

NiO Thin Film for Mercury Detection in Water by Square Wave Anodic Stripping Voltammetry

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NiO thin film thermally grown on Ni was investigated for the first time as an electrochemical sensor of mercury ions in water. The film was obtained by thermal oxidation in air of a commercial Ni foil. The influence of oxidation temperature, and time have been investigated by XRD, SEM, and EDS analysis. Square wave anodic stripping voltammetry was used for detecting Hg^{2+} ions in aqueous solution with different ion concentrations. In order to improve the response signal, all the operational parameters related to the sensing process such as pH, deposition time, potential, and square wave frequency, have been optimized. We obtained a detection limit of 4.4 ppb with a sensitivity of $1.1 \mu\text{A ppb}^{-1} \text{cm}^{-2}$.

1. Introduction

Despite the so-called heavy metals have been extensively used in the last decades for their tendency to form molecular complex and, above all, owing to their properties as catalyzers, to date, there is not a unique definition for identifying them. The most accepted definition is based on density, so that a metal with density higher than 5 g/cm^3 is considered as a heavy (Järup, 2003). Among this class, the most used metals are lead, cadmium, mercury, and arsenic, because find application in many areas. Lead is used as a building and fitting material, and, above all, in the battery industry; mercury is used as a disinfectant, for relieving tooth's disease, and for extracting gold from mines taking advantage of its tendency to form amalgam with gold (Lin et al., 2015). Unfortunately, heavy metals are highly toxic for both humans and environment. In particular, they can accumulate into human body and cause strong damages to the central nervous system, heart, kidneys, lungs, and immune system. The world's health organization (WHO) recognized mercury as one of the ten most dangerous chemical for human health (Ratner et al., 2015). In turn, The Environmental Protection Agency (EPA) imposed a 2ppb limit on overall concentration of mercury ions in drinking water (Jena et al., 2008). In this scenario, the development of a protocol for mercury determination in different media, such as water, food, blood, is of crucial importance, so that many researchers in the world are currently working in this area. The most modern analytical techniques for determination of mercury, as well as others heavy metals, are based on Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), Graphite Furnace Atomic Absorption Spectroscopy (GFAAS), and so on, which provide highly reliable results, with sensitivity less than 10ppb. Unfortunately, these techniques are very expensive in terms of both equipment and operating costs; in addition, they are time consuming, require highly skilled personnel, and cannot be used in-situ, therefore real time results are not available (Ratner et al., 2015). On the contrary, some high sensitivity electrochemical methods, such as Square Wave Anodic Stripping Voltammetry (SWASV), Differential Pulse Anodic Stripping Voltammetry (DPASV), and Cyclic Voltammetry (CV), have been recognized as valuable techniques for analytical determination of heavy metal. Their analytical response can be revealed through miniaturised, low power consumption, and use-friendliness devices, which can be preferentially used in place of expensive instruments, maintaining the same detection limits. In addition, analytical devices based on electrochemical methods are suitable for in-situ and real time analysis (Armas et al., 2016), and are extremely cheap. For these reasons, EPA recommends to use electrochemical methods for detecting heavy metal traces (Ratner et al., 2015). Among all the electrochemical methods, SWASV is considered the most powerful analytical technique for detecting heavy metals, owing to

its high sensitivity (limit of detection less than 10ppb), selectivity (each heavy metal has different stripping potential), and short analysis time. In the last decade, different materials, such as polymers (Kwang-Sik et al., 2003; Somerset et al., 2010), metals (Armas et al., 2016; Afkhami et al., 2015), DNA (Guerreiro et al., 2014; Liu et al., 2015), nanoparticles (Lin et al., 2015; Ratner et al., 2015), and carbon (Par et al., 2012; Nourifard et al., 2015) have been investigated as possible sensing materials for SWASV.

In this work, the attention is focused on nickel oxide that is a cheap material, easy to obtain from metallic nickel, and environmentally friendly. Due to these features, nickel (II) oxide has been extensively studied in the field of electrochemistry as an electrocatalyst (Wang et al., 2005), supercapacitor (Yuan et al., 2009), and active material for electrochemical sensor (Armas et al., 2016). NiO nanoparticles (NiO-NPs) were investigated as an electrode for sensing mercury ions through DPASV, showing a 8ppb detection limit with a linear range from 160ppb to 100ppm (Zhengcui et al., 2012).

Here, for the first time, at our best knowledge, the sensing properties of a NiO@Ni thin film for revealing mercury ion traces in water through the SWASV technique, which is a more powerful than those proposed by other authors, were investigated. The NiO thin film was obtained by thermal oxidation in air of a commercial Ni foil, and the effect of oxidation time and temperature were studied. All the oxide films were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD). Furthermore, all the parameters that affect the square wave voltammetry were optimized in order to achieve the highest possible sensitivity. Here, we present the preliminary results coming from this study, which are highly encouraging, because clearly evidence the potentiality of the electrochemical technique applied to a very simple and cheap sensing material for analytical determination of Hg in water.

2. Experimental

Fabrication of NiO thin film was performed by annealing a commercial Ni foil (Alfa Aesar Product, 127 μ m thick, purity higher than 99%) in an air oven. Mohanty et al. (2010) obtained 200nm of NiO-NPs after 3-6 hours of annealing at 500°C. On the other hand, Valladares et al. (2014) showed that just 3 hours of oxidation at 350°C are enough to obtain nickel (II) oxide from a commercial nickel foil. Because of this discrepancy, in this work, Ni foil was oxidized for 120 min at three different temperatures (350°C, 500°C and 700°C) and successively characterized through XRD, using a RIGAKU X-ray diffractometer (model: D-MAX 25600 HK), and SEM, using a FEI FEG-ESEM (mod. QUANTA 200) equipped with a detector for EDS. XRD patterns were obtained in the 2 θ range from 10° to 100° with a sampling width of 0.004° and a scan speed of 3 deg./min, using Ni-filtered Cu K α radiation (λ = 1.54 Å). Diffraction patterns were analyzed by comparison with ICDD database (International Centre for Diffraction Data, Power Diffraction File (2007), Pennsylvania USA).

The procedure for revealing Hg²⁺ ions consists of two successive steps. Initially, Hg is deposited on potentiostatically polarized NiO electrode, then, it is polarized through square wave anodic potential, recording the current response, and, in particular, the current stripping peak due to Hg dissolution. Through a calibration curve, the stripping current intensity can be correlated to the Hg²⁺ ion concentration in solution. NiO works as a cathode during the enrichment step (first step), while, it works as an anode in the second step (SWASV). The first step is very challenging because NiO is a p-type semiconductor therefore it tends to block cathodic current. For a correct working as a sensing element, it has been necessary to find a satisfying value of NiO thickness, which was sufficiently thin to avoid block effects in working as a cathode, and significant ohmic drop in working as an anode but, simultaneously, sufficiently high to don't dissolve under repeated SWASV cycles. In order to achieve this goal, two annealing times were investigated: 15 and 120 minutes, finding the last time as the best. After annealing, NiO@Ni was sealed with an insulating lacquer to expose a NiO geometric area of about 0.1 cm² that was tested as an electrochemical sensor for mercury ions. Electrochemical experiments were conducted in a 50ml three-electrode cell, where NiO@Ni was the working electrode, a Pt mesh was the counter electrode, and Ag/AgCl worked as a reference electrode. HgCl₂ solution was used as an analyte (solution containing the substance to be measured), which was buffered with citric acid and Na₂HPO₄ in different ratio depending on the desired pH, and was stirred at 600 rpm during deposition. Both deposition and square wave polarization parameters, such as deposition potential and time, frequency, potential step increment and duration were changed in a large range in order to find the best combination giving the highest stripping peak current. After optimization of the different parameters, a calibration curve was established, in order to find sensitivity and limit of detection (LOD) that are the key features of a sensor. For reliability purpose, the calibration curve was repeated for 5 times, at least, and the results here presented are averaged on 5 determinations. LOD was calculated through the equation (Di Natale, 2004)

$$LOD = 3 * \frac{SD}{S}$$

where SD is the standard error (μ A*cm⁻²) and S the sensitivity (μ A*ppb⁻¹ cm⁻²).

3. Results and discussion

Features of NiO thin film as a sensing material depend on annealing time and temperature. It has been necessary to find the right combination of these two parameters in order to form NiO without other nickel oxide or oxyhydroxide such as NiO₂ and/or NiOOH, and at the same time, to achieve a thickness ratio of NiO to Ni that guarantees good electrical conductivity of the electrode. Figure 1 shows XRD patterns of Ni foils annealed in different conditions. For comparison, the pattern of a not annealed Ni foil is also shown.

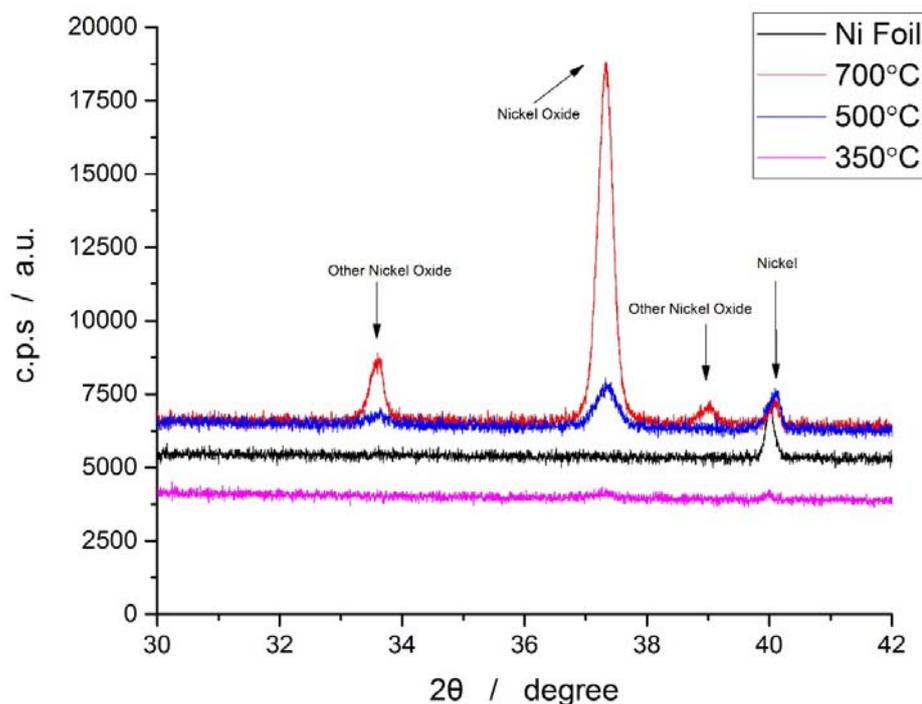


Figure 1: XRD patterns of Ni foil thermally oxidized in the air and at different temperatures for 120 minutes. For comparison, also the pattern of as received Ni foil is shown

Figure 1 show that the lowest temperature leading to visible formation of NiO is 350°C, but the kinetics of the process at this temperature is so slow that after 120 minutes of annealing the NiO peak is very weak. On the contrary, as annealing was conducted at 700°C, the Ni oxidation was very severe with formation of other oxidized species. The best annealing condition was found to be 120 minutes at 500°C, because the morphological analysis (see below) together with the successive tests as a sensor showed that NiO film thickness grown at 500 °C for 120 minutes is the best compromise between electrical conductivity and stability under SWASV. Only one NiO peak is shown in Figure 1 because the 2θ scale has been limited to a narrow interval for clarity purpose. Figure 2 shows two SEM images of a NiO surface after Ni oxidation at 500°C for 120 minutes, and EDS analysis. The ridges visible in the micrographs, likely, reproduce the initial Ni surface, so indicating that the film is thin, while the presence of fracture borders together with globular particles (see image at high magnification) suggest that the oxide film is well developed to be stable under SWASV, as confirmed by dedicated experiments. The EDS spectrum of Figure 2 shows the presence of only Ni and O peaks, so confirming in combination with XRD pattern, the purity of the oxide film. For testing the NiO sensing performance in detecting Hg²⁺ ions through the SWASV method, different parameters were investigated according to Armas et al. (2016). Figure 3 shows the influence of analyte pH (a), and Hg deposition potential (b) on SWASV curves of a NiO thermally grown at 500 °C for 120 minutes. Figure 3a shows that the current peak at 0.45 V increases as pH diminishes according to Pourbaix (1966). The optimum pH for detecting Hg was estimated to be 3 because at lower pH, NiO is unstable and tends to dissolve.

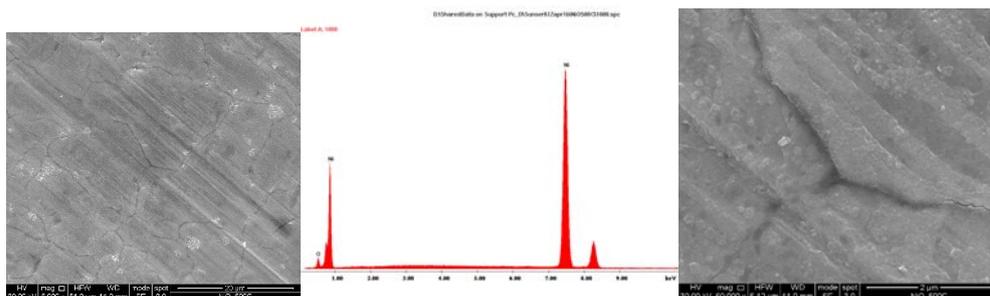


Figure 2: Surface SEM images of a NiO film grown through thermal oxidation at 500°C for 120 minutes, and EDS spectrum.

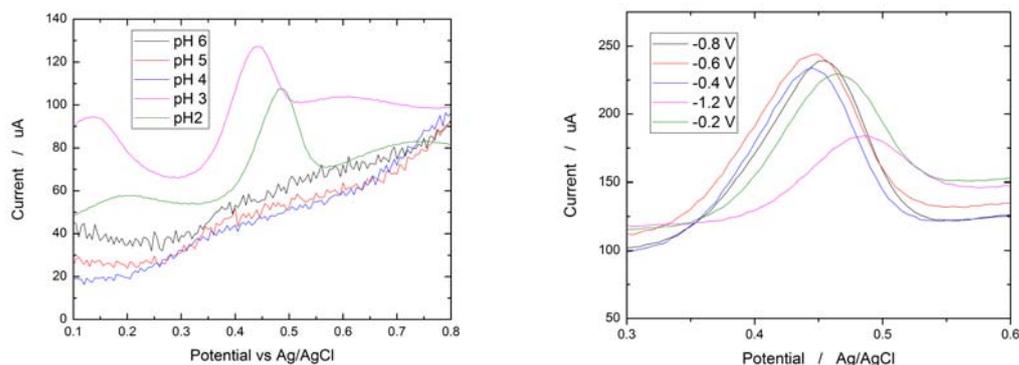


Figure 3: NiO SWASV curves at different a) analyte pH, and b) potential of Hg deposition on NiO

Therefore, the deposition potential of Hg on NiO was investigated at pH 3. In detail, deposition was conducted at different potentials for 3 minutes from a solution containing 4ppm of Hg^{2+} . After deposition, the sensing element was polarized through SWASV, and the current vs. potential curves showed in Figure 3b were recorded. It can be observed that the stripping current peak at 0.45 V is almost constant in the interval from -0.4 to -0.8 V, while for deposition at -0.2 V, the stripping peak is shifted at slightly higher potential. When deposition was conducted as to such a high potential of -1.2 V, likely, the reduction of H^+ ions strongly interfere with Hg^{2+} ones lowering Hg mass deposited on NiO. As a consequence, the stripping peak was weaker. According to these findings, -0.4 V was selected as the best deposition potential, because the lower potential guarantees higher selectivity of deposition and higher lifetime of the NiO film. Figure 4 shows the influence of deposition time on SWASV curves. The deposition was conducted at -0.4 V from a 4ppm Hg solution, at pH 3. According to the literature (Afkhami et al., 2015), the SWASV peak current vs. deposition time should be a sigmoid that reaches a plateau when the electrode surface is totally covered by the analyte. Figure 4 shows that after 350s of deposition at -0.4 V the peak current doesn't increase anymore, therefore this time was considered as the optimum one.

Also the SW parameters were optimized, achieving the best performance with 60Hz (step SW frequency), 5 mV (step extension) and 0.06V (step height). It has also been found that step height higher than 0.1mV and frequency higher than 120 Hz give distorted output signal so that analytical determination cannot be conducted. Conversely, it has been found that the stripping peak current was practically independent of step extension. Table I summarizes the optimized values of operational parameters controlling the analytical determination of Hg traces in water. Sensor calibration line was established by applying these parameters. Different HgCl_2 concentrations, from 6ppb to 5ppm, was exploited, and curves relative to only four concentrations are shown in Figure 5, for clarity purpose. The inset of Figure 5 shows a linear dependence of the peak stripping current on mercury concentration in a range from 15ppb to 1.8ppm with a sensitivity of $1.1 \mu\text{A ppb}^{-1} \text{cm}^{-2}$ and a limit of detection (LOD) of 4.4ppb (fig7a,b).

Despite the LOD value is higher than 2 proposed by EPA, it must be considered as satisfying, because it has been obtained in a preliminary study where the sensing process parameters were optimized for 4 ppm analyte concentration. The present results suggest to refine the study, using 4.4 ppb analyte concentration for

optimizing again the sensing process parameters and to find a new LOD value. Likely, to increase the sensing active surface of NiO can strongly help to improving the LOD value (Patella et al., 2016, and 2017).

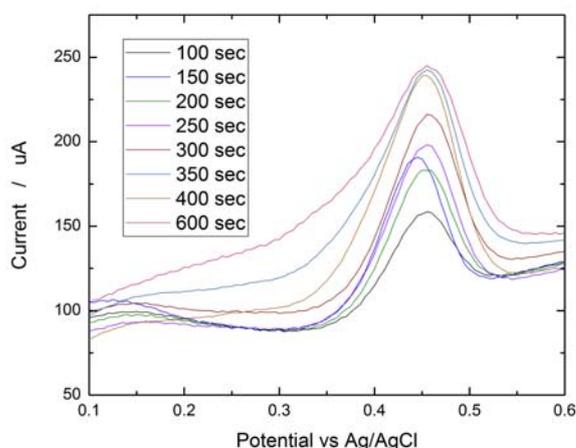


Figure 4: NiO SWASW curves after Hg deposition for different times

Table 1: Optimized values for analytical determination of Hg traces through SWASV

Oxidation temperature	Oxidation time	Analyte pH	Deposition potential	Deposition time
500 °C	120 minutes	3	-0.4V (Ag/AgCl)	350 s

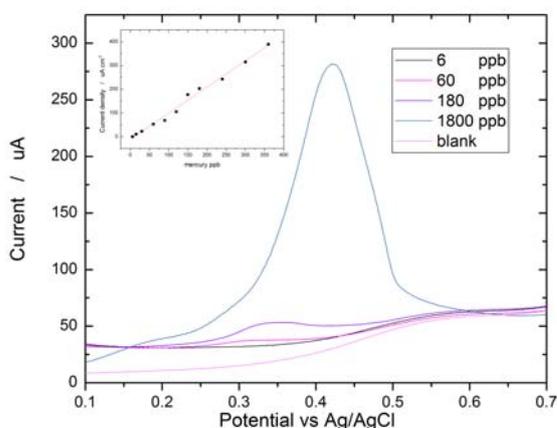


Figure 5: Stripping current peak at different Hg^{2+} concentration for establishing the calibration line shown in the inset, $i (\mu A cm^{-2}) = 1.1 C (ppb) - 11.31$, $R^2 = 0.995$

3. Conclusions

For the first time, it has been shown that NiO film, thermally grown on Ni, can be used as a sensing element for detecting Hg^{2+} in water through square wave anodic stripping voltammetry. Ni was oxidized in air at 500°C for 120 minutes giving a NiO film thickness suitable for the desired purpose. The optimization of the sensing process parameters using a 4 ppm analyte concentration gives a straight calibration line from 15ppb to 1.8 ppm with a LOD value of 4.4 ppb. Further work is in progress for diminishing this value below 2, that is the limit established by EPA for Hg in water. At this aim, new optimization of the sensing process parameters will be conducted using a 4.4 ppb analyte concentration. In addition, 1-D nanostructured NiO can help to reach the goal.

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