



# Electro and photoelectrochemical reduction of carbon dioxide on multimetallic porphyrins/polyoxotungstate modified electrodes



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## ABSTRACT

Electrochemical and photoelectrochemical reduction of carbon dioxide was studied in aqueous solution, using an ITO/multilayer modified electrode. The multilayer formation was carried out by the Layer-by-Layer method (LBL), using a  $\mu$ -(meso-5,10,15,20-tetra(pyril)porphyrin)tetrakis {bis(bipyridine)chloride ruthenium(II)} coordinated with Mn(III), Zn(II) and Ni(II) in its central cavity and an anionic polyoxotungstate  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ . The multilayer formation was corroborated by electrochemical methods and UV–visible spectroscopy. For this study, 3 multilayers were formed on the ITO surface. Carbon dioxide reduction was studied by linear sweep voltammetry at pseudo stationary state ( $5 \text{ mV s}^{-1}$ ) in a 0.1 M  $\text{NaClO}_4$ ,  $\text{CO}_2$  saturated solution. Photoelectrochemical reduction of carbon dioxide was studied in the same conditions described above under light irradiation at 440 nm. In dark conditions, an enhancement in current is detected at  $-0.75 \text{ V}$  indicating carbon dioxide reduction. Under light irradiation the reduction process shifts to  $-0.60 \text{ V}$ . Chemical analysis after controlled potential electrolysis shows that in dark conditions, formic acid, carbon monoxide and methanol are the reduction products. Under light irradiation there is a change in the product distribution and for some metals; formaldehyde can be detected, evidencing a change in the reduction mechanism. These results support the fact that  $[\text{MTRP}]^{n+}/[\text{SiW}_{12}\text{O}_{40}]^{4-}$  multilayer modified electrodes act as electrocatalysts for carbon dioxide reduction and that this activity is enhanced by a combination of light and potential where light produces excited states sites on the multilayer, that are more reactive toward carbon dioxide reduction.

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## 1. Introduction

The reduction of global  $\text{CO}_2$  emissions is currently an issue of major concern [1,2] due to its increase in the atmospheric concentration, caused by the dependence of human population on fossil fuels for energy sources, which is considered the major cause of the greenhouse effect [3–5]. This has stimulated the development of electrochemical and photoelectrochemical systems able to produce useful organic chemicals by reducing  $\text{CO}_2$  gas [6].

The electrochemical reduction of  $\text{CO}_2$  usually requires a high overpotential of approximately  $-2 \text{ V}$  vs NHE [7,8] for a one electron process. This potential can be lowered, by performing a two electron or proton coupled multi-electron  $\text{CO}_2$  reduction [8,9], with the necessary  $\text{CO}_2$  activation performed with the use of a catalyst.

This suggests that a multi-electron redox system is necessary for constructing a practical electrocatalytic system for  $\text{CO}_2$  reduction.

For the study of this reaction, a wide range of electrodes has been used: metallic cathodes such as Cu, Hg, Au, Ag, Ni, Pt [10–13] and semiconductors such p-CdTe, p-InP, p-GaAs [14–16]. The use of carbon electrodes, have also been studied, but in this case, a high overpotential is required and depending on the solvent, hydrogen evolution can compete as a secondary reaction [17]. This problem has been solved, using different kinds of catalyst such as transition metal complexes which can act as an electronic mediator and exhibit electro and photoelectrocatalytic activity toward  $\text{CO}_2$  reduction, in homogeneous media and confined on electrodes [9,17–24].

Macrocyclic metal complexes, such porphyrins and phthalocyanines have been widely studied as electrocatalysts in solution and forming parts of modified electrodes [21,25,26]. Results show that the efficiency and selectivity depend on different factors, for example the reaction media, applied potential, and microenvironment.

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Araki and coworkers synthesized a tetra-ruthenated porphyrin, consisting on a free base  $\mu$ -{meso-5,10,15,20-tetra(pyridyl)porphyrin}tetrakis{bis(bipyridine)chloride ruthenium (II)}(PF<sub>6</sub>)<sub>4</sub> (TRP) and the metal complexes derivatives (Co(II), Ni(II), Zn(II)) [27]. These types of supramolecular complexes have been used in electrocatalytic studies for sulfite reduction, nitrite oxidation and reduction, oxygen reduction and carbon dioxide reduction in solution [28–32]. Its capacity to act as an efficient electrocatalyst is mainly due to the combination of the catalytic and redox properties of porphyrins and the redox and photochemical properties of ruthenium polypyridyl complexes, which improve the electron transfer.

On the other hand, photoelectrochemical reduction of CO<sub>2</sub> has been studied with mixed systems such as [Ru(bipy)<sub>3</sub>]<sup>2+</sup> and [Ru(bipy)<sub>2</sub>(CO)<sub>2</sub>]<sup>+</sup> [7,33]. In this system, [Ru(bipy)<sub>3</sub>]<sup>2+</sup> acts as a photosensitizer and [Ru(bipy)<sub>2</sub>(CO)<sub>2</sub>]<sup>+</sup> as a catalyst in the presence of a reductant such a NAD(P)H model compound. [Co(tetraaza-macrocycles)]<sup>2+</sup> [34] and [Ni(cyclam)]<sup>2+</sup> [35,36] have also been used as catalysts in the presence of a photosensitizer obtaining CO as a major product, however, for this type of system, the efficiency of CO<sub>2</sub> reduction has several drawbacks, since hydrogen evolution from hydride complexes forms in the catalytic cycle. Different types of semiconductors have been used for CO<sub>2</sub> photoelectrochemical reduction [14–16,5,37] obtaining different reduction products such as methane, methanol, ethanol, formaldehyde and formic acid [14–16,5,37].

Polyoxometalates (POMs) are a group of early transition metal–oxygen clusters. Their versatile nature in terms of size, redox chemistry, structure, charge distribution and photochemistry means that polyoxometalate chemistry is arguably one of the many areas in inorganic chemistry that is developing most rapidly today [38]. Thin films of POMs in combination with water soluble cations [39], nanoparticles [40–42] and polymers [43,44] have been previously reported. In the last decade POMs have been recognized as important building blocks for highly efficient photocatalyst and photoelectrochemical devices when combined with semiconductors and organic/inorganic molecules [45]. It has been reported that in acid media a modified electrode with heteropoly and isopolyoxometalates shows high activity towards the hydrogen evolution reaction (HER) and molecular oxygen reduction [46], which has also been studied for nitrite, bromate and iodate reduction [47–49]. Cationic porphyrins combined with POMs give rise to an organic–inorganic film with very interesting electrocatalytic behavior for molecular oxygen reduction generating hydrogen peroxide as the reduction product and for hydrogen evolution in the range of –0.4/–0.5 V [46,50–52].

To the best of our knowledge there are no studies of carbon dioxide reduction and photoelectroreduction on multimetallc porphyrins/POMs films. The present work describes carbon dioxide reduction with an ITO/multilayer modified electrode. The multilayer was generated by a combination of cationic metal center Mn(III), Zn(II) and Ni(II)  $\mu$ -{meso-5, 10, 15, 20-tetra (pyridyl) porphyrin} tetrakis {bis(bipyridine)chloride ruthenium(II)} ([Mn(III)TRP]<sup>5+</sup>, [Zn(II)TRP]<sup>4+</sup> and [Ni(II)TRP]<sup>4+</sup>, respectively) and an anionic polyoxotungstate [SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> using a *layer-by-layer* method. Electroreduction and photoelectroreduction of carbon dioxide was studied in aqueous solution, by linear sweep voltammetry in the range between 0 and –0.9 V and controlled potential electrolysis.

Reduction products detection was carried out by colorimetric and chromatographic methods. Stability of these multilayer films was evaluated, before and after potential controlled electrolysis experiments.

These studies confirm the capability of these multilayer modified electrodes to act as electro and photoelectrocatalyst favoring single or multiple charge transfer process.

## 2. Experimental

### 2.1. Chemical reagents

All chemical reagents were of analytical grade. Polyoxotungstate anion [SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> and ammonium hexafluorophosphate were purchased from Fluka. Mn(III) acetate, Zn(II) acetate, Ni(II) acetate, 5,10,15,20-tetra pyridyl-21*H*, 23*H*-porphine, sodium perchlorate 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.

*N,N*-dimethylformamide (DMF), ethanol, methanol, acetone, glacial acetic acid 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 [53]. Supramolecular complexes [Mn(III)TRP]<sup>5+</sup>, [Zn(II)TRP]<sup>4+</sup> and [Ni(II)TRP]<sup>4+</sup> were prepared by a method described by Araki et al. [30,32,54–56]. 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 ITO electrode (Delta Technologies, USA) was used as the working electrode with Ag/AgCl (CH Instruments, TX, USA) as the reference electrode, and Pt wire as the counter.

All potentials values informed in this work are quoted against Ag/AgCl reference electrode. Photoelectrochemical experiments were carried out using a three compartment cell with a quartz window irradiated with light provided by a 500 W 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. Gas chromatography measurements were carried out using a DANI Master GC with a FID and a TCD detector. The columns used were a Supelcowax 10 (30 m × 0.32 mm × 0.25  $\mu$ m film thickness) and a Supelco mol sieve 5A° (30 m × 0.53 mm).

#### 2.2.1. Preparation of the [MTRP]<sup>n+</sup>/[SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> multilayer film

The ITO electrode was cleaned with methanol for one hour, and subsequently rinsed with deionized water for an additional hour.

Multilayer formation was carried out by a previously reported method [57]. A cleaned ITO electrode was dipped into a 0.5 mM methanolic solution of Ni(II), Zn(II) or Mn(III) porphyrin for 4 min. The electrode was rinsed with deionized water to avoid surface excess. The layer modified ITO electrode was dipped into a 0.5 mM water solution of [SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> for 4 min. The bilayer modified ITO electrode was rinsed and dried. The procedure was repeated three times, obtaining a multilayer [MTRP]<sup>n+</sup>/[SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> modified electrode.

The multilayer formation was monitored by cyclic voltammetry and UV–Vis spectroscopy.

The stability of multilayer modified electrode was evaluated in a 0.1 M NaClO<sub>4</sub> solution. The potential electrode was swept during 50 continuous cycles between –0.9 V and 1.0 V

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