Fabrication of Highly Ordered Arrays of Platinum Nanoparticles Using Direct Laser Interference Patterning

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ABSTRACT Highly ordered electrode arrays composed of lines of platinum nanoparticles deposited onto gold substrates have been made by direct laser interference patterning of polyaniline thin films, followed by electrochemical deposition of platinum nanoparticles. Nanostructured arrays of electrocatalytic platinum particles are built in that way.

KEYWORDS: nanoparticles array • interference patterning • polyaniline mask

INTRODUCTION

The synthesis of ordered nanomaterials is one of the key points in the development of novel nanotechnologies. For several applications, control of the distribution of the nanomaterials onto substrates is as essential as precisely controlling their size. One particularly interesting market is that of power sources for portable applications using micro fuel cells (1). In those systems, a careful design could improve significantly the performance, while the nature of the application allows for higher fabrication cost than that in larger cells. Previous investigations of the construction of micro fuel cells can be grossly separated into two approaches: (i) a top-down approach involving miniaturization of existing designs for polymer−electrolyte−membrane fuel cells (2) and (ii) a bottom-up approach employing microfabrication techniques developed for the semiconductor industry to fabricate fuel cell structures (3). Here we describe the development and testing of highly ordered electrodes built of nano/microlines of platinum nanoparticles electrodeposited onto gold substrates for its application in a direct methanol fuel cell. To do that, we use a combination of bottom-up and top-down techniques, similar to lithographic methods. Lithographic patterning of polyaniline (PANI) has been achieved by using acid (4) or base photogenerators (5). We have produced PANI patterns by hydrolyzing N-nitrosated PANI by chemical (6) and photochemical (7) routes.

Here, we used PANI patterns to mask the electrodeposition of platinum nanoparticles into periodic arrays. Direct laser interference patterning (DLIP) of PANI thin films is used to produce the PANI patterns. The technique has several advantages: (i) periodic patterns of features with a well-defined long-range order in the micro/nanoscale can be fabricated in a few seconds; (ii) areas ranging from square millimeters to square centimeters can be structured in each laser pulse; (iii) neither clean rooms nor special conditions are necessary; (iv) the size and periodicity can be adjusted easily in each pulse, allowing tailoring of the electrode to the application.

EXPERIMENTAL SECTION

Materials. Aniline (Merk) was distilled prior to polymerization using reduced pressure. The rest of the reagents, hexachloroplatinic acid ($PtCl_6H_2$), sodium sulfate (Na_2SO_4), *N*-methyl-2-pyrrolidone (NMP), and sodium hydroxide (NaOH), were used as received from the manufacturer.

Synthesis of PANI onto Gold Electrodes. The electrochemical synthesis of PANI was performed on the gold electrode by cycling (three times) the work electrode between −0.20 and +1.10 V vs SCE at 50 mV · s^{-1} in a solution consisting of 0.1 M aniline in 1 M HCl, using platinum as the counter electrode. The polymerization was completed by cycling (15 times) the electrode between −0.20 and +0.65 V vs SCE at 50 mV · s^{-1} in the same solution. The film was washed with 1 M HCl for ∼2 min to free it of aniline.

Laser Interference Experiments. A Q-switched Nd:YAG (YAG = yttrium aluminum Garnat) laser (Spectra Physics) with a frequency of 10 Hz and a pulse duration of 10 ns was used for the interference experiments. The laser beam was split into two subbeams that were guided by mirrors to interfere on the sample surface. The period of the linelike pattern was 4.2 μm, and the utilized wavelength was 355 nm.

Platinum Deposition. The platinum strips were electrodeposited in a 1×10^{-3} M $PtCl_6H_2$ + 0.1 M Na_2SO_4 electrolyte, adjusting to pH 11 by adding NaOH. The potential was cycled between 0.0 and 1.25 V at 100 mV · s^{-1} for 25 min (step 2).

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Methanol Oxidation. The electrochemical oxidation of methanol was carried out using a conventional cell of three electrodes using a 0.5 M H_2SO_4 + 0.1 M methanol solution. The counter and reference electrodes were a platinum foil and a hydrogen reversible electrode immersed in the same working solution, respectively. A structured platinum nanoparticle array on gold and the platinum nanoparticles onto flat gold were used as working electrodes. The scan rate was 100 $mV \cdot s^{-1}$ in all experiments.

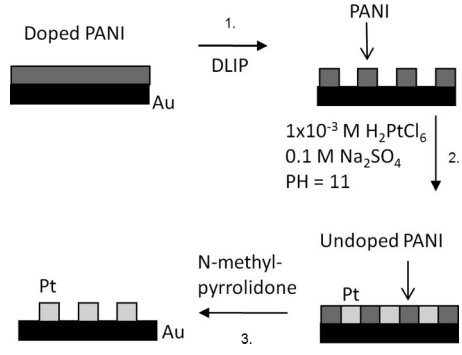
RESULTS AND DISCUSSION

The sequential procedure to obtain the patterned electrodes is depicted in Scheme 1. First, a thin film of PANI is electropolymerized onto the gold electrode. Very thin (>10 nm) and uniform films can be deposited in such a way (8). Then the PANI film was patterned using DLIP at ambient conditions, producing regular line arrays of PANI (Scheme 1, step 1) (9). Because the photothermal and thermal stabilities of gold and PANI are quite different, it is possible to fabricate sets of regular lines of PANI and clean gold, separated by a fixed distance (period).

Taking into account that PANI behaves as an electrical insulator in neutral or alkaline solutions (10), we electrodeposited metals (in this work platinum) selectively onto the free gold lines (Scheme 1, step 2). The polymer mask allows deposition of the platinum only onto the ablated areas (see the Experimental Section for details). After that, PANI was removed using an appropriate solvent, NMP, leaving the electrode composed of alternating lines of platinum and gold (Scheme 1, step 3).

The topography of the electrode after the laser interference local ablation of PANI has been analyzed by white light interferometry (WLI). Well-defined arrays of PANI lines could be fabricated in one single laser pulse because the local and periodic ablation of the polymer at the interference maxima positions (Figure S1a in the Supporting Information). Moreover, the width of the lines and their separation are very regular (Figure S1b in the Supporting Information). We measured a spatial period and height of 4.2 μm and 347 nm, respectively. Figure 1a shows the scanning electron microscopy (SEM) image of the structure obtained after ablation of the PANI film. The surface shows homogenous and ordered lines of polymer and gold of ca. 3 and 2 μm, respectively. In addition, the micrographs reveal that the entire polymer was removed at the position where the light pattern has a maximum intensity because of the local and periodical ablation. After that, platinum nanoparticles were deposited by electrochemical reduction of $PtCl_6^{-2}$ ions. Figure 1b shows the SEM micrograph of the structure obtained after electrodeposition of platinum and dissolution of the PANI with NMP. Quite regular lines of platinum nanoparticles that are electrodeposited only on the gold lines could be observed. The presence of nanoparticles is related to the metal nucleation in specific sites. The size of the lines of platinum particles built in this easy way has a width of ca. 2 μm, corresponding to the size of the free gold lines. The results show that arrays of platinum nanoparticles could be straightforwardly fabricated using DLIP of PANI to produce a mask. The method could be easily extended to other substrates, e.g., platinum, glassy carbon, and indium–tin oxide. It also could be used to deposit nanoparticles of other active metals such as ruthenium, palladium, or iridium.

Scheme 1. Fabrication Procedure of the Patterned Gold–Platinum Electrodes: (1) DLIP of PANI; (2) Electrochemical Deposition of Platinum; (3) Removal of the Remnant PANI Lines



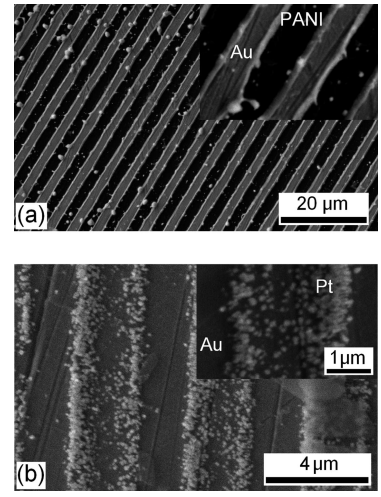


FIGURE 1. SEMs of the electrodes: (a) PANI patterned by DLIP on gold; (b) platinum nanoparticle array produced after platinum deposition on part a and removal of the PANI lines.

Additionally, it has been shown that DLIP is able to ablate spots and other patterns, beside lines (11). Therefore, the structured deposit could be in the form of dot arrays or other periodic patterns.

Finally, we tested the ability of the periodic arrays to act as electrodes. Because methanol is electrochemically oxidized on platinum and not on gold, we used the reaction to detect the presence of platinum. The performance of the electrode for the methanol oxidation was evaluated using cyclic voltammetry (Figure 2). To ensure that platinum nanoparticles have the same size, two regions, one flat and the other patterned, of the same gold electrodes were compared. The voltammograms display the typical behavior for methanol oxidation on platinum (Figure 2). However, the patterned array of nanoparticles shows a current density, calculated using only the area actually covered by particles, which is ca. 4.9 times larger than the one measured with an electrode made of nanoparticles deposited onto a nonpatterned surface.

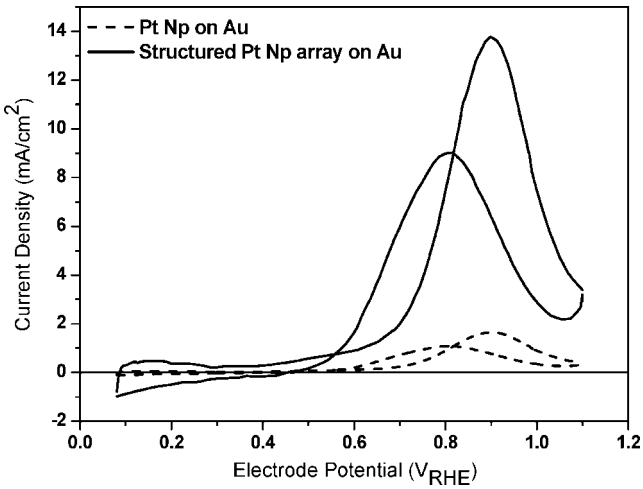


FIGURE 2. Cyclic voltammograms of methanol (0.1 M CH_3OH in 0.5 M H_2SO_4) oxidation on platinum particles deposited onto flat gold (dashed line) and platinum nanoparticles deposited on a patterned electrode (solid line). Scan rate = 100 mV · s^{-1}. The current density is calculated using only the area covered by platinum nanoparticles in each case.

A possible explanation to the observed behavior is that the array of 2 μm wide platinum nanoparticle strips on gold acts as an array of ultramicroelectrodes (12). Therefore, the mass transfer of reactants and products to/from individual lines is cylindrical instead of planar, as in a flat surface. Therefore, the reaction occurs at a faster rate on ultramicroelectrodes than on flat electrodes. Because methanol oxidation is controlled by the heterogeneous rate constant, it is unlikely that only increased diffusion of the reactant alters the current. On the other hand, it is known that poisoning of the platinum surface by CO and other side products of the oxidation controls the methanol oxidation rate (13). Therefore, an enhanced diffusion of those products could free the platinum surface, increasing the methanol turnover on platinum.

We have demonstrated a robust method for the fabrication of highly ordered electrode arrays composed of strips of platinum nanoparticles deposited onto gold substrates. It is suggested that the patterned gold–platinum electrode acts as an array of ultramicroelectrodes. The method allows the production of nanostructured patterns that could be useful in different research fields. Using the method, it is possible to fabricate structures made of electroactive oxides (NiOx, CoOx) or even other conductive polymers such as polypyrrole, polythiophene, or poly(3,4-ethylenedioxythiophene). In that way, nanostructured electrodes useful in batteries, supercapacitors, could be easily built.

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Supporting Information Available: WLI images of a patterned PANI layer on gold using 126.75 mJ/cm^2 of laser fluence. This material is available free of charge via the Internet at http://pubs.acs.org.

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