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Platinum nanoparticle-modified electrodes, morphologic, and electrochemical studies concerning electroactive materials deposition

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Abstract The present work describes the synthesis of platinum nanoparticles followed by their electrophoretic deposition onto transparent fluorine-doped tin oxide electrodes. The nano-Pt-modified electrodes were characterized by voltammetric studies in acidic solutions showing a great electrocatalytic behavior towards H^+ reduction being very interesting for fuel cell applications. Morphological characterization was performed by atomic force microscopy on different modified electrodes showing a very rough surface which can be tuned by means of time of deposition. Also, nickel hydroxide thin films were galvanostatically grown onto these electrodes showing an interesting electrochemical behavior as sharper peaks, indicating a faster ionic exchange from the electrolyte to the film.

Keywords Platinum nanoparticles · Electrophoretic deposition · AFM · Nickel hydroxide

Introduction

The development of nanoscience has been grown very fast over the last few years. Traditional areas of technology have

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been boosted due to the great advantages that nanoparticulate-based materials may offer [1–3]. In the field of electrochemistry, these advantages are reached by both the enhancement of the total rate of diffusional processes due to the surface to volume ratio [4, 5] and/or leading to a higher number of molecules that can be attached or adsorbed on the inorganic nanoparticles [6, 7]. These features have lead to new advances in traditional areas of chemistry as analytical [8, 9], batteries [10], composite materials [11, 12], solar cells [13], and electrochromism [14].

In the field of catalysis, nanotechnology has a special role. Gold has always been considered as poor catalytic material, but Haruta and coworkers reported that Au nanoparticles adsorbed onto Co_3O4, Fe_2O_3, or TiO_2 showed great catalytic activity for CO, methanol, and H_2 oxidation [15, 16]. Among classical catalytic metals, platinum nanoparticles have been extensively studied [17, 18]. Crooks et al. developed a simple way to obtain Pt nanoparticles by using dendrimers as templates [19] where metallic cations are attached inside the macromolecule followed by chemical reduction. This technique is very interesting as bimetallic nanoparticles can also be obtained such as Pt-Pd, Au-Pt, or Au-Pd [20]. The utilization of Pt nanoparticles has also attracted great interest in analytical chemistry [21] and also in composite materials [22].

In order to immobilize nanoparticles onto conducting substrates, several methods have been described in literature; the simplest one is the direct dropping of colloidal solution. An important contribution was made by Decher's layer-by-layer technique [23]. Although layer-by-layer deposition is very useful in several applications, some problems may occur when using non-electroactive polymers intercalated between conducting materials [24] although some advances have been made by using conducting

polymers in some applications [25, 26]; by this way, better electrochemical performance (by improving both easy diffusion of ionic species and direct electron transfer) must be encountered with the direct contact between the conducting substrate and the nanomaterials. This feature can be reached by using the electrophoretic deposition (EPD) which is a reliable, easy handling, and low cost methodology for the immobilization of materials.

Electrophoresis has been studied since the beginning of twentieth century being vastly employed in ceramic materials technology, where materials with different volumes, sizes, and forms can be easily obtained [27–29]. Electrophoretic deposition is achieved by motion of charged particles under an electric field, forming a deposit onto one of the electrodes, where the roughness of the formed film can be controlled by either electric field or time of deposition. This phenomenon could be applied to nanoparticles deposition once normally nanoparticles present an excess of negative charges on their surface [7, 29]. A scheme of electrophoretic deposition is shown in Fig. 1.

The development of a nanostructured electrode is very important once it can be used as substrate for deposition of many materials where the nanostructured modified surface must be kept. Among many materials studied in nanometer range, nickel hydroxide has been the subject of intense studies due to its varied field of applications such as secondary batteries [30, 31], sensors [32], and electrochromic devices [33]. But, for our purpose, nickel hydroxide is extremely interesting once it can be deposited by simple electrochemical technique in less than 1 min in an inexpensive and easy handling synthesis.

In this work, the synthesis of Pt nanoparticles by reduction of $[PtCl_6]^{2-}$ in presence of methanol is shown. These nanoparticles were immobilized onto electrodes by using elecrophoretic deposition, which was followed by electro-chemical and physical characterization. Also, the electrode-position of nickel hydroxide thin films onto these modified substrates is shown.
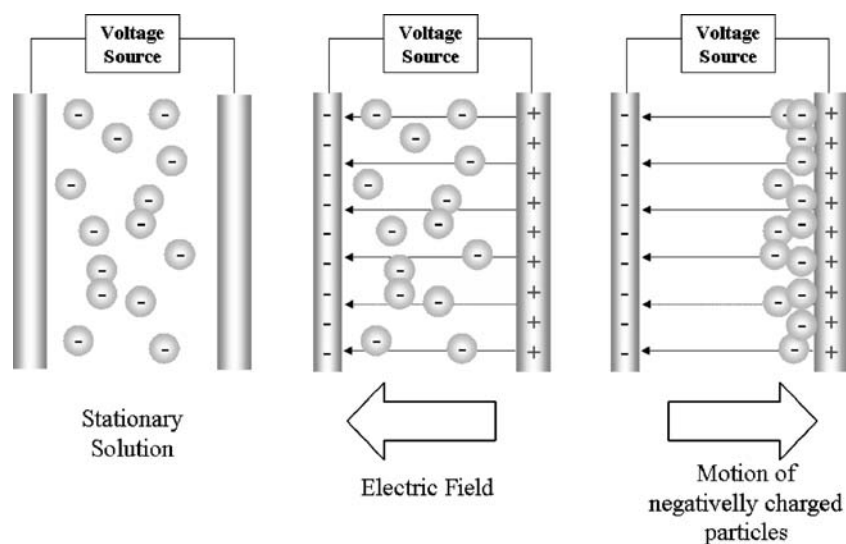
Experimental

All solutions were prepared by using deionized water purified by UHQ Elga System. H_2SO_4 (Shynth), $Ni(NO_3)_2$ (CPQ), KOH (Shynth), Methanol (Merck), H_2PtCl_6 (Aldrich), poly(vinyl pyrrolidone) (PVP) (Aldrich) M_W of 40,000 were used as received without further purification. Pt nanoparticles were obtained by using the method proposed by Teranishi [29]: a mixture of 5 mL of 6.0 m mol L^{-1} H_2PtCl_6 aqueous solution (30 μmol Pt) was added in a 45 mL reflux solution methanol/water (9:1 v/v) containing PVP (PVP/Pt=10 mol/mol). The refluxing time was about 3 h; according to this work, 3-nm particles were obtained.

The nanoparticle-containing solution obtained was used for electrophoretic deposition, where two electrodes (transparent fluorine-doped tin oxide (FTO) or Au ultra-flat) were placed in parallel to each other, and an electric field of 2.0 V cm^{-1} was applied between them for various durations in order to obtain different amounts of deposited nanoparticles. After deposition, the modified Pt electrodes were gently washed with deionized water and dried with N_2.

$Ni(OH)_2$ thin films were grown galvanostatically onto FTO substrates and FTO-Pt modified electrode (120 min of deposition), according to Corrigan's method [34], from 10× 10^{-3} mol L^{-1} $Ni(NO_3)_2$ aqueous solution was supplied a cathodic apparent current density of −0.1 mA cm^{-2} for 50 s. Precipitation of metal hydroxides onto the electrode surface takes place because of the increase of interfacial pH, due to

**Fig. 1** Schematically representation of electrophoretic deposition

the electrochemical reduction of NO_3^- anions, producing OH^- (Eqs. 1 and 2).

$$NO_3^- + 7H_2O + 8_e^- \rightarrow NH_4^+ + 10\,OH^- \qquad (1)$$

$$2\,OH^- + Ni^{2+} \rightarrow Ni(OH)_2 \qquad (2)$$
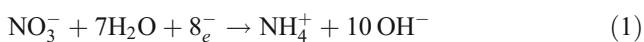
UV-Vis experiments were performed in a HP 8453 Diode Array Spectrophotometer using a quartz cuvette (1 mm optical path). All electrochemical experiments were performed in an Autolab PGSTAT 30 (Ecochemie) potentiostat. Atomic force micrographs (AFM) were taken in a Nanoscope IIIA (Veeco) microscopy in "tapping" mode where at least five points of the sample were analyzed in order to verify the homogeneity of electrode surface, in micrometer scale. The cantilever was driven at resonance frequency (~315 Hz).

Results and discussion

Pt nanoparticles formation was followed by UV-Vis; spectra were taken in different times as seen in Fig. 2. It can be seen that when the refluxing time increases, the band centered in 263 nm decreases becoming unchanged after 90 min of synthesis; this band is related to ligand-to-metal charge transfer transition in $[PtCl_6]^{2-}$ ions, indicating the formation of Pt metallic [29], according to Eq. 3. The solution was initially light-yellow turning brown after synthesis indicating the formation of metallic nanostructures.

$$H_2PtCl_6 + 2\,RCH_2OH \rightarrow Pt^0 + 2\,RCHO + 6\,HCl \qquad (3)$$
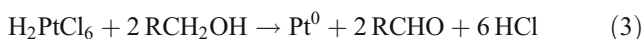
The immobilization of Pt nanoparticles was performed by EPD, applying an electric field of 2.0 V cm^{-1} for
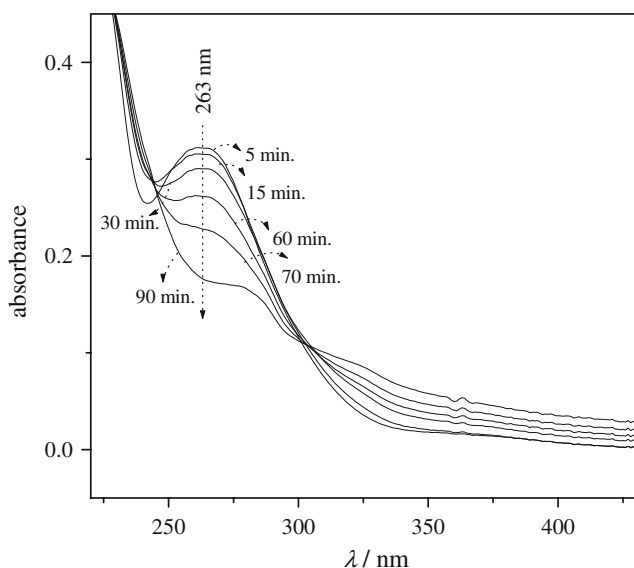

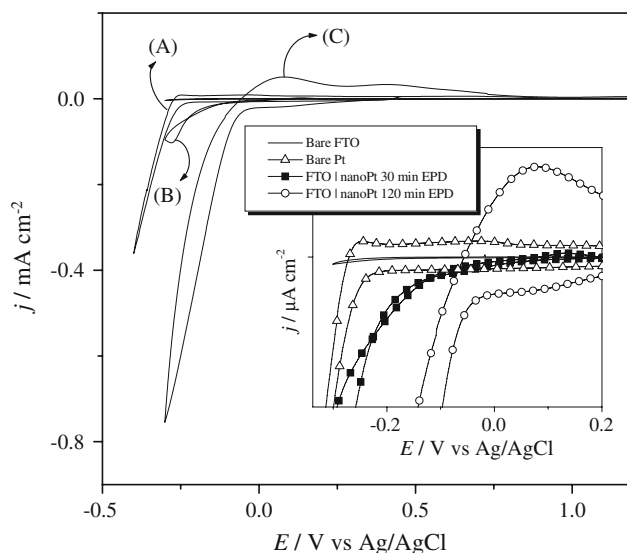**Fig. 2** UV-Vis Spectra from synthetic solution taken in different times of nano-Pt synthesis

Fig. 3 Cyclic voltammograms obtained in H_2SO_4 0.1 mol L^{-1} solution for *A* Bare Pt electrode, *B* nanoPt-FTO EPD electrode modified by 30 min of EPD, *C* Pt-FTO EPD electrode modified by 2 h of EPD. *Inset* more magnification in the region of hydrogen reduction. Scan rate: 5 mV s^{-1}, Pt foil as counter electrode

different durations in order to achieve different amounts of deposited nanoparticles. Here, an important point must be raised that obviously, at higher applied potentials the electric field and the amount of deposited particles will be higher as well, but in this case, higher potentials led to the formation of metallic tin on the negative electrode as well as the formation of gaseous products in both electrodes. These undesirable reactions affected the nanoparticles deposition and led to inhomogeneous deposits and unreliable results; 2.0 V cm^{-1} was chosen as the maximum applied field as none of the above reactions occurred. Figure 3 shows cyclic voltammograms performed in H_2SO_4 0.1 mol L^{-1} solution, each one corresponding to a different amount of nano-Pt (deposited for 30 min and 2 h); for the sake of comparison, the voltammetric behavior of both bare FTO electrode and a Pt bare electrode are also shown.

It can be seen that the bare FTO electrode does not show any electrochemical reaction in the range of applied potential, but for FTO-Pt-modified electrodes, it is very clear that H$^+$ reduction occurs at ca. 0.0 V. When the number of Pt nanoparticles increases the reduction, reaction is enhanced as can be seen by a higher cathodic current due to a higher electroactive surface area; also, the potential of the hydrogen reaction is slight shifted in the positive direction as compared to bare Pt electrode.

To verify the electrode nano-Pt-modified morphology, EPD was carried on Au ultraflat substrates with the same experimental conditions described for FTO electrodes. Ultra-flat electrodes were employed due to the intrinsic roughness of FTO surface which could mask the morphologic surface of Pt deposited. The electrodes were modified using different

lengths of EPD: 30, 60, and 120 min. In Fig. 4, AFM images of the modified Au surfaces are shown.

Increasing deposition times yields higher amounts of deposited material, corroborating the electrochemical experiments. Also, it can be seen that the deposited nanoparticles
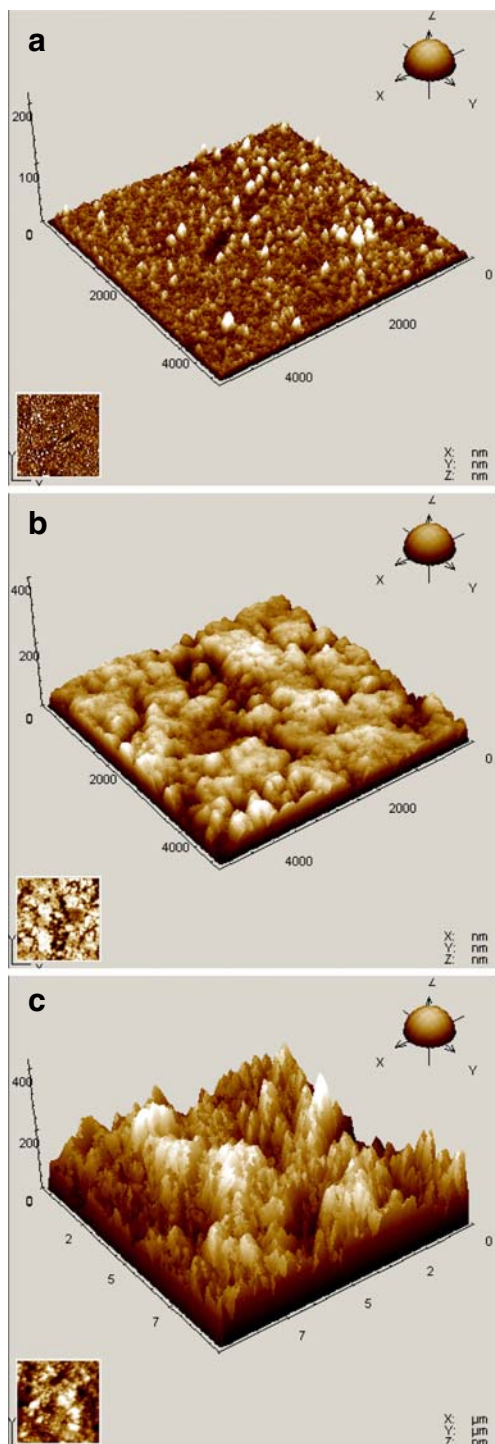

Fig. 4 AFM images obtained from Au ultraflat electrodes modified by Pt nanoparticles deposited by different times of EPD: **a** 30 min, **b** 60 min, and **c** 120 min. Z axis in the nanometer scale
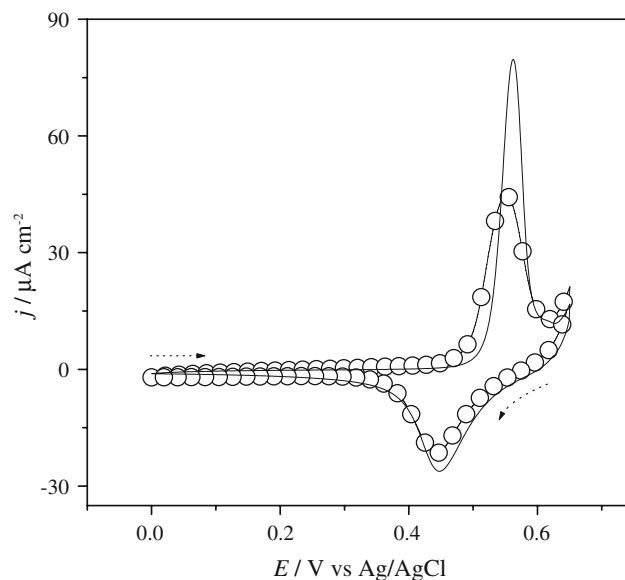

Fig. 5 Cyclic voltammograms obtained in KOH 0.1 mol L^{-1}. Ni(OH)$_2$ electrodeposited onto (*solid lines with circles*) FTO bare electrode and (*solid lines*) nanoPt-FTO electrode. Scan rate: 5 mV s^{-1}, Pt foil as counter electrode

led to a very rough surface and that the roughness can be tuned by the length of the deposition time.

Nickel hydroxide thin films were galvanostatically grown onto nanoPt-FTO-modified electrodes. The galvanostatic method is an interesting way to control the total amount of nickel hydroxide deposited onto electrodes. In Fig. 5 is shown the voltammetric behavior of nickel hydroxide films deposited by a total amount of charge of 5.0 mC cm^{-2} onto bare FTO electrode and nanoPt-FTO electrode (EPD of 120 min).

For the bare FTO electrode modified with nickel hydroxide, the electrochemical behavior is very similar to that showed in literature [33–35]. The redox behavior of nickel hydroxide is well reported where the reduced form is less conductive and its oxidation is accomplished by the insertion of cations (in this case, K$^+$) from electrolyte into the film; on the other hand, during the reduction, these cations are expelled from the film [35, 36]. For nanoPt-FTO nickel hydroxide-modified electrode, a thicker anodic wave can be observed indicating a faster compensation of ionic species and a slight enhancement for the reduced state. This behavior was achieved due to the deposited Pt nanoparticles which provided a very rough surface for the subsequent deposition of nickel hydroxide film.

Conclusions

A simple method for Pt nanoparticle immobilization using electrophoretic deposition was described. Using AFM experiments, it was shown that the electrode surface

roughness can be easily tuned by the deposition time. The modified electrodes showed a very interesting behavior for H^+ reduction; also, the further deposit nickel hydroxide thin films on the Pt nanoparticles leading to a fast ionic exchange from the electrolyte to the inorganic structure was possible. These features show that EPD is a promising tool for the deposition of electroactive materials for high performance devices.

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