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Photoactivity and scattering behavior of anodically and cathodically deposited hematite photoanodes – a comparison by scanning photoelectrochemical microscopy

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ABSTRACT

Two differently processed nanostructured hematite electrodes were prepared by anodic and cathodic electrodeposition in presence of small organic molecules as structure-directing agents on a divided conductive glass. As the materials were on the same support, all subsequent processing steps were identical. The materials were characterized with respect to light absorption. Raman spectroscopy and X-ray photoelectron spectroscopy were used for structural characterization. The morphology was assessed by scanning electron microscopy. The photoelectrochemical properties of both materials were compared by scanning photoelectrochemical microscopy in one experiment. Besides absorption properties, the scatttering properties of the materials were compared. It is found that the more rough cathodically deposited material exhibited higher light scattering efficiency and thus showed a 4.5 times higher average photocurrent.

1. Introduction

Photoelectrochemical production of hydrogen as fuel or storage vector is one contribution to the decarbonization of the economy [1]. There is an intensive search for new photocatalysts for the water splitting reaction. Due to the high overpotential at the photoanode, the oxygen evolution reaction (OER, eq. (1)) limits the overall efficiency of the conversion, whereas the hydrogen evolution reaction (HER, eq. (2)) is much faster [2].

$$4\ OH^- \rightleftharpoons O_2 + 2\,H_2O + 4\,e^- \qquad (1)$$

$$2\ H_2O + 2\,e^- \rightleftharpoons H_2 + 2\ OH^- \qquad (2)$$

Compounds based on iron oxides have been proposed as one of the prospective materials for photoelectrochemical water splitting of photoanode catalysts because it satisfies most of the stringent requirements for semiconductors utilized in photoelectrochemical (PEC) devices namely chemical stability (in alkaline electrolytes), good visible light absorption properties, suitable valence band edge alignment to perform the water oxidation and low production cost [3,4]. Owing to these promising properties, significant progress has been made regarding methods to improve hematite photoanode performance (nanostructuring, doping, co-catalyst and oxide passivation layers) [5–8], the mechanistic understanding of the water oxidation process [9,10] and charge transport [11,12]. Nevertheless, today the best performing hematite photoanode can deliver only photocurrent densities around 4.5 mA cm^{-2} at 1.23 V vs. RHE at optimized conditions which is considerably lower than the theoretical predictions [13]. Factors limiting the efficiency include short hole diffusion length, large light absorption cross section due to its low absorptivity, and mismatch of the conduction band edge for the water reduction. Most importantly, the water oxidation reaction is inherently sluggish at the hematite interface.

Structural details and methods of preparation are mainly responsible for the enhanced photonic performance reported in the literature over the last years [3], but also lead to strong variations. Although vapor phase synthesis routes yield generally highly crystalline and well controlled hematite films with better performance [3,6], such preparation requires vacuum equipment,

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is expensive and hard to scale up. We, therefore, used two different solution processed films. In order to understand, how the structural details of the resultant films influence the photoactivity, spatially resolved *in-situ* characterization techniques are invaluable.

A localized comparison of photoanode materials would allow the evaluation of the intrinsic homogeneity after preparation. If different materials can be united on one support, even a comparison between different materials is possible. Scanning photoelectrochemical microscopy (SPECM) measures the photocurrent of an macroscopic electrode as a function of the horizontal (x, y) coordinates of a microscopic light source [14]. It is related to laser scanning [15] and scanning optical droplet cell systems [16] as well as microtiter plates filled with photocatalyst that are prepared and tested with a pipet robot [17]. All these methods have been used extensively for combinatorial screening of oxygen evolution catalysts [18,19]. Among those techniques, SPECM offers the particular advantage that it is very fast because no translocation positioning or settling of a droplet cell is required nor is there a need for dissolved compounds to diffuse from the photoelectrode to a microscopic detector electrode as it is the case in the sample-generation-tip-collection mode of scanning electrochemical microscopy (SG/TC SECM) [20]. Furthermore, SG/TC SECM with a microelectrode of 25 μm diameter will change the signal and the response time substantially for distance variations between 100 and 250 μm. SPECM is much less sensitive to such variations of the working distance which are difficult to avoid when working on large samples [21]. Taken together, these advantages render SPECM a suitable technique for exploring local properties of rather large samples which is problematic for other electrochemical scanning techniques because of the prohibitive long measuring times [22]. Here a new concept for substrates for such tests is introduced, by which a conducting glass is subdivided into macroscopic, electrically insulated regions onto which materials can be electrodeposited under different conditions, but processed and characterized afterwards under identical conditions (washing, drying, calcination, activation, SPECM). As the individual regions are large, the technique is suitable to detect local variations in electrochemical performance that might be related to the process conditions and would remain undetected when relying exclusively on integral electrochemical techniques. To demonstrate the working principle and exploit the capacity of the method, nanostructured hematite photoanodes were selected. The hematite photoanodes are prepared by electrochemical deposition because this method offers several attractive features such as simple instrumentation, high flexibility in terms of composition and experimental parameters as well as easy scale-up for fabrication of large area electrodes [23–25]. Recently, it was shown that addition of small organic molecules (e.g. glucoronic acid and coumarin C343) during the electrodeposition of hematite films can tune the structure, improve the mechanical stability of the films and lead to enhanced photoactivity [26]. In the present study, these films are prepared following anodic and cathodic electrodeposition processes and are used as photoanode materials for SPECM investigation.

2. Experimental

2.1. Chemicals

Fluorine-doped tin oxide (FTO) coated glass slides (Sigma-Aldrich Steinheim, Germany) with surface resistivity of $\sim 7\,\Omega$/sq were used as conductive support. The reference sample was purchased from Pilkington Deutschland AG, Weiherhammer, Germany. A platinum wire (Goodfellow, Bad Nauheim, Germany) was used as counter electrode and a reversible hydrogen electrode as a reference electrode. The electrolyte solutions were prepared by dissolving sodium hydroxide 99.0% (Roth, Karlsruhe, Germany) or sodium sulfate p.a. anhydrous 99.0% (Fluka, Steinheim, Germany) in deionized water taken from a Purelab classic UV (Elga, High Wycombe, United Kingdom). Ammonium iron (II) sulfate hexahydrate, sodium acetate, γ-glucuronic acid (GA) were with analytical grade purchased from Sigma-Aldrich and used as received.

2.2. Sample preparation

Patterned FTO slides were obtained by the following process: The area for the two working electrodes was masked by scotch tape (NITTO tape, Osaka, Japan) leaving a gap of ca. 5 mm between them. The exposed area was then treated with a mixture of Zn powder and 1 M HCl to remove the conducting FTO layer. After removing the mask the two conductive regions were separately contacted by a copper wire attached to FTO by silver epoxy glue (type number: 530042, Ferro GmbH, Hanau, Germany) that was sealed by a layer of two-component epoxy glue (R&G Faserverbundwerkstoffe GmbH, Waldenbuch, Germany). The hematite samples were sequentially electrodeposited potentiostatically from the same deposition bath. The deposition was carried out with an AMEL Potentiostat/Galvanostat 7050 interfaced with a computer running under Junior Assist software for Windows, version V3 (AMEL, Milano, Italy). A conventional three-electrode electrochemical cell was used with FTO glass as a working electrode, coiled Pt wire as counter electrode and an Ag/AgCl/$KCl_{sat.}$ (XR300 Radiometer Analytical, Villeurbanne, France) electrode separated by a salt bridge as a reference electrode. The deposition solution consisted of 0.1 M CH_3COONa and 1 mM GA and the solution was bubbled with N_2 for 10–15 min prior to adding 0.02 M $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ and kept at 45 °C to facilitate the deposition. Anodic deposition was performed at 0.4 V vs. Ag/AgCl and the process involves the oxidation of Fe(II) to Fe(III) and subsequent precipitation as hydroxide [27] (hereafter this electrode is denoted as AnD). During the cathodic deposition at −1.2 V vs. Ag/AgCl complete reduction of Fe(II) to Fe (0) resulted in a thin layer of gray Fe film on the electrode (hereafter this electrode is denoted as CaD). The films were rinsed with distilled water and dried in a N_2 stream. The amount of charge was fixed (0.13 C for AnD and 0.16 C for CaD) to obtain the same amount of photoactive material and later cross-checked spectrophotometrically by dissolving specific areas (1 cm^2) of the film in conc. HCl solution. For annealing the films in a tube furnace they were mounted in a quartz tube closed with mineral wool at both sides. The temperature was controlled by a thermostat (JUMO, Fulda, Germany) via a thermocouple (901250/32, JUMO). The samples were annealed in ambient atmosphere with a temperature program first heating them up to 600 °C with a ramp of 2 °C/min and then holding the temperature at 600 °C for 60 min [26].

2.3. Instrumentation

The SPECM setup was developed on the basis of an existing instrument for scanning electrochemical microscopy running with an three-axis positioning system (Maerzhaeuser, Wetzlar, Germany, closed loop for x, and y axes, open loop for z axis) a Jaissle bipotentiostat (PG-10, IPS Elektroniklabor GmbH & Co. KG, Muenster, Germany) and in-house SECMx software [28] (Fig. 1C-E). This setup was expanded by a super continuum laser consisting of a laser source (SuperK Extreme EXB4 4W, NKT Photonics GmbH, Cologne, Germany) with a repetition rate of 78.9 MHz with a pulse width of 10 ps and an integrated pulse picker with a variable dividing factor of 1-40. The light intensity was adjusted via the pulse picker and the wavelength was controlled with a Varia