems benefit from the very good catalytic activity of RuO_2 and the high electrochemical stability supplied by IrO_2 [18]. Therefore, in this work it was applied very thin layers of IrO_2/RuO_2 co-catalysts in a thermally treated hematite thin film; to the best knowledge of the authors there are no published results using IrO_2/RuO_2 metal oxides as co-catalysts for enhancing the performance of hematite photoelectrodes. This new photoelectrode proved to be stable in an alkaline electrolyte displaying an onset potential of *ca.* 0.48 V_{RHE} and a photocurrent of 1.52 mA cm^{-2} at 1.23 V_{RHE}. Complementarily, the effect of the co-catalysts was studied by electrochemical impedance spectroscopy to improve the fundamental understanding of the water oxidation mechanism in this new hematite-based photoelectrode.

2. Experimental section

2.1. Hematite photoanodes preparation and co-catalysts deposition

Ultrathin films of hematite were deposited on 1 mm thick, 10 Ω square^{-1} conducting fluorine doped tin oxide (F:SnO$_2$) coated glass substrates (Solaronix, Switzerland) by spray pyrolysis using the in-house assembled setup [2]. The FTO-glasses were adequately cleaned [27] and pretreated with a diluted tetraethyl orthosilicate (TEOS) solution (10% volume in ethanol) [2]. The hematite deposition conditions on TEOS treated FTO-glass substrates were optimized following a design of experiments approach as reported elsewhere [2]. After the hematite deposition, samples were air-annealed for 30 min at 550 °C, before being cooled down to the room temperature. The hematite thin films were then subjected to a high-temperature annealing at 800 °C in air for various periods of time (5 min, 10 min and 20 min); FTO-glass substrates are made of aluminoborosilicate, which only undergo melting above 1000 °C.

RuO_2 co-catalyst was electrodeposited on hematite thin film photoelectrodes using an aqueous solution of 1.3 mM $KRuO_4$; the deposition was made at room temperature and using a platinum wire as counter-electrode. Since the initial pH of the deposition bath strongly influences the rate of RuO_2 electrodeposition [33], a fresh $KRuO_4$ solution was made before each deposition. The range of conditions used for optimizing the galvanostatic electrodeposition were: i) applied current density, in the range of 5−30 μA cm^{-2} and ii) deposition time (5 min, 15 min, 30 min, 1 h, 2 h, 4 h and 8 h). The current densities applied for the catalyst electrodeposition took place at relatively low potentials, insufficient for water oxidation [34].

The IrO_2 coating solution was prepared as described elsewhere [35]. IrO_2 co-catalyst layer was deposited by two successive electrodeposition techniques: pulsed anodic electrodeposition and constant applied current density. Briefly, pulsed electrodeposition consisted in applying 500 cycles of a charge density of 5 mC cm^{-2} during 0.5 s and zero current during 0.5 s for each cycle; the galvanostatic electrodeposition was performed applying a constant charge density of 5 mC cm^{-2} over 500 s. The electrodeposited films were then sintered at 200 °C over 2 h.

2.2. Electrochemical characterization

A PEC cell device known as "cappuccino" was chosen to perform the electrochemical characterization of the prepared hematite photoanodes [2]. The cell was filled with 1 M KOH (pH 13.6) electrolyte aqueous solution and the surface area illuminated was 0.283 cm^2 defined by an internal mask. A standard three-electrode configuration was used: Ag/AgCl/Sat. KCl (Metrohm, Switzerland) as a reference electrode, 99.9% pure platinum wire (Alfa Aesar®, Germany) as counter-electrode.

A ZENNIUM workstation (Zahner Elektrik, Germany) controlled by Thales software package (Thales Z 2.0) was used to perform the current density voltage (*J-V*) characteristic curves, cyclic voltammetry (*CV*) curves, steady state *J-V* curves, stability test and electrochemical impedance measurements. The applied potential bias was reported as a function of the reversible hydrogen electrode (RHE). *J-V* and *CV* measurements were performed at room temperature in dark and under 1-sun simulated sunlight (illuminating from the front-side), at a scan rate of 10 mV s^{-1}. A class B solar simulator equipped with a 150 W Xenon lamp (Oriel, Newport, USA) and an AM 1.5 G filter (100 mW cm^{-2}; Newport, USA) was used; the light beam was calibrated with a c-Si photodiode (Newport, USA). For steady-state measurements, the photocurrent was sampled after stabilizing over