



# Water oxidation electrocatalysis with iron oxide nanoparticles prepared via laser ablation<sup>☆</sup>

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## ABSTRACT

Iron oxide nanoparticles (FeO<sub>x</sub> NPs, 5–30 nm size) prepared via laser ablation in liquid were supported onto Indium Tin Oxide conductive glass slides by magnetophoretic deposition (MD) technique. The resulting FeO<sub>x</sub>/ITO electrodes are characterized by a low amount of iron coverage of 16–50 nmol/cm<sup>2</sup>, and show electrocatalytic activity towards water oxidation in neutral phosphate buffer pH 7 with 0.58 V overpotential and quantitative Faradaic efficiency towards oxygen production. XPS analysis on the oxygen region of the FeO<sub>x</sub> films reveals a substantial hydration of the surface after catalysis, recognized as a crucial step to access reactivity.

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## 1. Introduction

Artificial photosynthesis aims at the production of renewable solar fuels, via the light-induced water splitting into hydrogen and oxygen (Eq. 1) [1]. In this process, water oxidation to dioxygen is an essential step [2], since through this reaction (Eq. 2) water provides the electrons required to feed the reductive side of the overall process, where hydrogen is ideally generated from proton reduction (Eq. 3).



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However, the complexity of water oxidation, associated to a 4e<sup>-</sup>/4H<sup>+</sup> removal and to the formation of a new oxygen–oxygen bond, implies severe kinetic hurdles and high activation energy, which can be overcome by the employment of suitable catalysts [2,3]. In recent years, there has been an explosion of reports in this field, and extended relevance was given to water oxidation catalysts (WOCs) based on first row transition metals, due to their natural abundance and limited cost [4]. Among these, iron appears as an optimal choice, due to its biocompatibility and low environmental impact. Consequently, water oxidation catalysis by iron compounds was investigated with molecular complexes employing polydentate nitrogen based ligands [5], or with extended iron oxides (FeO<sub>x</sub>) phases [6–14]. In this latter case, the FeO<sub>x</sub> layer is supported onto conductive (or semiconductive) electrodes, and water oxidation is electrochemically (or photoelectrochemically) accessed. Current state-of-the-art materials are amorphous FeO<sub>x</sub> films prepared by photochemical metal-organic deposition (PMOD) [6], by electro- or photoelectrochemical deposition [7–9,12,14], by Successive Ionic Layer Adsorption and Reaction (SILAR) [10,11], or by Pulsed-Laser deposition [13]. Typically, water oxidation was investigated in alkaline aqueous media (pH 9–13) to guarantee stability of the oxide layer, while only recently catalysis was investigated in ideal neutral phosphate buffer (pH 7), with a low loading FeO<sub>x</sub> film (10–12 nmol Fe/cm<sup>2</sup>) electrodeposited onto Indium Tin Oxide (ITO) slides by means of cyclic voltammetry in neutral acetate buffer [14]. This material catalyzes water oxidation at a low overpotential of 0.48 V, reaching a total turnover

number (TON: ratio between evolved  $O_2$  mols and deposited Fe mols) of  $1.5\text{--}5.2 \times 10^4$ , with a turnover frequency (TOF is defined as the TON per unit of time) of  $750\text{--}1500\text{ h}^{-1}$ . A limitation of the system is the dependence of its stability upon operating conditions, and in particular a major loss of activity at high applied bias. In this work, we investigate the electrocatalytic behavior of magnetic  $FeO_x$  nanoparticles (NPs,  $d < 30\text{ nm}$ ) prepared by laser ablation in liquid and casted onto ITO electrodes by magnetophoretic deposition (MD) [15].  $FeO_x$  NPs provide a nanostructured morphology of the electroactive layer, with an enhanced surface area compared to a 2D compact film surface. Moreover, among different deposition techniques from liquid solution, MD does not require an additional application of an external bias. This method provides indeed a stable, low-amount loading of the  $FeO_x$  NPs onto an ITO electrode; the resulting film catalyzes water oxidation in neutral media at a low overpotential of  $0.58\text{ V}$  and with a quantitative Faradaic efficiency; a Tafel slope of  $110\text{ mV/decade}$  suggests the first electron transfer to the electrode as the rate determining step; evolution of the catalyst with formation of surface Fe-OH moieties upon prolonged electrocatalysis is also discussed.

## 2. Experimental

### 2.1. General procedures

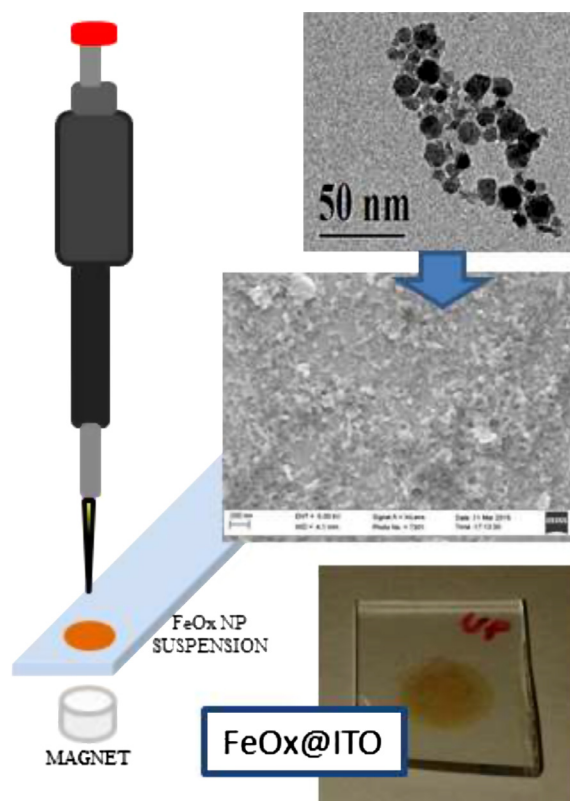
Iron concentration of  $FeO_x$  NPs was determined by the o-phenanthroline method, previously calibrated against inductively coupled plasma assisted mass spectrometry (ICP-MS) measurements. Briefly,  $FeO_x$  NPs were dissolved adding concentrated  $H_2SO_4$  and heating at  $90\text{ }^\circ\text{C}$  for 90 min. After setting the pH to 3.9 with NaOH, the o-phenanthroline solution ( $1\text{ g/L}$ ) was added with a ratio of  $250\text{ }\mu\text{L}$  per mL of  $FeO_x$  NPs dispersion. A buffer of potassium hydrogenphthalate was used to bring the final volume to  $5\text{ mL}$ . After 20 min, UV–vis spectra were recorded. The absorbance at  $396\text{ nm}$  gives the total iron in solution.

TEM analysis was performed with a JEOL JEM 3010 microscope operating at  $300\text{ keV}$  and equipped with a Gatan Multiscan CCD Camera model 794 a.  $FeO_x$  NPs were deposited by drop casting on a copper grid coated with an holey carbon film and left drying in air at room temperature, in the same ambient conditions exploited for deposition of  $FeO_x@ITO$  films.

Cyclic voltammetry and Controlled Potential Electrolysis experiments were performed using a BAS EC-epsilon potentiostat and an AMEL Potentiostat-Galvanostat, model 7050. A custom designed air-tight three-electrode cell was employed for all experiments. The custom designed cell used was assembled starting from a  $100\text{ mL}$  commercial threaded flask equipped with a Teflon cap, in which three copper wires ( $1.5\text{ mm}$  diameter) were welded, bearing the clips that allow connections with the electrodes. In the Teflon cap the FOXY-R oxygen probe was inserted, in order to allow oxygen measurement in solution. A silicon O-ring between the Teflon cap and the flask ensures the tightness of the cell. A Pt wire and an Ag/AgCl were used as counter and reference electrodes, respectively.

Dissolved oxygen measurements were performed using an Ocean Optics FOXY-R fluorescence probe coupled with NeoFox-GT phase fluorimeter and NeoFox Viewer software. The oxygen probe was calibrated using the two points calibration procedure of NeoFox Viewer software, employing a  $2.0\text{ M}$  sodium sulfite as  $0\text{ mg/L}$  dissolved oxygen value, and an aerated aqueous solution for which the amount of dissolved oxygen is reported, depending on the temperature and pressure.

Characterization of  $FeO_x$  NPs, complementary electrochemical and XPS experiments are available in the Supplementary Material.



**Scheme 1.** Schematic representation of deposition of  $FeO_x$  NP, picture of a  $FeO_x@ITO$  electrode, TEM image of  $FeO_x$  NP and SEM image of  $FeO_x@ITO$  electrode.

## 3. Results and discussion

### 3.1. Preparation of the $FeO_x@ITO$ electrodes

Synthesis of  $FeO_x$  NPs via laser ablation in liquid solution (LASiS) was carried out according to a well-established protocol [16], exploiting the first harmonic ( $1064\text{ nm}$ ) of a  $9\text{ ns}$  Nd-YAG laser focused on bulk  $\alpha\text{-Fe}$  target immersed in pure water. Remarkably, LASiS does not require the use of undesired chemical precursors or additives to obtain  $FeO_x$  NPs [16,17]. Laser synthesized crystalline  $FeO_x$  NPs are purified from the amorphous iron hydroxides byproducts with an heat treatment at  $60\text{ }^\circ\text{C}$  for  $1\text{ h}$  in a disodium ethylenediaminetetraacetate (EDTA) aqueous solution, then collected by centrifugation and repeatedly washed with distilled water. By transmission electron microscopy (TEM, Scheme 1 and Figure S1), the particles size was observed in the  $5\text{--}30\text{ nm}$  range, with a polycrystalline structure typical of LA-SiS products, and single crystal domains of the order of  $5\text{ nm}$  [17a]. According to selected area electron diffraction (SAED, Figure S1b), Raman and FTIR spectroscopy (Figure S2a–b), final  $FeO_x$  NPs are prevalently composed by the magnetic phase magnetite ( $Fe_3O_4$ ), although Fe(III) oxide and hydroxides are also present, especially at the particles surface, as expected after the heat treatment in water. The  $FeO_x$  NPs were deposited onto glass coated with ITO ( $8\text{--}12\text{ }\Omega/\text{sq}$  surface resistivity) slides, by drop-casting  $8\text{--}25\text{ }\mu\text{L}$  of a  $1\text{ mM}$  (total amount of Iron) aqueous suspension, previously sonicated for  $30\text{ min}$ , followed by slow evaporation of the solvent at room temperature. The magnetic particles in the electrodes (hereafter  $FeO_x@ITO$ ) were distributed in a round area (diameter =  $0.8\text{ cm}$ , geometric surface area =  $0.5\text{ cm}^2$ ) with the aid of a magnet kept below the glass slide, while water was let to evaporate overnight, at room temperature (Scheme 1). This procedure allowed to achieve an Iron coverage in the range

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