Chimica & Ricerca

THINKING ABOUT 'RUST' NOT ONLY AS A WASTE[*]

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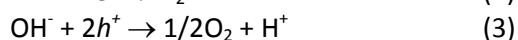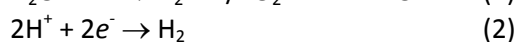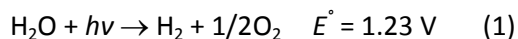*e farmaceutiche*
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Hematite (α-Fe$_2$O$_3$, 'rust') thin films were prepared on FTO glass and then functionalized with an amorphous iron(III) water oxidation catalyst (Fe-OEC). The improved performances of the catalyst modified photoanodes were investigated with Electrochemical Impedance Spectroscopy (EIS), showing an enhanced kinetic of charge transfer from the semiconductor to the solution.

Non sempre la 'ruggine' rappresenta un problema
Nel presente studio sono stati preparati film di ematite (α-Fe$_2$O$_3$, 'ruggine') su FTO funzionalizzati successivamente con un catalizzatore amorfo per l'ossidazione dell'acqua a base di Fe(III) (Fe-OEC). Le migliori prestazioni dei fotoanodi in presenza del catalizzatore sono state indagate mediante Spettroscopia di Impedenza Elettrochimica (EIS), evidenziando una più efficiente cinetica di trasferimento delle buche in soluzione.

In the last 40 years, since the pioneering experiments of Fujishima and Honda[1], solar water splitting using semiconductors has become one of the most challenging goal in the scientific academy. The possibility to convert the solar energy not directly into electricity (photovoltaic cells), that has to be used instantaneously or stored into batteries, but in chemical bonds, represents a more robust and efficient way to exploit the unlimited power of the sun and gives us a needful tool to reduce the dependence of our economy from fossil fuels.

Photoelectrochemical devices (PEC) represent probably the simplest way to achieve the splitting of water molecules into H$_2$ and O$_2$ using solar irradiation (1)[2]. Like for conventional electrolysis, they employ two separate electrodes connected through an external circuit and immersed into an electrolyte solution. At least, one of the two electrodes has to be a photoactive semiconductor which can generate an electron (e^-)/hole (h^+) couple, respectively in the conduction (CB) and in the valence band (VB), after the absorption of a suitable energetic radiation. These carriers have to reach the interface between the electrode and the electrolyte solution and then be transferred to the solution to drive the water reduction (2) (photocathode) or the water oxidation (3) (photoanode) reaction:

$$H_2O + h\nu \rightarrow H_2 + 1/2O_2 \quad E^° = 1.23 \text{ V} \quad (1)$$
$$2H^+ + 2e^- \rightarrow H_2 \quad (2)$$
$$OH^- + 2h^+ \rightarrow 1/2O_2 + H^+ \quad (3)$$

Among various candidates to achieve photoinduced water splitting (e.g. WO$_3$[3,4], and TaON[5]), hematite (α-Fe$_2$O$_3$)[6,7] is one of the most investigated material to realize efficient photoanodes made of very cheap and earth-abundant materials, due to its band gap of ca. 2.2 eV, to the energetic position of its VB with respect to the O$_2$/H$_2$O potential and to its high stability in basic solution under photo-oxidation conditions. Unfortunately, α-Fe$_2$O$_3$ electrodes suffer from very fast electron-hole recombination[8] and slow hole transfer interfacial kinetics[9]. This means that only a few of the photogenerated holes are actually involved in the water oxidation reaction (3), limiting the full exploit of hematite performance[10]. Given that, we planned our work in order to overcome the above mentioned unfavourable features[11].

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We prepared nanocrystalline wormlike hematite thin film on FTO (Fluorine-doped Tin Oxide) according to a simple hydrothermal procedure, based on the hydrolysis of a ionic Fe(III) precursor ($FeCl_3 \cdot 6H_2O$) in the presence of an electrolyte buffer ($NaNO_3$)[12]. This results in the nucleation and growth of an homogeneous layer of iron (III) oxo-hydroxyde nanoparticles on the FTO, that decompose in nanocrystalline hematite after the annealing at 500 °C. A subsequent heat treatment at 800 °C is required to improve the photoanodic response of either hydrothermal or colloidal hematite, probably due to the Sn^{4+} diffusion and doping from the underlying FTO/glass substrate to the hematite layer[13].
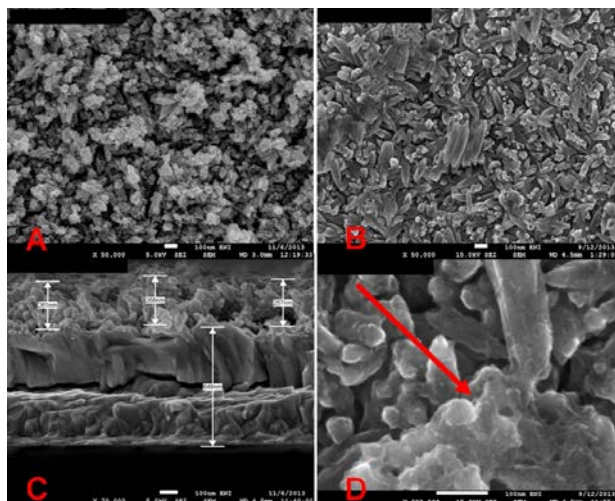

Fig. 1 - SEM images of: hematite thin film surface annealed at (A) 500 °C and (B) 800 °C;
(C) cross sectional view of A; (D) magnified image of hematite thin film functionalized with Fe-OEC

The SEM image of α-Fe_2O_3 thin films annealed at 500 °C (Fig. 1A) shows elongated irregular features (ca. 100x20 nm) partially aggregated in larger conglomerates. The following treatment at 800 °C increases both the size of these agglomerates (ca. 300x50 nm) and the crystallinity of the film (Fig. 1B). The thickness of hematite films is about 250-270 nm, clearly distinguishable from the underlying FTO (Fig. 1C). Nanostructuring and doping are two key strategies to reduce electron-hole recombination for many photoelectrode materials. The improvement of the surface area promotes charge transfer across the semiconductor-liquid-junction (SCLJ), due not only to a more intimate contact between the semiconductor and the solution, but also to the reduction of their charge transport pathways. In addition, the very low electron mobility in hematite can be greatly enhanced adding sufficient levels of atom like Sn^{4+}, Ti^{4+} and Si^{4+} [14,15] that act as electronic dopants.

After the synthesis, we functionalized hematite thin film with an amorphous iron(III) oxygen evolving catalyst (Fe-OEC) through a simple SILAR (Surface Ionic Layer Absorption and Reaction) method[16], consisting in subsequent immersions of the electrode in a $FeCl_3$ solution followed by the dipping in NaOH. This led to the deposition of mixed iron(III) oxide/hydroxide above the nanocrystalline hematite, identifiable from the SEM image as irregular and porous encrustations (Fig. 1D). Surface modification of hematite thin film with either oxygen evolving catalyst[17,18,19,20] or passivating overlayers[21] has been showed to enhance the photo-oxidation performance of the semiconductor both increasing the photocurrent and shifting the photo onset potential to less positive values, probably due to an aiding in the electron/hole separation.

It can be observed from the JV curves (Fig. 2) that the surface modification of hematite thin film with the iron(III) catalyst (Fe-OEC) nearly doubles the photoanodic response in the whole explored potential interval, whit a maximum photocurrent that reaches ca. 0.8 mA/cm^2 at 0.8 V vs SCE, whereas the unmodified hematite is limited to ca. 0.35 mA/cm^2. Because the photoanodic current begins at ca. 0 V vs SCE for both the samples, no modifications occur on the Fermi level of hematite due to the presence of Fe-OEC. Same results have been obtained in different buffer solutions (Na_2CO_3, NaOH), ruling out specific electrolyte effects on the charge transfer. In addition, no significant variation of the steady state photocurrent have been observed under prolonged illumination conditions, confirming the great stability of this semiconductor in photo-oxidation environment. In good agreement with JV data, also IPCE values more

than doubles in the presence of the catalyst, showing instead non modification of the shape of the spectra between the two sample (Fe-OEC modified and unmodified hematite) (inset in Fig. 2).
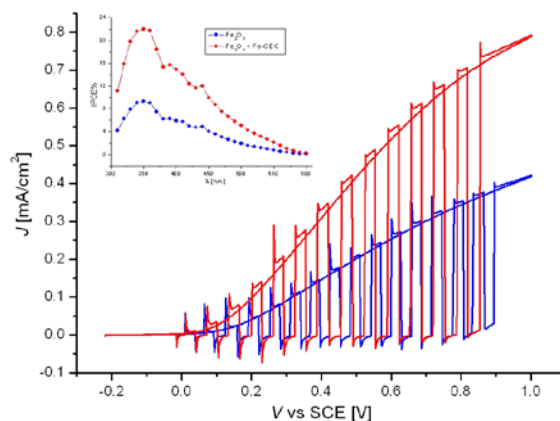

Fig. 2 - JV curves under continuous and shuttered illumination (100 mW/cm², AM 1.5 G filter)
of Fe-OEC modified (red line) and unmodified hematite (blue line) in 0.5 M sodium borate buffer (pH 11.5).
Inset: IPCE recorded in borate buffer under 0.7 V vs SCE potential bias

Significant key information about the involvement of the Fe-OEC catalyst in the hole transfer dynamics have emerged from Electrochemical Impedance Spectroscopy (EIS) experiments. Both Fe-OEC modified and unmodified hematite show similar impedance features, characterized by two semicircles in the complex plane at intermediate (100-10 Hz) and low frequencies (10-1 Hz) (Fig. 3).
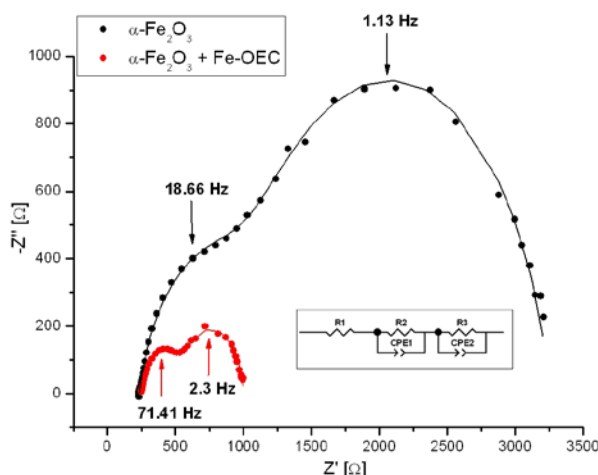

Fig. 3 - Complex plane plot of Fe-OEC modified (red circles) and unmodified hematite thin film (black circles)
under AM 1.5 G illumination recorded at 0.3 V vs SCE in 0.5 M sodium borate buffer (pH 11.5).
Data are fitted (solid lines) with the inset reported circuit model

We first assigned the loop at intermediate frequencies to the FTO/hematite interface and the loop at low frequencies to the hematite/electrolyte one, evaluating the match between charge transfer resistances measured by EIS with the inverse of the differential resistance ($\partial j/\partial V$) obtained from the JV curve. Then, we studied the capacitance behaviour at the two interfaces of the photoanode under different bias potentials in the dark and under illumination conditions (100 mW/cm², AM 1.5 G), ascertaining that at the FTO/hematite interface the capacitance is dominated by the space charge region developed in the FTO, accordingly to the reasonably linear Mott-Schottky plot ($1/C^2$ vs V) and the calculating donor density (N_d), in agreement with the value reported in literature for fluorine-doped tin oxide[14]. At the hematite/electrolyte interface, instead, the super linear Mott-Schottky plot and the observed increase in the capacitance under illumination (both for the modified and unmodified hematite thin film) can't be explained with the formation of a depletion layer in the semiconductor but, accordingly to what has been already proposed by Hamann and Bisquert[22], with the trapping of photoinduced holes in highly valent surface states. The ca. 2.5 factor increasing capacitance of hematite electrode in the presence of the Fe-OEC (Fig. 4) attests a more

favourable transfer of holes to the catalyst that, being an amorphous hydrated oxide (unlike the Fe(III) ions in hematite lattice), easily undergoes to proton couple electron transfer (PCET) reaction (4):

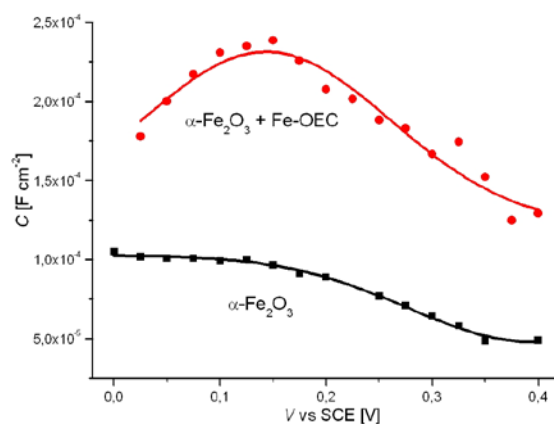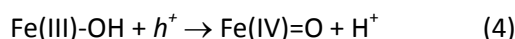$$Fe(III)\text{-}OH + h^+ \rightarrow Fe(IV)\text{=}O + H^+ \qquad (4)$$

Fig. 4 - Capacitance of the semiconductor/electrolyte interface under AM 1.5 G illumination of Fe-OEC modified (red circles) and unmodified hematite thin film (black squares) measured in 0.5 M sodium borate buffer (pH 11.5)

The Fe(IV)=O centres may be subsequent attacked from water molecules, leading to peroxide intermediates which then decompose to O_2, through a sequence of steps not already clarified for hematite, but well documented for other metal complexes (i.e. Ru(II) aquo-complexes)[23].

Hematite photoanodes can be easily prepared and functionalized with simple equipment and cheap reactants, showing good performance and excellent stability. The presence of catalytic iron(III) species on the hematite surface allows the transfer of photogenerated holes in centres that, due to the their amorphous nature, can led to the oxidation of water molecules. But even if the Fe-OEC greatly improves the performance of pristine hematite, the majority of holes still recombine with electrons, as it can be appreciate from poor IPCE values (Fig. 2). Given that, much work remain to be done in order to exploit the full potentialities of hematite as a successful photoanodic material.

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