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were performed using an EmStat^{3+} from PalmSens company (Netherlands). Electrochemical impedance spectroscopy was carried out using Zahner/Zennium potentiostat-galvanostat (Zahner, Germany).

Results and Discussion

We synthesized **1** in according to the previously report by the reaction of anhydrous $FeCl_3$ with 1,4,7,10-tetraazacyclododecane in methanol produces **1**.[27] Iron oxides at pH ~ 9-13 are efficient water-oxidizing catalysts toward water oxidation.[28-31] To find out the true catalyst for water oxidation in the presence of **1** at pH = 11, the bulk electrolysis of **1** at ~ 1.5 V (vs. Ag|AgCl|KCl$_{sat}$) was performed with Fluorine doped tin oxide (FTO) and Pt wire as working and auxiliary electrode, respectively. The Glassy carbon electrode is decomposed under water oxidation and thus the identification of true catalyst on the surface of this electrode is not easy.[32]

Interestingly, in this condition a film was appeared on the FTO electrode during 10 h in the bulk electrolysis of **1** at 1.5 V. The film was characterized by scanning electron microscopy, energy-dispersive X-ray analysis and X-ray diffraction.

As shown in Fig. S3 (ESI†), the SEM images of the film show nano-sized particles of SnO_2 from FTO. The EDX data from (FTO-**1**) shows that the obtained film at pH = 11 contains O and Sn with low amounts of Fe (~ 0.3%), which disperse on the surface of electrode. However, XRD only shows FTO peaks (Fig. S1, ESI†). It is not surprising that SnO_2 and many metal oxides with a nano-sized structure absorbs metal ions or complexes on its surface at least by electrostatic interaction (**Fig. 2**). Such attachments convert homogeneous catalyst to heterogeneous one and most probably decompose a metal complex to a metal oxide (**Fig. 2**). Fe oxide on FTO electrode in this condition is an efficient catalyst toward water oxidation.
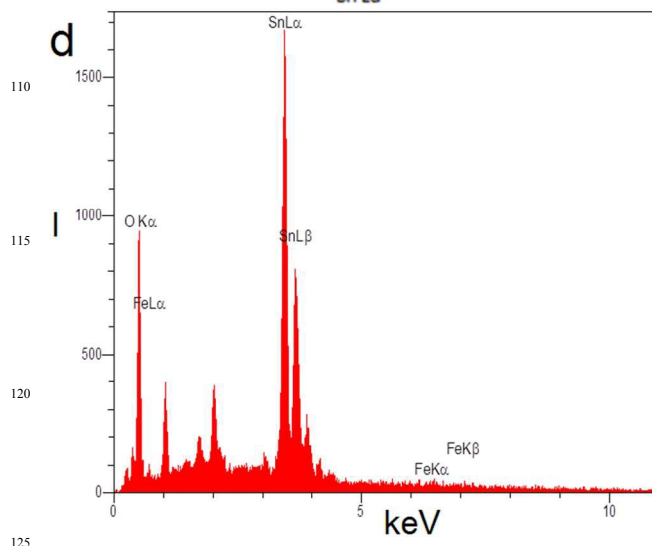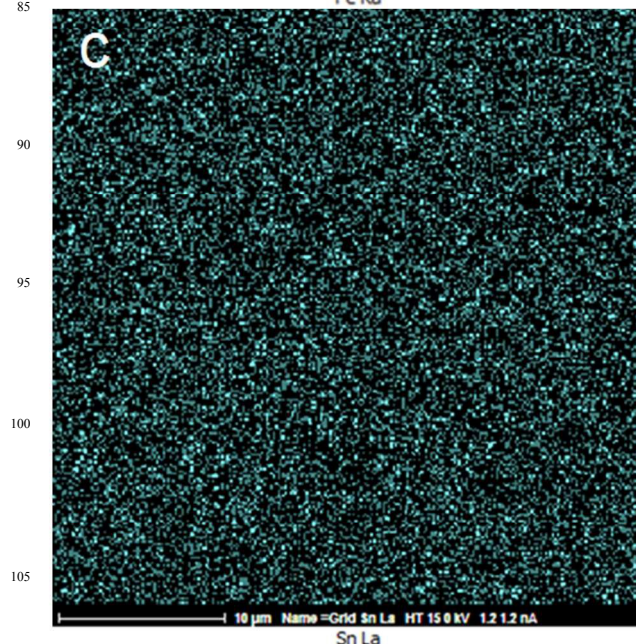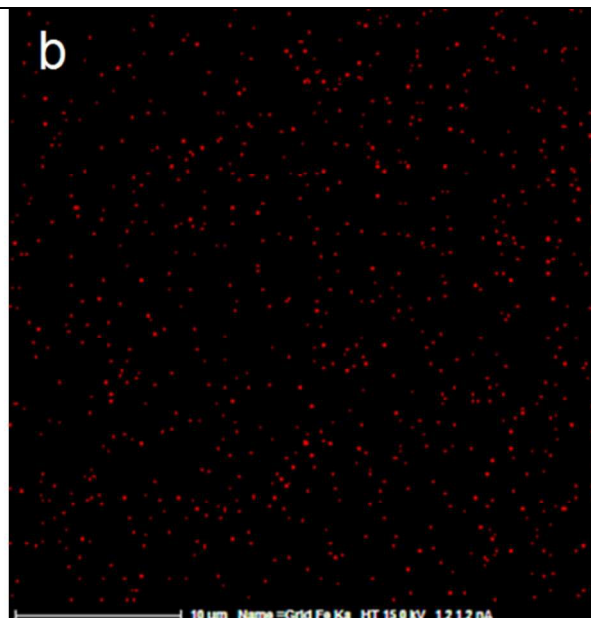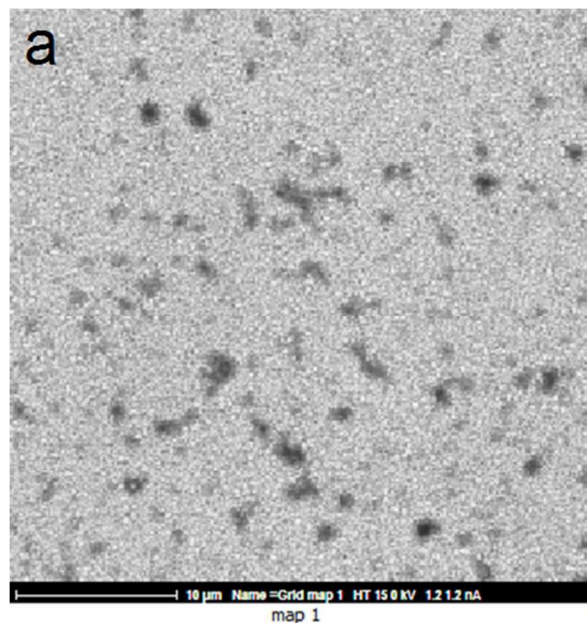
Fig. 2 SEM (a) and EDX-Mapping of Fe (red) (b) and Sn (blue) (c) for appeared film (FTO-**1**) electrode during 10 hours under water oxidation in 0.25 M phosphate buffer (pH = 11.0) in the bulk electrolysis of **1** at 1.5 (vs. Ag|AgCl|KCl$_{sat}$). The scale bar is 10 μm. EDX for the electrode
5 shows a few amounts of iron (d).

As shown in **Fig. 3**, cyclic voltammograms (CVs) of FTO and FTO after water-oxidation reaction in the presence of **1** (FTO-**1**) is different (see **Fig. 3**), which, similar to EDX results, shows Fe
10 ions present on the surface of electrode. Although the amounts of Fe on the surface of FTO is low, FTO-**1** shows efficient water-oxidizing activity. The stability of iron layer film was examined by consecutive cyclic voltammetry for FTO-**1** (see **Fig. 3b**). The film is stable, but recycling potential in the range between +1.2
15 and +1.7 V (vs. Ag|AgCl|KCl$_{sat}$) with a scan rate of 50 mV s^{-1} for 100 cycles in a Ar-saturated in LiClO$_4$ (pH = 6.9) causes a few decreasing in voltammetric currents, which is related to decrease iron oxide on the surface of the electrode.
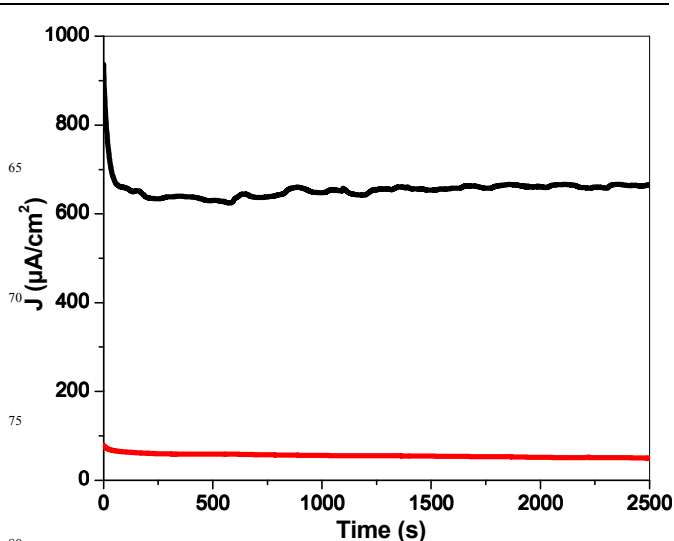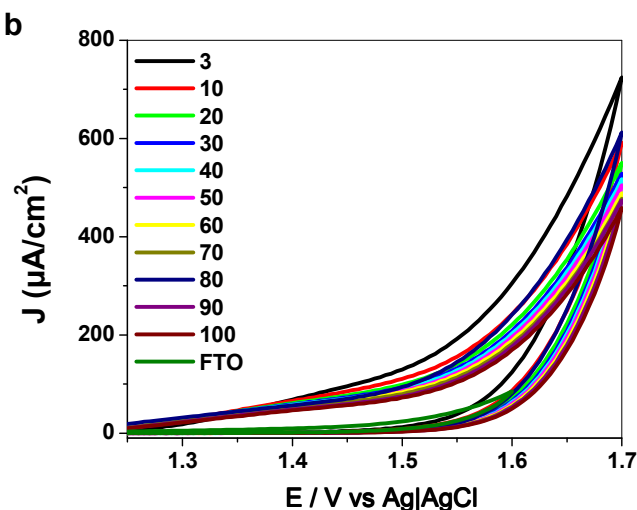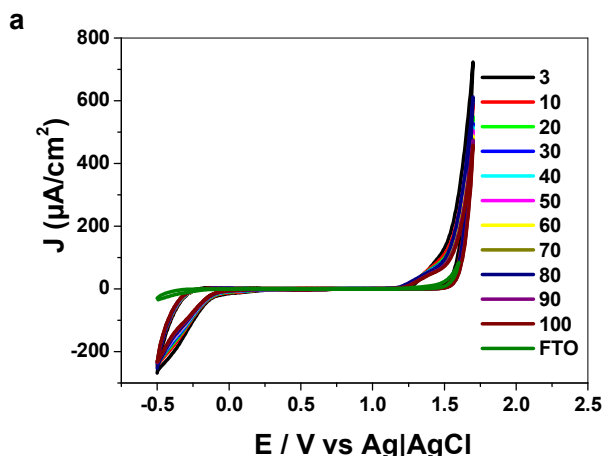
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c

Fig. 3 The different cyclic voltammograms for a clean FTO electrode and FTO in a solution of **1** (FTO-**1**) after 10 hours under water oxidation in 0.25 M phosphate buffer solution (pH = 11.0) at a scan rate of 100 mVs^{-1} (1.5 vs. Ag|AgCl|KClsat) (a,b). Chronoamperometry for FTO (red) and
85 FTO-**1** (black) electrodes, see **Fig. 2b**, in a N$_2$-saturated phosphate buffer 0.25 M at 1.5 V (c). Cyclic voltammetry studies were carried out with a conventional three-electrode setup, in which a FTO, an Ag|AgCl|KCl$_{sat}$ and a platinum rod served as the working, reference and auxiliary electrodes, respectively.

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Among the different techniques used for characterization of the thin film layers, electrochemical impedance spectroscopy (EIS) is an effective tool for the study of electrochemical properties and interfacial characteristics of the electrode.[33] With this in mind, the
95 electrochemical impedance response of FTO electrodes was recorded during the 96 cycles in order to evaluate and understand the mechanism of water oxidation. EIS was conducted under an AC voltage amplitude of 10 mV in the frequency range of 10^5– 0.01 Hz.
100 Nyquist plots relevant to the effect of cycle numbers upon the Nyquist parameters, Z′ and Z″ (real and imaginary impedance components, respectively) in a solution containing **1** (**Fig. 4**). Impedance spectra were obtained after each 5 cycles in order to follow the changes in the FTO interface during the scanning in
105 voltammetric studies

Afterwards, the raw impedance data was fitted by proposing equivalent circuit wich is compatible with the Nyquist diagram (**Fig. 4**). In order to analyze the impedance data in the complex plane, the measured data were simulated using the software of
110 Zview (II). This circuit describes the three time constants in each state.

Two parallel combinations of R$_1$, CPE-1 and R$_2$, CPE-2 features representing the film formation during scanning of voltammetry and double layer interface of the solution and FTO electrode,
115 respectively.

Also, the semicircle in series with this (R$_3$, CPE-3) is attributed to FTO electrode. Since the behavior of such systems is not ideal resulting in the replacement of capacitors by constant phase elements (CPE) which is related to account for non-
120 homogeneties and their geometry very complicated. CPE can be defined by the equation:[34]

$$Z_{CPE} = \frac{1}{Y^0 (j\omega)^n}$$

a

b

where Y^0 is the CPE constants, ω is the angular frequency (in rad s^{-1}), and n is the CPE exponent. This equation can describe an impedance of a pure capacitance of a capacitor (C) for a condition Y^0=C and the exponent n=1.

Table S1 (ESI†) reports the proposed equivalent circuit parameters obtained from the experimental impedance data fitting after different cycle numbers. With respect to the data in Table S1 (ESI†) and related Fig. S3 (ESI†), it is clear that during the first 6 cycles, the equivalent resistances increased and Nyquist plots shifted to higher values, which can be attributed to the complex decomposition and therefore the formation of thin film on the electrode surface. After six voltammetric cycles in LiClO$_4$ containing solution of **1** solution, the R$_1$ values reduced, which can be owing to formed film contribute in water oxidation process and so lead to increasing in film resistance. As well as, R$_2$ values, which are related to charge transfer resistance decreased after 6 cycles. This fact indicates that the formed film has a significant catalytic activity toward water oxidation (Fig. S4, ESI†). After these electrochemical experiments, we observed white crystals, which is precipitated from solution. Surprising, ^{1}HNMR spectra of this compound shows the related peaks for cyclen and other peaks in aromatic area. The patterns show decoordination of iron because iron as a paramagnetic ion has a signifant effect on ^{1}HNMR spectrum of organic compounds (Fig. S2, ESI†). We related the peaks to oxidation of cyclen under electro-water oxidation condition. Such changes in cyclen under electrochemical condition can induce decoordination of iron ions, and in the next step iron oxide formation.
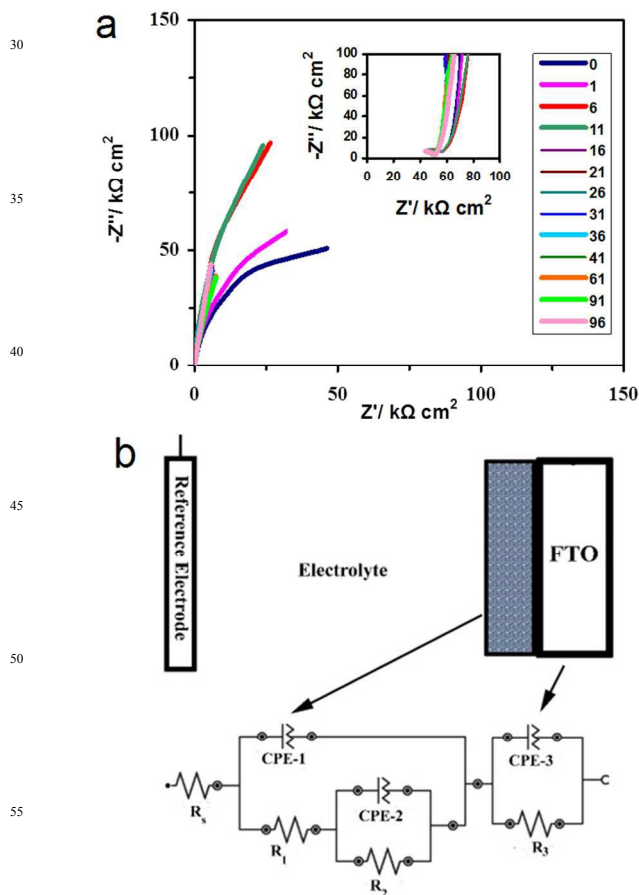

Fig. 4 Nyquist diagrams recorded at various cycle numbers in LiClO$_4$ containing **1** and FTO electrode (a). Equivalent circuit used in fitting of the impedance data presented in a (b). The range of CV is 0.5-1.8 V vs. Ag/AgCl|KClsat. Cyclic voltammograms recorded for a clean FTO electrode and (FTO-**1**). Conditions: supporting electrolyte, N$_2$-saturated LiClO$_4$ (0.25 M); scan rate, 5 mV s^{-1}, in the range of 0.5-1.8 V. Cyclic voltammetry studies were carried out with a conventional three-electrode setup, in which a FTO, an Ag|AgCl|KClsat and a platinum rod served as the working, reference and auxiliary electrodes, respectively.

All these evidences clearly show that a heterogeneous catalyst is responsible for water oxidation in the electrochemical condition based (**Scheme 2**). Such mechanisms should be carefully checked for many metal complexes in the water-oxidation condition because ligands usually are not stable in the oxidizing-condition related to water oxidation.[35-43] In this condition, released metal ions from the metal complexes form nano-sized metal oxides on the surface of electrode. The surface of FTO and ITO can easily and strongly bind to released metal ions and form a metal oxide that could oxidize water. In the case of iron ions, Cao's group reported an iron-based films as a highly efficient water-oxidation catalysts.[31] Interestingly, the extremely low iron loading on the electrodes is critical for improved efficiency for catalysis.[31]

Such results can show:

- The extremely low concentration of metal ions, which releases from metal complexes can be formed an efficient catalyst on the surface of electrode.[31,44]

-In contrast to high concentration, the extremely low concentration of metal ions provides better catalytic sites for water oxidation. Such low concentration of metal ions can be obtained by the decoordinaton of metal ions from metal complexes:
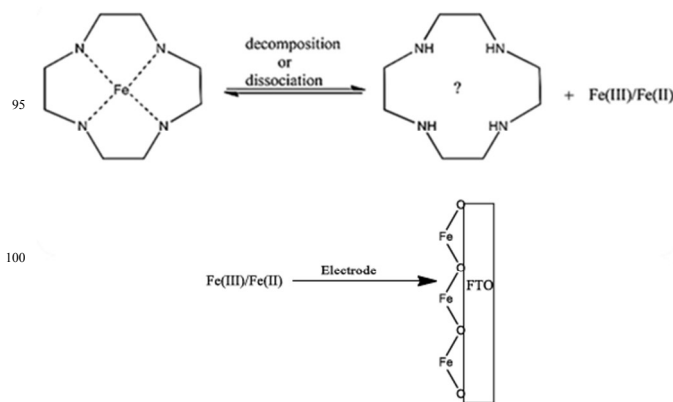
Scheme 2 A simple scheme to propose a very small formation of Fe oxide on the surface of electrode by decomposition or dissociation of **1**.

The results consistent with the result for water oxidation by Fe complex in the presence of chemical oxidants in high pH[26] and indicates Fe oxides are response for water oxidation.

Conclusions

We studied the water-oxidizing activity of an iron complex with 1,4,7,10-tetraazacyclododecane as ligand. Electro-water oxidation at pH = 11 is observed, which we related it to Fe oxide formation. We propose that to find true catalyst in related condition, the

stability of metal complex in the water-oxidation and other oxidation/reduction condition should be carefully checked because in these conditions organic ligands are usually decomposed and very low amounts of metal ions form very small metal oxides, which are efficient catalysts toward water oxidation. We believe that these results are worthy of consideration since many metal complexes, most probably, are not stable in water-oxidation condition.

Notes and references

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