A facile method for the fabrication of hierarchical nanosized metal catalysts

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ABSTRACT

Fabrication of well-defined metal nanoparticles with homogeneous distribution is of great importance to enhance the catalysts' effectiveness and to minimize their cost. Here we report the electrodeposition of palladium on modified carbon substrates with an aryl-based organic monolayer and its electrocatalytic performance towards two model reactions with high involvement in energy storage and production systems, i.e. the oxygen reduction reaction (ORR) and the hydrogen evolution reaction (HER) in alkaline medium. Main results indicate that the organic layer dramatically affects the growth, size and distribution of palladium nanoparticles on the conductive substrate, which provokes a great enhancement of the catalytic performance for both studied reactions. These results demonstrate the potential of synthetic methodology for cost-effective production of metallic catalysts.

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1. Introduction

Metallic nanoparticles (MNPs) consist on one of the most widely extended, versatile and effective materials used in electrocatalysis. It is well known that shape, size and distribution of MNPs have strong effect on the catalytic performance. Physical and chemical methods are the most employed strategies to produce MNPs. On the other hand, metal electrodeposition may produce MNPs with well-defined shape and size [1,2].

Metal electrodeposition on carbon substrates such as highly oriented pyrolytic graphite (HOPG) and glassy carbon (GC) is commonly found in bibliography [3,4]. Defect and edge surface sites at HOPG are usually the preferred nucleation sites for the growth of MNPs. The latter leads to a non-homogeneous distribution of MNPs on the carbon-based surface. Furthermore, low carbon-MNPs adhesion is frequently observed, and therefore very unstable systems are commonly achieved [3,4].

Modification of the electrode surface with organic layers has been proposed as a very convenient method to improve the stability and the control of the arrangement when metallic nanoparticles are incorporated on a conductive surface [5–7].

One of the most extended strategies to modify electrode surfaces is the use of aryl diazonium salts [7–11]. However, a full control of the organic monolayer growth onto the electrode surface has not been reported. The latter is due to the well-known polymerization mechanism when electrografting of these molecules is carried out [12]. Thus, a thick layer with slow electron transfer rates on the electrode surface is obtained. In this sense, a strategy to control the thickness of the monolayer is needed, and the most simple and easy method is the use of radical scavengers [13–15].

In a previous work, gold electrodeposition on modified HOPG with an organic layer based on aryl diazonium salts was carried out [16]. Main results indicated the formation of Au nanoparticles with well-defined size and homogeneous distribution onto the organic layer. The opposite happened on bare HOPG, where randomly distributed MNPs were observed at step and defect surface sites. However, the electrocatalytic behavior of this new type of materials was not studied.

Having this in mind, palladium was electrodeposited on unmodified and aryl-modified carbon substrates and their electrochemical performance toward two model reactions (oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER)) in alkaline medium was scrutinized.

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2. Experimental section

2.1. Materials

4-Nitrobenzenediazonium tetrafluoroborate (NBD) (Aldrich, 97%), tetrabutylammonium tetrafluoroborate ($TBAFB_4$) (Sigma-Aldrich, 99%), acetonitrile anhydrous (ACN) (Sigma-Aldrich, 99.8%), 2,2-Diphenyl-1-picrylhydrazyl (DPPH, Sigma-Aldrich, 98%), KCl (Merck, 99.5%), CH_3CH_2OH (Merck, p.a.), $PdCl_2$ (Sigma-Aldrich, 99.9%), $HClO_4$ (Merck, 70–72%), $NaClO_4$ (Sigma-Aldrich, 98%) and NaOH (99.99%; Sigma-Aldrich were used as received. Ultra pure water (18.2 MΩ·cm; Milli-Q, Millipore) was employed to prepare all the solutions. Before each measurement, Argon (N50, Air Liquide) was bubbled through the solution to avoid dissolved oxygen. For the oxygen reduction reaction (ORR) experiments, the electrolyte was saturated with O_2 (Air Liquide, 99.995%). HOPG samples (Grade SPI-2) were obtained from SPI Supplies. GC electrode tips from Methrom Autolab (diameter 3 mm) were used.

2.2. Sample preparation

In order to modify the GC surface, three voltammetric cycles from 0.75 to −0.60 V at 0.10 V s^{-1} in 1 mM NBD + 2 mM of DPPH + 0.1 M $TBAFB_4$/ACN solution was carried out. After that, the sample was sonicated in ACN solution and rinsed with ultra pure water. Nitro groups exposed to the medium were reduced in CH_3CH_2OH/H_2O 10:90 + 0.1 M KCl solution by cycling the potential three times from 0.0 to −1.2 V at 0.05 V s^{-1}. Palladium electrodeposition was performed through a potential pulse from 0.80 V to −0.20 V for 10 s in bare and modified GC electrodes in 0.1 mM $PdCl_2$ + 0.1 M $NaClO_4$ + 1 mM $HClO_4$ solution. The charge corresponding to Pd deposition on bare and modified GC electrodes was determined by integration of the current transient in presence of Pd in solution, subtracted by the integrated current in the blank current transient in absence of Pd.

2.3. AFM analysis

HOPG substrates were used due to the high roughness of GC electrodes. Modification of the HOPG surface was carried out with the same procedure described for GC electrodes (2.4), although a platinum foil was used as counter electrode due to the small space design of the cell. Topographic AFM images were acquired in PeakForce Tapping mode using a multimode microscope with a Nanoscope V control unit from Bruker. Scan rates of 0.5–1.2 Hz were used. Measurements were done with Scan-Asyst HR (100–160 kHz, and 0.4 N/m) tips (from Bruker). AFM images were analyzed with Nanoscope Analysis 1.5 software.

2.4. Electrochemical experiments

The electrochemical experiments were carried out at room temperature using a three-electrode glass cell, a carbon rod as counter-electrode and an Ag/AgCl(sat) electrode as a reference. All the recorded potentials are referred to the Ag/AgCl scale. The working electrode consisted in a glassy carbon disc (0.07 cm^2) embedded in a rotating disk electrode (RDE) tip (Metrohm).

Electrochemical measurements were performed using an Eco Chemie Autolab PGSTAT302 potentiostat/galvanostat in 0.1 M NaOH electrolyte solution. For the ORR, the electrolyte was saturated with O_2 over 20 min at a controlled disk potential of 0.15 V. The steady polarization curves were recorded in a potential range from 0.15 to −1.2 V at rotating speeds of 100, 400, 600, 900, 1600 and 2500 rpm at 0.005 V s^{-1}. Before HER experiments, argon

was bubbled through the solution to avoid dissolved oxygen, and a linear sweep voltammetry (LSV) from 0.4 to −1.7 V was performed.

3. Results and discussion

3.1. Modification of carbon surfaces by an organic layer

Surface modification of carbon electrodes in this work consists of the deposition of an aryl-based organic layer and the subsequent electrodeposition of palladium on the modified surface. Fig. 1 summarizes the principal steps of the modification process.
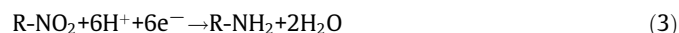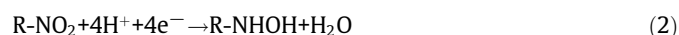
The electrografting process is based on the formation of an aryl radical through the reduction of a precursor. This radical can bind to the surface forming a C—C bond. The high efficiency of the process leads to the generation of multilayered films without control of thickness. In order to impede the formation of multilayers on the surface, a radical scavenger (DPPH) is added to the solution. This radical scavenger acts as a molecule that bonds to the excess aryl radicals (grafting specie) in the electrode-solution interface, promoting the formation of a film of aryl groups in a monolayer structure [13,14]. Employing this procedure, a sub-monolayer with free substrate areas on HOPG has been previously reported [16,17]. AFM images revealed that the height of this layer is around 0.8 nm, in agreement with the height of a molecule perpendicular attached to the surface [16,17]. This process leaves a carbon surface covered by nitrophenyl groups, which is employed in the current work.

Fig. 1a shows the cyclic voltammograms for the electrografting of the diazonium salt on the GC surface. The first negative going sweep direction (black line) reveals a cathodic peak at ca. 0.45 V related to the NBD reduction and anchorage on the GC surface. It should be noted that the charge associated with this cathodic peak decreases with subsequent scans, which is related to the non-full coverage of the GC surface during the first scan. Indeed, it is well known that complete coverage of the GC surface by NBD in absence of DPPH is reached during the first scan, and consequently the cathodic peak is absent during the subsequent cyclic voltammograms [17]. Additionally, Fig. 1a depicts the reversible DPPH/DPPH$^-$ redox couple at ca. 0.3 V [13,16].

Fig. 1b depicts the second step of the GC surface modification, which consists of electrochemical reduction of the NO_2 groups. This reduction of NO_2 groups is a complex mechanism where different reactions can take place. The reduction process is pH dependent and may proceed by a 4 or 6-electrons mechanism to produce NHOH or NH_2 groups, respectively [17]. In our case, electrochemical reduction of NO_2 groups has been carried out in a neutral media according to ref. [18]. Fig. 1b reveals a broad cathodic wave associated with the massive reduction of NO_2 groups during the first negative going sweep potential. After the strong reduction step, a reversible redox couple at ca. −0.3 V becomes apparent during the subsequent cyclic voltammograms. The reversible redox couple is related to the NHOH – NO redox system, as shown in Eq. (1):

$$R\text{-}NO + 2H^+ + 2e^- \leftrightarrow R\text{-}NHOH \tag{1}$$

Noticeable is the absence of the cathodic current associated to the reduction of NO_2 after the first cyclic voltammogram, which indicates that all nitrogen-containing groups anchored to the GC surface have been reduced to NHOH (via 4 electrons, Eq. (2)) or NH_2 (via 6 electrons, Eq. (3)):

$$R\text{-}NO_2 + 4H^+ + 4e^- \rightarrow R\text{-}NHOH + H_2O \tag{2}$$

$$R\text{-}NO_2 + 6H^+ + 6e^- \rightarrow R\text{-}NH_2 + 2H_2O \tag{3}$$

The latter was confirmed by XPS analysis, in which the signal of NO_2 groups located at 406 eV disappears after the reduction step in aqueous media (EtOH/H_2O 10:90 in 0.1 M KCl solution) [16]. After