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Nitrite reduction on a multimetallic porphyrin/polyoxotungstate layer-by-layer modified electrodes

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ABSTRACT

Electro and photoelectrochemical reduction of nitrite in aqueous solution was studied using a multielectrocatalysts modified ITO electrode. ITO modification was carried out using the layer-by-layer (LBL) method, where sequential electrostatic assemblies were formed using a μ-(meso-5,10,15,20-tetra (pirydil)porphyrin)tetrakis{bis(bipyridine)chloride ruthenium (II)} $[MTRP]^{n+}$, coordinated in its central cavity with Mn(III), Zn(II) or Ni(II) as a cationic layer, and polyoxotungstate $[SiW_{12}O_{40}]^{4-}$ as the anionic layer. Electrochemical measurements and UV–vis spectroscopy were used to monitor the modification process. Optimal results were obtained when three layers were deposited onto the ITO surface and were stable in aqueous solution. The order of the multilayer formation was explored by comparing a modified electrode where $[Zn(II)TRP]^{4+}$ was the outermost layer with an electrode where $[SiW_{12}O_{40}]^{4-}$ was the outer layer. Results show that the best performing electrode is one with $[SiW_{12}O_{40}]^{4-}$ as the outer layer. Nitrite reduction on these electrode surfaces was studied in dark conditions and under light irradiation. Potential controlled electrolysis experiments were also performed, finding hydroxylamine, hydrazine and ammonia as the reduction products in dark conditions. Under light irradiation, only hydrazine and ammonia were found and, we observed an increase in the amount of obtained product. In this case, the electrolysis was carried out 150 mV less and half of time than in dark conditions. These results show that the combination of light and potential give rise to an improvement in the electrocatalytic properties of the modified electrodes. Continuous photolysis and IR spectroelectrochemical experiments were carried out to determinate the nature of this phenomena, evidencing the formation of an intermediary species between nitrite and $[Mn(III)TRP]^{5+}$.

1. INTRODUCTION

Nitrite ion, NO_2^-, is an intermediate species in the nitrogen cycle resulting from the oxidation of ammonia or from reduction of nitrate [1,2]. Nitrite is strongly related to human life because it is used as a preservative of foods and a color fixative for meats [3]. On the other hand, atmospheric nitrite is oxidized to HNO_3 by $OH^{\bullet}$ radicals. Nitric acid is a component of acid rain, which in contact with soils, generates nitrites and nitrates increasing their concentration in this complex environmental matrix [4,5] and in ground water [3,4]. The removal or conversion of nitrites and nitrates in water to harmless compounds, is one of the current issues in environmental remediation [3].

The influence of nitrite in human health has been recognized since nitrite contained in drinking water and foods is a serious health risk for human beings such as metahemoglobinemia, where Fe(II) present in hemoglobin (Hb) protein is oxidized to Fe(III) generating methahemoglobin (metHb) which is incapable of perform its

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physiologic functions [6]. On the other hand, nitrite ion is able to react with secondary amines or amides to form nitrosamines or nitrosamides, that can act as carcinogenic agents [7].

Several analytical methods have been proposed to determine nitrite including spectrophotometry [8,9] and chromatography [10,11]. Nitrite has been important from the point of view of electrochemistry, because is oxidized to nitrate and reduced to nitric oxide or other compounds [3]. In most common electrodic surfaces, nitrite reduction is thermodinamically favorable, but the charge transfer kinetics associated with the reaction is slow, and needs high overpotentials [2]. For this reason, the use of an electrocatalyst is necessary. In this sense, nitrite reduction has been reported using different kinds of modified surfaces with metals [12–14], metal oxides [15–18] and diferent types of transition metal complexes like porphyrins [5,19–25], phtalocyanines [26], corrols [27], cyclams [28] among others.

Recently Winther-Jensen et al. described a method to reduce nitrite using PEDOT-bipyridinium-Fe-complex electrodes, finding that it is possible to reduce nitrite at −0,65 V vs Ag/AgCl, in aqueous media, giving only ammonia as reaction product. The system selectivity have been explained in terms of the formation of an Fe-nitrosyl complex, which is reduced to ammonia in a five electron step, giving an important evidence about the effect of coordination chemistry in the design of an efficient electrocatalyst for the reduction of nitrite [29].

Polyoxometalates (POMs) are oligomeric aggregates formed by metal cations and bridged by oxygen atoms. Due to its unique structure POMs are very versatile compounds. Their properties such as size, redox chemistry, charge distribution and photochemical activity can be modulated according to its chemical composition; for these reasons their chemical reactivity has been studied in many applications such as biologic assays [30] or as catalysts in chemical reactions with technological interest [31].

POMs (heteropoly and isopolyoxometalates) have been used as material to modify electrodic surfaces, its activity in acid media toward the hydrogen evolution and oxygen [32], nitrite [33], bromate [34] and iodate reduction [35] have been tested.

Recently, Liu et al [36]. have reported the use of POM in hybrid fuel cells, which uses the previously mentioned catalyst to degrade biomass under light irradiation, and to reduce oxygen in the same device, showing the photoelectrocatalytic activity of this kind of clusters.

In 1993, Araki and coworkers synthesized the μ-{meso-5, 10, 15, 20-tetra (pyridyl) porphyrin} tetrakis {bis(bipyridine) chloride ruthenium(II)}$(PF_6)_4$ (TRP) and its respective metal complexes with Co(II), Ni(II) and Zn(II) [37] starting from a free base pyridyl porphyrin and the corresponding ruthenium complex. These kind of compounds have been previously used in a wide range of electrochemical studies including environmental and technological applications such as sulfite, nitrite, oxygen and carbon dioxide reduction using the above mentioned complexes as an homogeneous catalyst in several solvents [38–42]. Its capacity to act as an efficient electrocatalyst is mainly due to the combination of the coordination and redox properties of porphyrins and the redox and photochemical properties of ruthenium polypyridyl substituents, which improve electron transfer, hence, this kind of compounds can be used to achieve multielectronic redox processes.

It was previously demonstrated that ITO electrodes modified with bilayers containing $[SiW_{12}O_{40}]^{4-}$ and tetraruthenated porphyrins present strong photoelectrocatalytic behavior toward carbon dioxide reduction, showing that at −0,8 V vs Ag/AgCl this kind of electrodes can lead to multielectronic reduction of CO_2, producing high reduced compounds such as methanol, formic acid or formaldehyde in dark conditions; changing to a more selective product distribution when the system is under irradiation of 440 nm [43].

In the present work multimetallic porphyrins/POMs films have been investigated toward the electrocatalytic reduction of nitrite.

2. EXPERIMENTAL

2.1. Chemical reagents

All chemical reagents were of analytical grade or better. Silicontungstinic acid $[H_4SiW_{12}O_{40}]$ and ammonium hexafluorophosphate were purchased from Fluka. Mn(III) acetate, Zn(II) acetate, Ni(II) acetate, 5,10,15,20-tetra pyridyl-21H, 23H-porphine, sodium perchlorate, tetrabuthylammoniun nitrite (TBAN), triethanolamine (TEA), and 2,2-dipyridyl were purchased from Sigma-Aldrich. Lithium chloride was purchased from Fisher Scientific. Ruthenium (III) chloride trihydrate was purchased from Pressure Chemical Co. Sodium nitrite was purchased from Riedel-deHaën. N,N-dimethylformamide (DMF), ethanol, methanol, acetone, glacial acetic acid, deuterated acetonitrile and neutral alumina were purchased from Merck.

The synthesis of the precursor complex cis-dichloro (2,2-bipyridine) ruthenium (II) dihydrate was carried out based on a procedure previously described in the literature [44]. Supramolecular complexes μ-{meso-5, 10, 15, 20-tetra (pyridyl) porphyrin} tetrakis {bis(bipyridine) chloride ruthenium(II)}$(PF_6)_4$ and its respective metal complexes with Mn(III), Ni(II) and Zn(II) defined as $[Mn(III)TRP]^{5+}$, $[Zn(II)TRP]^{4+}$ and $[Ni(II)TRP]^{4+}$ were prepared by a method described by Araki et al [40,45–48]. The purity of these compounds was checked by optical absorption spectroscopy, elemental analysis and cyclic voltammetry.

2.2. Procedures

Electrochemical experiments were carried out in a CH Instruments model 620B electrochemical workstation using a three-compartment Pyrex glass cell. An Indium Tin Oxide (ITO) electrode (Delta Technologies, MN U.S.A) was used as the working electrode with Ag/AgCl (3 M KCl) (CH Instruments, TX, U.S.A.) as the reference and Pt wire as the counter electrodes respectively.

All potentials values informed in this work are quoted against Ag/AgCl (3MKCl) reference electrode. Photoelectrochemical experiments were carried out using a three compartment cell with a quartz window irradiated with light of 440 nm, provided by a 500W Xenon-Mercury lamp system (Oriel Co) coupled to a monochromator (Jarrell Ash, Czerny-turner).

Controlled potential electrolysis experiments were carried out on a BASI POWER MODULE PWR-3 potentiostat. The experiments were performed in a gastight H type cell. UV-Visible data were recorded on a Shimadzu Multispec 1501 spectrophotometer.

IR-SEC measurements were carried out in a Bruker Equinox 55 spectrometer along with a Pine Biopotentiostat Model AFCBP1.

Continuous photolysis experiments were carried out on a sealed quartz cell irradiated with white light provides by a 500W Xenon-Mercury lamp system (Oriel Co).

AFM images were registered on a Bruker NanoScope Innova AFM along with NanoDrive v8.01 software.

All XPS spectra were obtained by a XPS spectrometer, Physical Electronic model 1257.

2.2.1. Preparation of the $[MTRP]^{n+}/[SiW_{12}O_{40}]^{4-}$ bilayers film

The ITO electrode was cleaned with methanol for one hour, and subsequently rinsed with deionized water. Modification process was carried out by a previously reported method [43,49] A cleaned ITO electrode was dipped into a 0.5 mM methanolic solution of Ni (II), Zn(II) or Mn(III) tetraruthenated porphyrin for four minutes. After that, the electrode surface was rinsed with deionized water to avoid surface excess. The “layer” modified ITO electrode was