

Photo-assisted water splitting using Ni-Fe oxyhydroxide-modified mesoporous titania thin films (O-17H)

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1. Introduction

The serious effects of global warming make the transition towards renewable energy sources a crucial step for society. One way to tackle this issue is the production of green hydrogen via water splitting.[1] One major challenge in the development of efficient water splitting devices is the sluggish oxygen evolution reaction (OER), which hinders the overall efficiency. Extensive literature covers the search for efficient OER catalysts. However, conventional methods for improvement of these catalysts are reaching the theoretical limitations. In particular, in alkaline conditions, state-of-the-art catalysts can only reach overpotentials about 0.3 V at 10 mA.cm⁻², a value very close to that given by theoretical volcano plots.[2,3] An interesting way forward is the use of photo-assisted electrocatalysis, where an additional input of solar energy can boost the catalytic performance even further.[4] Here, illumination of a light-absorbing semiconductor leads to photo-generated carriers, which can interact with the electrocatalyst and lower the overpotential.

Titanium dioxide (TiO₂) is a robust semiconductor, largely used in photocatalytic applications due to its high availability and low toxicity. In particular, mesoporous titania thin films (MTTF) have high surface areas, which can be easily tuned or functionalized.[5,6] This makes them a promising semiconductor platform for the integration with electrocatalysts.

Ni-Fe oxyhydroxides (NiFeO_x) are excellent OER electrocatalysts in alkaline conditions.[7] Iron content, i.e., the Ni:Fe ratio, is a critical variable in the response of these catalysts. Even low amounts of iron impurities in KOH electrolyte can cause iron incorporation in the material, drastically improving the activity.[8] Typically, iron content between 10 and 50% achieve the best catalytic activities.

Here, we combined NiFeO_x and MTTF in a nanostructured photoanode aimed at photo-assisted water splitting. Highly ordered thin mesoporous TiO₂ films were prepared via a sol-gel approach and further electrochemically modified by NiFeO_x. The structural and (photo)electrochemical properties of these materials were systematically studied, by changing the Ni:Fe ratio and concentration.

2. Experimental

2.1 Materials synthesis

Mesoporous titania thin films (MTTF) were fabricated onto FTO coated glass substrates by evaporation induced self assembly. Two solutions containing Ti(iPrO)₄, acetylacetonate (acac), HCl, ethanol and water in a 1:1:4:40:14 molar ratio were prepared (A). Pluronic F127 was added as pore template to solution A, in a Ti:F127 1:0.005 molar ratio, to make the solution B for mesoporous layer deposition. A first layer of dense TiO₂ was prepared by spin coating solution A at 8000 rpm, followed by stabilization at 200 °C for 30 min. Afterwards, mesoporous TiO₂ layer was deposited by spin coating solution B at 4000 rpm. Films were stabilized and calcined under air atmosphere at 200 °C for 30 min, 2 h at 350 °C and 30 min at 550 °C, to remove the template and crystallize.

NiFe oxyhydroxides were electrochemically deposited at -0.1 mA.cm⁻² from a 0.1 M total metal content solution containing Ni(NO₃)₂·6H₂O and FeCl₂·H₂O in the corresponding Ni:Fe ratio (0-30% of iron). After deposition, films were rinsed with Milli-Q water.

2.2 Characterization

Surface morphology was determined by Field Emission Scanning Electron Microscopy (FE-SEM, Zeiss Merlin), from CIME-EPFL. AFM images were obtained with a FastScan Bio AFM (Bruker) using FastScan-B tips. X-ray Absorption Spectroscopy (XAFS) measurements were conducted at the XAS beamline at Elettra-Sincrotrone Trieste (Italy).

Electrochemical performance was measured in a custom photoelectrochemical cell and VersaStat potentiostat. The light source was a Newport Oriel lamp (AM 1.5G, 100 mW/cm²). MTTF samples were used as the working electrode, Au wire as the counter electrode and HydroFlex[®] standard hydrogen reference electrode (Gaskatel) was used as the reference electrode. 0.1 M KOH was used as electrolyte. For Fe-free measurements, the KOH electrolyte was purified as described elsewhere.[8] Current densities refer to the geometrical area.

3. Results

3.1 Structural characterization

The synthesized MTTF are optically homogeneous and crack free, with an ordered grid-like structure. MTTF is formed by 50 nm of a dense TiO₂ layer and 75 nm of mesoporous layer. FE-SEM images of NiFeO_x modified MTTF show no significant change in the morphology after 10- and 30-seconds deposition, while flakes of NiFeO_x appear after longer deposition times.

3.2 Electrochemical characterization

Cyclic voltammetry measurements of the modified electrodes in the dark show an anodic current characteristic of OER at potentials above 1.4 V vs RHE, which is not seen in bare MTTF. This dark current is dependent on the catalyst composition (Table 1), with 60 s deposited Ni_{0.9}Fe_{0.1}O_x being the most active sample.

Table 1. Current (mA) obtained at 1.50 V vs RHE for the NiFeO_x modified MTTF. Data extracted from CVs performed at 10 mV/s, in the dark, in 0.1 M Fe-free KOH.

Dep. time (s)	Ni(OH) ₂	Ni _{0.9} Fe _{0.1} O _x	Ni _{0.8} Fe _{0.2} O _x	Ni _{0.7} Fe _{0.3} O _x
10	0.05	0.08	0.08	0.04
30	0.02	0.15	0.09	0.04
60	0.03	0.53	0.31	0.10

3.3 Photo-assisted electrocatalysis

The changes in the current after sample illumination was studied to assess the ability of TiO₂ to photo-assist the electrocatalyst. A plot of the difference between illuminated and dark currents is shown in Fig. 1.

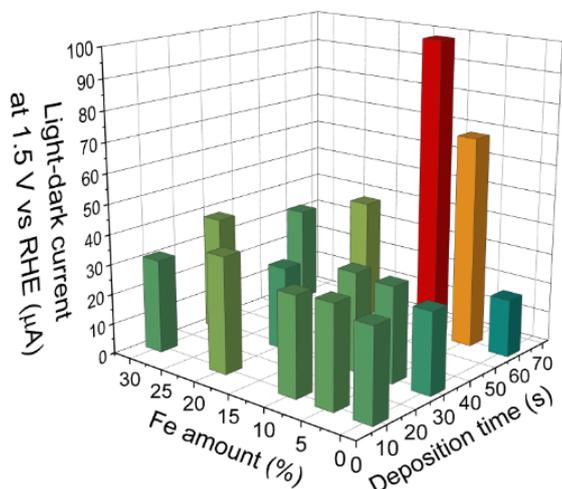


Fig. 1. Difference between illuminated and dark current of the NiFeO_x modified MTTFs at 1.50 V, measured from illuminated and dark CVs. The dependence on the Fe content and deposition time is shown.

4. Discussion

When comparing the difference in the illuminated and dark currents at 1.50 V, the photo-assisted current is very similar to that obtained with bare TiO₂ in most samples (c.a. 40 μA), except for the one modified with Ni_{0.9}Fe_{0.1}O_x, depos-

ited for 60 seconds. In this case, a synergistic effect is observed: the total current is greater than the sum of the dark current and the photocurrent provided by the TiO₂. An enhancement in of ca. 18 % is obtained. Increasing the amount of deposited catalyst further does not raise this enhancement, possibly because of increased resistance, as a thick layer of catalyst forms in this case. These results demonstrate that the amount and composition of the catalyst are critical for evaluation of photo-assisted electrocatalysis.

5. Conclusions

We have developed a promising nanostructured material through a facile and scalable method, composed of mesoporous TiO₂ thin films and Ni-Fe oxyhydroxides, to be used in photo-assisted water splitting. This material shows a synergy between the photo-activity of the TiO₂ substrate and Ni-Fe oxyhydroxide catalytic activity. An increase of 18% in the OER current when illuminated at 1.50 V, after optimizing the Ni:Fe ratio (9:1) and deposition time (60 s). Our findings expand the development of novel composite nanostructures for photo-assisted oxygen evolution.

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