Electrochimica Acta 116 (2014) 194–202

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Simple fabrication of active electrodes using direct laser transference

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ARTICLE INFO

Article history:
Received 20 May 2013
Received in revised form 15 October 2013
Accepted 20 October 2013
Available online 13 November 2013

Keywords:
Modified electrodes
Laser ablation
Polyaniline
Noble metals
Nanoparticles desposition

ABSTRACT

Direct laser transference (DLT) method is applied to obtain electrodes modified with thin films of conducting polymers (CPs) or catalytic metals. A short (6–10 ns) pulse of laser light (second harmonic of Nd-YAG Laser, $\lambda = 532$ nm) is shined on the backside of a thin (<200 nm) film of the material to be transferred, which is deposited on a transparent substrate. The illuminated region heats up and the material (conducting polymer or metal) is thermally transferred to a solid target placed at short distance in air. In that ways, CPs are transferred onto polypropylene, glass, indium doped tin oxide (ITO), glassy carbon and gold films. In the same manner, electrocatalytic metals (platinum or gold) are transferred onto conductive substrates (glassy carbon or ITO films on glass). The films have been characterized by scanning electron microscopy, cyclic voltammetry, atomic force microscopy, UV-visible and Fourier Transform Infrared spectroscopies. The chemical, electrical and redox properties of the polymeric materials transferred remain unaltered after the transfer. Moreover, CP multilayers can be built applying DLT several times onto the same substrate. Besides polyaniline, it is shown that it is also possible to transfer functionalized polyanilines. The electrode modified with transferred Pt shows electrocatalytic activity toward methanol oxidation while ferricyanide shows a quasireversible behavior on electrodes modified with transferred Au. The method is simple and fast, works in air without complex environmental conditions and can produce active electrodes on different conductive materials. It only requires a pulsed high power Nd-YAG laser, which presently is available at low cost, and thin films on transparent substrata as source. In this way DLT seems to be a general and straightforward method to build technological devices based on CPs and/or electrocatalytic metals including electrodes for direct methanol fuel cells and sensors.

1. Introduction

Electrochemical electrodes are made of an electrical conductor where an electrochemical reaction occurs at some large enough rates to use in the intended application. The reaction rate is directly related to the charge transfer across the interface. Moreover, in some applications (sensors, batteries, electrosynthesis) the electrode should be active for a specific reaction (e.g. oxidation of the analyte) while significantly less active to other reactions (e.g. oxidation of the interference). Such a behavior is linked to the catalytic activity of the material at the interface. In plain solid materials (e.g. active metals), this activity usually involves the adsorption of the solution redox species on the surface changing the redox mechanism from outer sphere to inner sphere. Another possibility is to place a redox solid species on the electrode surface which reacts with the solution redox species in an outer sphere redox reaction. In the latter case, the redox species could be inorganic (e.g. a redox oxide) or organic (e.g. an electroactive polymer) extending greatly the quantity of different catalysts. Moreover, redox catalysts are active only on soluble redox couples lower than its redox potential bringing on specificity to the catalytic electrode. However, the redox catalysts have low electronic conductivity and have to be deposited on a cheap electronic conductor.

On the other hand, while there are electrode materials (e.g. Pt) which are active for most reactions and good electronic conductors, they are too expensive to be used in bulk form to build technological devices. Therefore, a method to deposit small amounts of the catalyst on a cheap electronic conductor is of interest.

In real applications it is usually necessary to place the electrocatalyst only in some region of the electrode to be able to contact the conductor in another region. Obviously, some redox catalyst (e.g. conducting polymers) and active metals (e.g. Pt) can be easily electrodeposited. However, the procedure has poor reproducibility and complex masking procedures are required to deposit the material only in one electrode region.

Conducting polymers (CP) are interesting materials for a variety of technological applications, including electrochemical devices. Most conducting polymers (e.g. polyaniline) are not soluble in common solvents and can only be deposited by in situ chemical or electrochemical polymerization [1]. The in situ procedure has poor reproducibility and it is difficult to produce patterns of the polymers on the electrodes. Additionally, functionalized

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http://dx.doi.org/10.1016/j.electacta.2013.10.146

conducting polymers which cannot be produced by electrochemical or chemical copolymerization can be produced by chemical post modification [2]. Therefore, a physical method to deposit thin polymer films would be of great interest [3–5].

Laser technology has introduced a number of advantages in many fields of industrial production and research. The properties of the laser are high speed, high power density, facility of automation, non-contact system, possibility to operate in a clean way without the necessity of additional workings, and adaptability to various types of material such as steel, aluminum alloys, plastic, wood and textile materials. Taking into account these advantages, the laser has been used for TiO_2 transference onto glass materials [6]. On the other hand, there are a lot of experimental works that involve ablation of metals surface [7–9]. For all these reasons, the laser technology applied to metals materials is a powerful method for the synthesis of high quality multicomponent thin films [10]. Also the laser technology has been used by Gleason et al. who show that it is possible to deposit thin films of conducting polymers by physical sublimation at high vacuum [11]. It has been also shown that frozen solutions of polyaniline (PANI) can be used as sources for laser transference methods in vacuum [4]. It has been shown that conducting polymers can be ablated by short laser pulses, removing the polymer without degradation [12–14]. Taking into account the early results, it is reasonable to think that the physically removed material could be deposited on a nearby object, effectively transferring the material polymer. In the best of our knowledge, laser has not been used to fabricate electrodes for electrochemical devices (sensors, micro-batteries, super-capacitors, electrochromic displays, etc.). In that sense, the transference of metals by laser ablation is well known. However, its use to produce electrochemical devices is limited.

In the present communication we describe a general method to produce electrodes for electrochemical devices by laser induced transfer. The direct laser transference (DLT) method shows to be able to fabricate electrodes modified with conducting polymers or electrocatalytic metals.

The method is simple, fast, and works in air without complex environmental conditions. It only requires a pulsed high power Nd-YAG laser, which presently is available at low cost, and thin source films on transparent substrata, which can be easily prepared by available methods. Obviously, there are plenty of chemical deposition methods, such as electrochemical deposition, layer by layer self assembly, in situ polymerization, etc. In the same way, physical vapor deposition or sputtering methods are able to produce metal deposits on different surfaces. However, besides the fact that laser techniques are able to produce small surface patterns which are difficult to make by other methods, the extreme simplicity of the method makes it suitable for different applications where other methods are difficult to apply. Moreover, it is able to produce active electrodes by deposition onto different conductive materials (gold, ITO, glassy carbon) which is not the case of other deposition methods.

2. Experimental

2.1. Direct laser transfer method (DLT)

A high power (>1000 mJ) Q-switched Nd:YAG (YAG: Yttrium Aluminum garnet) laser (1064 nm frequency doubled to 532 nm) with a repetition rate of 10 Hz and pulse duration of 6 ns was used for performing DLT. The laser is commercialized for tattoo removal and is available at low cost (<2000 USD). All the samples were performed using one laser single pulse per transfer and the substrate was held at room temperature in air during transfer. The same laser was used to transfer platinum and gold. The laser fluence was adjusted by controlling the pumping flashlamp voltage of the laser. It was set at different values depending of the material to transfer, as stated in each experience description. The laser energy was measured with a pyroelectric energy meter (Melles-Griot model 13PEM001).

2.2. Polymerization onto transparent substrates

Aniline and Pyrrole (Merk) were distilled prior to polymerization using reduced pressure. Ammonium persulphate (Aldrich) was used as received from the manufacturer. All aqueous solutions were prepared using twice-distilled water. All the other reagents were of analytical quality. Polyethylene (PE) and Polypropylene (PP) films (1 mm thick) were purchased from Goodfellow and used as transparent substrates.

2.3. Synthesis of polyaniline (PANI) thin films

PANI was prepared by oxidation of aniline (0.1 M) in 1 M HCl with ammonium persulphate (equimolar to aniline) following the procedure published elsewhere [15]. The reactor was immersed in an ice-water bath to keep the temperatures below 5 °C. In order to produce PANI onto polyethylene (PE) or polypropylene (PP), 4 cm × 4 cm of each polymer film were immersed in the polymerization solution. In that way, thin (200–600 nm) films of PANI are deposited onto the transparent substrates [16]. After the polymerization finished, the films of PANI on the plastic substrates were washed for 15 min in pure water to ensure that no reactant was retained in the film.

Due to the mechanism of polymer growth, the polyaniline is obtained in its half oxidized (emeraldine salt) form. By thoroughly washing with ammonia solution, the film can be converted into its emeraldine base form.

2.4. Synthesis of functionalized PANI films

The functionalized PANI films (F-PANI) were produced by coupling of diazonium ions with PANI in base form thin films [17]. The amines were diazotized with sodium nitrite and concentrated HCl in an ice bath [18]. PANI films were suspended in TRIS® buffer (pH = 8) and mixed with the diazonium salt solution in an ice bath. The modified films were washed first with 1 L of 1 mol L^{-1} HCl solution and then with 1 L distilled water. Then the films were dried (dynamic vacuum for 48 h). Metals (gold or platinum) thin films were deposited on glass by physical vapor deposition (PVD) at U. Saarland (Saarbrucken, Germany).

2.5. Polymer characterization

2.5.1. UV-visible Spectroscopy

The UV–visible (UV–visible) spectra of the transferred polymer onto Polypropylene, ITO substrate or quartz were recorded by transmission using a HP 8452 UV-visible Spectrophotometer. The spectra is taken ex situ using films dried with air after being stabilized in aqueous solution of defined pH, which is specified in the text.

2.5.2. FTIR-spectroscopy

The Fourier transform infrared spectroscopy (FITR) spectra were performed in a Bruker Tensor 27 FTIR spectrometer with a resolution of 4 cm^{-1}. The Fourier Transform Spectra of the polymer were obtained by transferring the CP onto a KBr pellet. The pellets were obtained by pressing finely milled KBr (Aldrich) powder for 15 min at 15 Tn/cm^2 under dynamic vacuum. The polymer was transferred using 350 mJ cm^{-2} of fluence.