

# Electroless Nano-Plating in Ion-track Etched Polymers: Iridium- and Bismuth-coated Membranes for Catalysis and Sensing Applications

Martin Christoph Scheuerlein<sup>1</sup>, Wolfgang Ensinger<sup>1</sup>

<sup>1</sup>Department of Materials and Earth Sciences, Technical University of Darmstadt  
Alarich-Weiss-Str. 2, 64287 Darmstadt, Germany  
scheuerlein@ma.tu-darmstadt.de

**Abstract** – Nanostructured materials are of ever-increasing research interest for a variety of applications, from (electro-)catalysis to sensing. In particular, ion-track etched polymer membranes provide a versatile, nanostructured platform due to the variety of realizable pore shapes and dimensions. In order to coat these membranes with active materials, electroless plating is commonly employed, due to its ability to conformally coat even recessed pores in porous materials. Our paper briefly discusses two recently developed nanoscale electroless plating procedures for two vastly different materials, i.e. Iridium and Bismuth. Coatings are applied onto ion-track etched polycarbonate to verify their nanofabrication capabilities. The coated membranes are then used as heterogeneous catalysts for the degradation of methyl orange (in the case of Ir) and to sense Pb in water (in the case of Bi).

**Keywords:** Electroless plating, Ion-track etched polymers, heterogeneous catalysis, heavy metals sensing, Iridium, Bismuth

## 1. Introduction

Due to their high surface-to-volume ratio and unique properties, nanostructured materials and free-standing nanostructures have been of increasing interest over the last decades, especially in the fields of catalysis, energy conversion and chemical sensing.[1], [2] Nanoporous membranes coated with catalytically active metals are particularly interesting for these applications, as they combine a very high active surface area with the added stability benefits of a solid support structure. Electroless plating is the coating method of choice, due to its technical simplicity, scalability and mild reaction conditions. Generally, the term electroless plating refers to the coating of surfaces by an autocatalytic redox-reaction between a metal precursor (usually complexed metal ions) and a reducing agent. Due to kinetic hindrance, the reaction only proceeds on catalytically active surfaces and the deposited metal film itself. This enables the efficient and conformal plating of a wide variety of substrate materials, including insulators and porous materials. Over the last years, many different nanoscale electroless plating procedures have been developed, covering a wide range of possible materials, including the iron-group and more noble transition metals. In this paper, we introduce two recent developments in electroless plating of ion-track etched membranes, namely the coating with Iridium and Bismuth. While Ir is interesting for (electro-)catalytic applications (e.g. oxygen-evolution reactions, 4-nitrophenol (4-NP) reduction, degradation of hazardous substances),[3], [4] Bi is considered a viable alternative to mercury electrodes for heavy metals sensing in waste water[5]. This is mainly due to its pronounced tendency to form alloys and intermetallic phases with various relevant heavy metals, such as Pb, Cd and Sn[6].

Ir and Bi coated membranes are fabricated by procedures developed in our group [7], [8] by electroless plating on commercially available ion-track etched polycarbonate membranes (ipPORE<sup>TM</sup>, *it4ip*, Belgium) with a nominal pore diameter and membrane thickness of 400 nm and 25  $\mu\text{m}$ , respectively. In the case of Ir, the coated membranes are then used for catalyzing the degradation of methyl orange in the presence of  $\text{NaBH}_4$ , while the Bi coated polymer is used as a proof-of-concept device to detect Pb in water.

## 2. Results and Discussion

### 2.1. Synthesis: Electroless Ir Plating

While electroless plating procedures for other noble transition metals, such as Pt, Au and Ag have been the subject of several studies over the last years, there is a noticeable lack of reports concerning the more exotic platinum group metals (PGMs) such as Ir, Os and Ru. This can be attributed to their intricate aqueous chemistry, which is governed by remarkably low ligand exchange rates, a plethora of possible oxidation states, and in the case of Ir the tendency to form insoluble oxides

in alkaline media.[9], [10] Recently, we showed that nanoscale electroless Ir plating is possible as long as the choice of metal precursor, complexing agent and reducing agent is carefully considered.[7] In this case, either citrate or ethylene diamine (EDA) proved to be suitable stabilizers, when  $\text{NaBH}_4$  is used as reducer. Figure 1a shows SEM images of Ir-coated ion-track etched polycarbonate membranes, prepared using a citrate stabilized plating bath. The deposit is remarkably homogenous, consisting of crystallites multiple nanometers in size. XPS and XRD measurements on a similar deposit have confirmed that metallic Ir is deposited predominantly.[7] However, small amounts of surface oxides are to be expected, due to the comparatively high oxygen affinity of Ir. Interestingly, the presence of both Ir and  $\text{IrO}_x$  has been linked to an increased catalytic activity of the material.[4]

## 2.2. Application: Degradation of Methyl Orange

The Ir coated membrane can then be used as a catalyst e.g. for various hydrogenation reactions such as the reduction of 4-NP or the degradation of organic dyes, such as methyl orange or rhodamine B. In our case, we assessed the activity of the deposit by utilizing it in the reduction of 4-NP[7] as well as the degradation of methyl orange (shown here). The coated membranes can be used in a flow-through configuration, in which the reaction solution is pumped through the membrane, as well as in a more conventional way, by simply submerging the catalyst in the solution under constant agitation. In the case of methyl orange, the reaction can be easily followed by UV-Vis spectroscopy, due to the strong and characteristic absorbance of the dye. Assuming Lambert-Beer's law, the reduction in absorbance before and after reaction on the catalyst is proportional to the decrease in educt concentration. Figures 1b and c show schematics of the experimental setup as well as UV-Vis spectra before, during and after the reaction, for (b) the flow-catalysis and (c) the conventional method. Using the membrane as a flow-catalyst enables a remarkable conversion even at a comparatively high flow rate of  $5 \text{ ml min}^{-1}$ . After one pass of the membrane, about 93% of the methyl orange has been converted. With the conventional method, a similar conversion requires much more time (Fig. 1c). This can be ascribed to the limited accessibility of the 400 nm diameter pores by diffusion. It can be concluded, that in order to unlock the full potential of the catalyst material, it is necessary to mechanically push the solution through the membrane. From the data shown in Fig. 1b, the apparent rate constant  $k_{\text{app}}$  of the reaction can be determined, which amounts to  $0.059 \text{ min}^{-1}$ . [7]

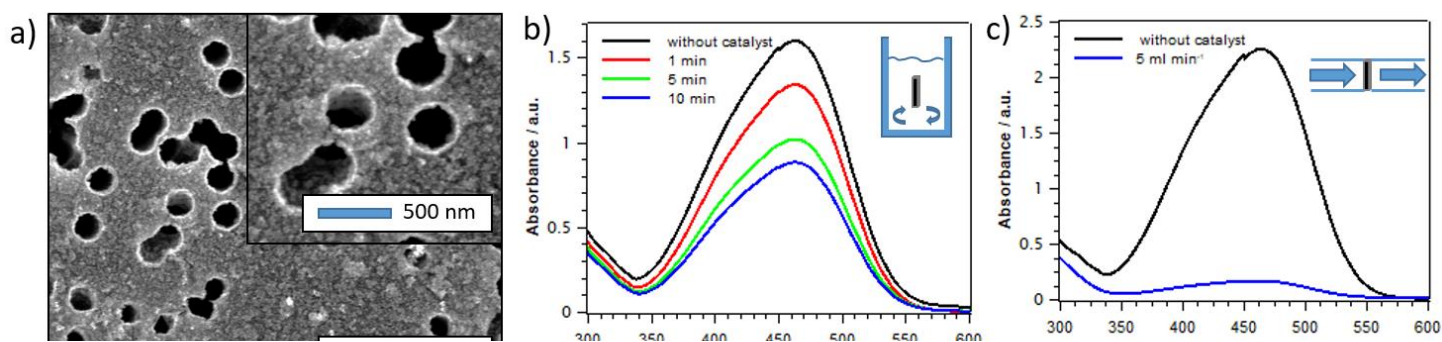


Figure 1: a) SEM images of Ir-coated ion-track etched polycarbonate membranes; b) characteristic absorbance of methyl orange after treatment with the catalyst for different times in stirred solution; c) absorbance of methyl orange/ $\text{NaBH}_4$  solution before and after passing the membrane in a flow reactor setup at  $5 \text{ ml min}^{-1}$  (adapted from [8]).

### 2.3. Synthesis: Electroless Bi Plating

As stated before, regarding many of the transition metals, multiple nanoscale electroless plating procedures have been developed over the last decades. In case of the main-group or post-transition metals, however, reports on electroless plating are very limited. During the early 1990s, Senda *et al.* reported the successful electroless deposition of Bi (among other main-group elements).[11] Their approach relies on the usage of Sn(II) complexes as reducing agent, which enables the fast fabrication of relatively thick Bi films consisting of micrometer sized grains. Despite some optimization in the following decades, the method still isn't suitable for controlled nanoscale synthesis. One of the challenges is Bismuth's low catalytic activity towards the decomposition of many of the typical reducing agents employed in electroless plating. Recently, we found that a plating bath based on the remarkably stable EDTA complex of Bi(III) in combination with borane dimethylamine (DMAB) as reducer is suitable for nanoscale Bi plating.[8] Figure 2a shows electroless Bi deposits in ion-track etched polycarbonate membranes. The amount of deposited Bi can be controlled by adjusting the deposition time. XRD analysis of the material corroborates that zerovalent, rhombohedral Bi is formed predominantly, although small amounts of superficial oxides are likely present as well.[8]

### 2.3. Application: Pb(II) Sensing

One possible application for nanostructured Bi materials is their use as electrodes in heavy metal sensors. Currently, this role is often filled by Hg electrodes due to their high sensitivity, despite the obvious toxicity issues. Bi-based materials have been proposed as an environment-friendly alternative, with ever improving sensory performance.[5] Sensing is usually performed by means of square-wave anodic stripping voltammetry (SWASV) after a preconcentration step at a constant potential. As a proof-of-concept, we performed SWASV sensing of Pb with one of our coated membranes. Measurements were performed in a 0.1 M acetate buffer at pH 4.6 with increasing concentrations of Pb-acetate. In a typical three-electrode setup, the membrane (geometric area: 0.25 cm<sup>2</sup>) was contacted as the working electrode, while an Ag/AgCl electrode and a glassy carbon rod were used as reference and counter electrodes, respectively. SWASV was performed after a preconcentration step at -1.2 V for 300 s. Stripping was then conducted with a step size of 4 mV, a pulse amplitude of 25 mV and a pulse frequency of 20 Hz. The recorded differential current response during the anodic stripping step is given in Figure 2b. It can be observed that the current response at the characteristic stripping peak for Pb scales linearly with the Pb concentration in the solution (Fig. 2c). While sensitivity certainly needs to be improved in order to detect Pb concentrations below the relevant exposure limits in drinking water, the first experiments show that electrolessly plated Bi can be used to detect Pb. We assume that sensor performance can be improved by using a larger pore diameter to enable faster diffusion of the analyte inside the pores, or, analogous to the catalysis experiments, a flow-through setup for detection.

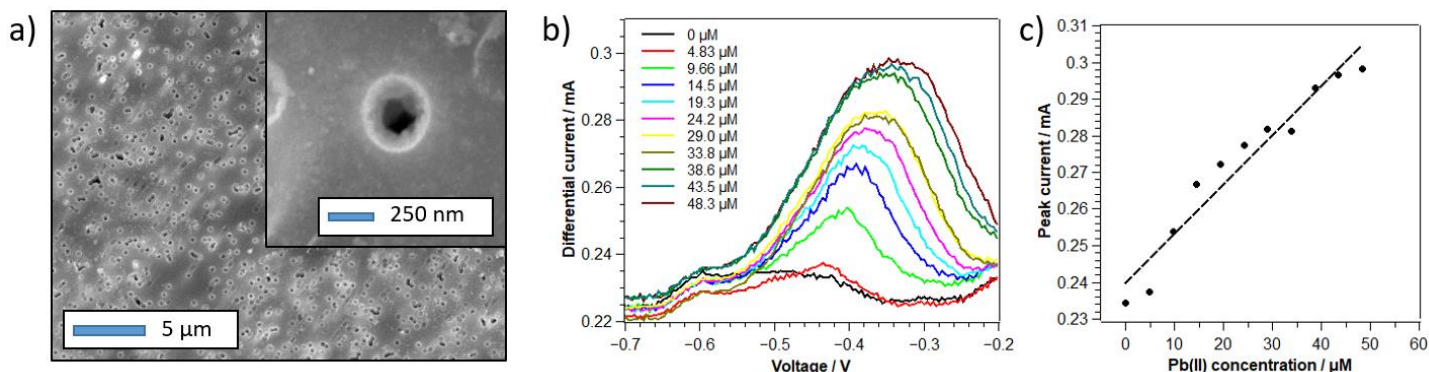


Figure 2: a) SEM images of Bi-coated ion-track etched polycarbonate membranes; b) differential current measured during SWASV measurements with increasing concentrations of Pb(II); c) peak differential current in relation to Pb(II) concentration.

### 3. Conclusion

In this paper, we briefly introduced two recently developed electroless plating routines for Ir and Bi. Their nanofabrication potential was shown by coating ion-track etched polymer membranes with a nominal pore diameter of nm. Our results show that due to the wide variety of possible coating materials, coated polymer membranes are promising various applications from heterogeneous catalysis to heavy metals sensing. In the case of catalysis, using the membranes a flow-reactor proved to be a significant improvement over the conventional method in which the catalyst is simply submerged in the stirred solution. For heavy metals sensing on Bi-coated membranes, future investigations should focus on improving sensitivity by optimization of membrane properties and electrical contacting of the sample.

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