



Simple fabrication of active electrodes using direct laser transference



P. Cavallo, R. Coneo Rodriguez, M. Broglia, D.F. Acevedo*, C.A. Barbero*

Departamento de Química, Universidad Nacional de Río Cuarto, Ruta 8, km 601, Agencia postal No 3, 5800 Río Cuarto, Argentina

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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.

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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

* Corresponding authors.

E-mail address: cbarbero@exa.unrc.edu.ar (C.A. Barbero).

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 TiO₂ 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 (Saarbrücken, 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 (FTIR) 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/cm² under dynamic vacuum. The polymer was transferred using 350 mJ cm⁻² of fluence.

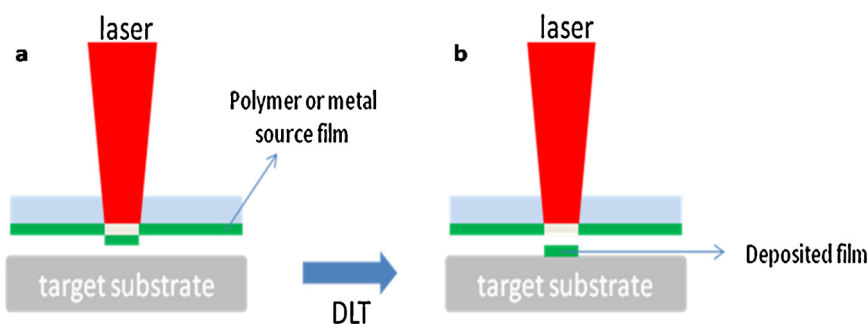


Fig. 1. Schematic description of the direct laser transfer method (DLT). (Left) the material (metal or conducting polymer), deposited onto a transparent substrate, is heated by a laser beam and vaporizes at the material/substrate interface. The vaporized material closest to the interface pushes the non-vaporized material away from the substrate and into the target substrate, (right) where it is deposited.

2.5.3. Scanning electron microscopy

The polymer was transferred onto a flat silicon substrate using 350 mJ cm^{-2} of fluence and then the morphology was studied using scanning electron microscope (SEM). A high-resolution scanning electron microscope FEI Strata DB 235 at 5 kV acceleration voltage was used.

2.5.4. Cyclic voltammetry

The electrochemical experiments were performed using a PC controlled Autolab PGSTAT30 potentiostat–galvanostat. A conventional three-electrode cell involving Pt as counter electrode, a saturated calomel electrode (SCE) as reference and a conductive substrate (gold, glassy carbon, ITO) as a working electrode, was used. The PANI salt form was transferred onto the conductive substrate, using 350 mJ cm^{-2} of fluence. Electrochemical measurements of the PANI transferred (PANI-T) were carried out in an aqueous solution of 1 M HCl and the voltammograms were recorded at 50 mV/s between 0.05 V and 0.6 V vs. SCE.

2.5.5. Atomic force microscopy

The atomic force microscopy (AFM) measurements were made with an Agilent 5420 AFM/STM microscope. A commercial Point Probe® Plus Contact/Tapping Mode with a force constant of 6 N m^{-1} , 156 Hz was used in contact mode.

3. Results and discussion

3.1. Direct laser transference method (DLT)

A first step to apply the DLT involves the generation of a source film of the material to be transferred deposited on a transparent substrate (see Fig. 1a). In this work we use polyaniline, modified polyanilines, and metals (Pt and Au). The laser beam is shined onto the source film, which is placed $500 \mu\text{m}$ above the target substrate (Fig. 1b). When the laser beam impacts to the source substrate, the materials are transferred to acceptor substrate (Fig. 1c).

The method of direct laser transfer could be explained as follows: (1) the material to be transferred is heated by a laser beam; (2) the material is vaporized at the interface between the transparent and the source material; (3) the vaporized material closest to the interface pushes the non-vaporized material away from the substrate to the acceptor substrate; (4) the transfer material is collected on the accepted substrate. Fig. 1 shows the mechanism of the laser transfer technique. During the process of laser transfer, the some part of the material is sublimated or melted.

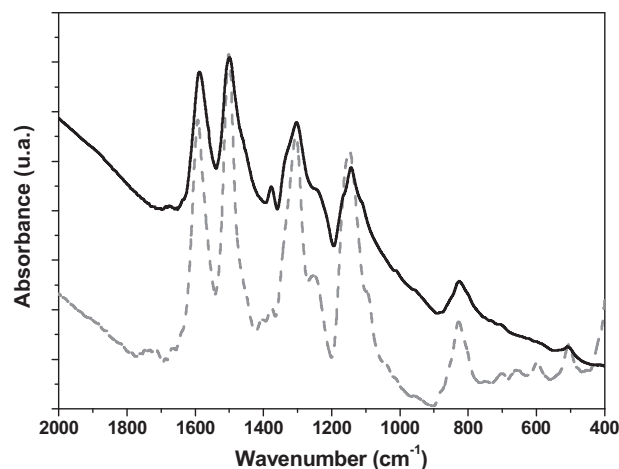


Fig. 2. FTIR spectra of doped PANI (source, black continuous line) and transferred doped PANI (gray dashed line).

3.2. Direct laser transference method applied to conducting polymers

PANI salt form was chemically deposited onto PP or PE, and these films were employed as a source substrate. The plastic film covered with PANI is placed close ($500 \mu\text{m}$) to the target substrate, as described in Fig. 1. Then a single laser pulse (532 nm , 350 mJ cm^{-2} , 6 ns pulse width) is applied. It can be seen that a green circular spot appears in the target substrate and a circular hole is made on the source film. To check if the conducting polymer suffers degradation during transfer, the material is transferred onto a KBr pellet, a material transparent to medium infrared radiation, to be able to measure the infrared spectrum of the deposited layer. For comparison, the PANI on the source film is rubbed with KBr powder and the spectrum of a KBr pellet containing the source polymer is also measured.

The FTIR spectra of polymer source and transferred PANI (emeraldine salt form) are shown in Fig. 2. Both spectra present characteristic bands of doped PANI: at 1574 cm^{-1} assigned to the C=N stretching of the quinoid rings, at 1490 cm^{-1} assigned to the C=C stretching of benzenoid rings, at 1288 cm^{-1} assigned to C–N stretching, at 1157 cm^{-1} assigned to imine (C=N–H) vibration and at 800 cm^{-1} assigned to out of plane vibrations of the C–H in the aromatic rings [2]. Both the similarity of the spectra and the absence of bands usually due to degradation (e.g. at $1650\text{--}1750 \text{ cm}^{-1}$ assigned to C=O vibrations of quinines [19]), in

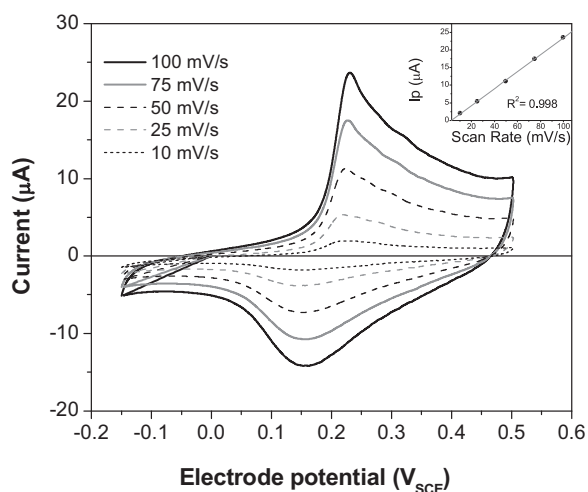


Fig. 3. Cyclic voltammogram of polyaniline emeraldine salt form transferred on gold electrode = 2 M HCl, scan rate 10, 25, 50, 75, 100 mV/s. Insert: peak current vs. scan rate.

the target spectra suggest that no changes in the chemical structure occur during transfer.

3.2.1. Electrochemical and electronic properties of transferred PANI (PANI-T)

To measure the cyclic voltammogram of transferred PANI, the same source film was used but a gold film on glass was used as target substrate. The cyclic voltammograms of PANI-T, at different scan rate, are shown in Fig. 3. The redox response of the PANI-T electrode agrees with those previously reported for electrochemically or chemically deposited polyaniline [2,20]. The CV shows a typical anodic peak at 230 mV, corresponding to the oxidation from leucoemeraldine to emeraldine state, and a cathodic peak at 150 mV, corresponding to the reverse reaction. As it can be seen, PANI transferred onto gold electrode shows the typical electrochemical response of a polymer film synthesized in a conventional manner (e.g. electrochemical polymerization). Moreover, the film does not show the so called “middle peak” at ca. 0.6 V vs. SCE which is related to degradation processes [21]. The peak current is linear with the scan rate (10–100 mV/s), suggesting that all the film is oxidized during the potential excursion (insert Fig. 3).

To measure the UV–visible spectra, the film was transferred from the same source film but onto a polypropylene film which is transparent in the range from 280 to 1100 nm. Fig. 4 shows the UV–visible spectrum of transferred polyaniline (PANI-T) in salt (doped) state (denoted by gray line) and PANI-T in base (undoped) state (black line). The spectrum of salt form does not change upon exposure of the film to 1 M HCl solution, suggesting that the film is transferred in its doped state. The spectrum of the base form of PANI-T is obtained by exposing the film to 0.1 M NH_4OH solution. In both cases, the exposure time is of 15 min. In the spectrum of doped PANI-T (Fig. 4, gray line) it is possible to observe three characteristic bands at ca. 349, ca. 413, and ca. 1000 nm of the polymer. The shoulder at ca. 349 nm is attributed to the $\pi \rightarrow \pi^*$ transition of the aniline ring and the band at ca. 413 nm is assigned to the $n \rightarrow \pi^*$ transition of the localized radical cation. The band at ca. 1000 nm is assigned to the excitation from the highest occupied molecular orbital (HOMO) of the benzenoid rings (pb) to the lowest unoccupied molecular orbital (LUMO) of the quinoid rings (pq) in the quinoneimine units [22]. The UV–vis spectrum of the undoped PANI-T (Fig. 4, black line) shows a typical shift of the polaron band from 1000 to 700 nm. This behavior is characteristic of conductive and electroactive PANI. Since the UV–vis spectrum is directly related to the electronic state of the polymer, the agreement with the spectrum of doped PANI

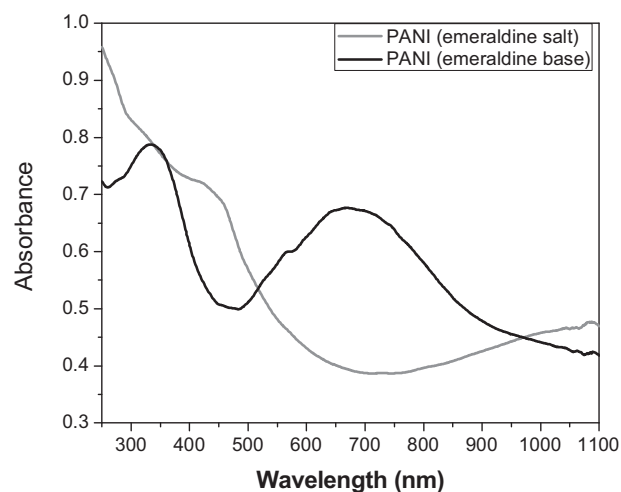


Fig. 4. Ex situ UV–vis spectra of PANI transferred on PP in the protonated (gray line) and undoped state (black line).

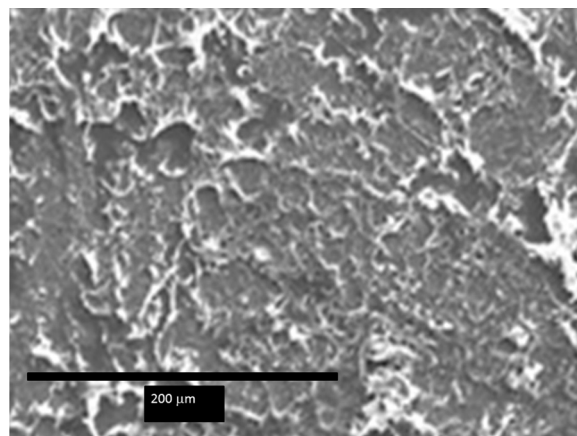


Fig. 5. Scanning electron microscopy images of transferred PANI on silicon.

suggests that the polymer electronic structure is not affected when the polymer is transferred to the substrate. Besides that, the change of spectrum due to the external pH and the cyclic voltammogram suggests that all the film is accessible to the external solution. On the other hand, the timescale for the voltammetric excursion is much smaller than the one for protonation/deprotonation.

3.2.2. Scanning electronic microscopy (SEM) of transferred PANI (PANI-T)

The DLT method was applied to the same source film, but a flat silicon wafer as a target substrate to study the topography of the PANI-T using SEM. In Fig. 5, it is shown the scanning electron microscopy images of transferred polyaniline (single pulse) on a silicon substrate, at room temperature. As it can be seen, a wrinkled deposit of conducting polymer is obtained. However, the polymers transferred maintain the connectivity that is important to some applications.

3.2.3. DLT applied to functionalized polyanilines

Recently, we show a successful incorporation of azo linkages by coupling PANI in base form, with diazonium ion and the elimination of the attached group by degradative reduction of the azo linkage [2]. In that way, novel properties such as additional charge storage or the ability to release drugs inside living bodies could be incorporated. Since the chemical modification could be made directly on a PANI film (as far as the modification does not make the polymer

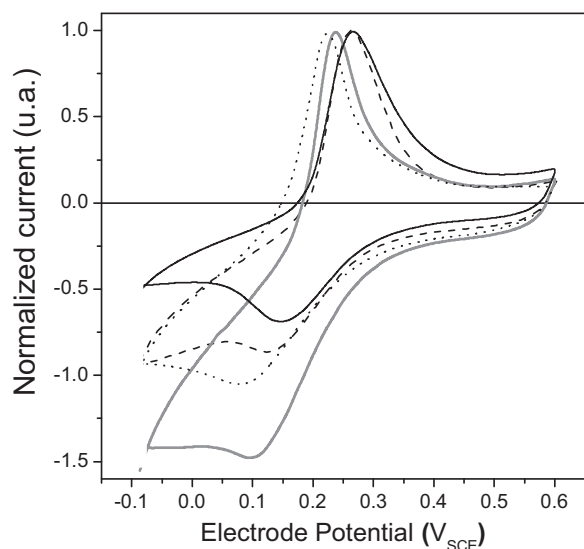


Fig. 6. Cyclic voltammogram of different polyanilines: PANI (black line), 4-nitroaniline azo 2-chloro aniline azo doped PANI (full black line), 4-trifluoroaniline azo 2-toluidine azo doped PANI (full gray line), 3-aminobenzylalcohol azo anisidine azo doped PANI (dotted black line). Electrolyte = 1 M HCl, scan rate = 50 mV/s. For easy comparison, the current in all the curves are normalized to the maximum value of the anodic current.

soluble in water), it is possible to produce a functionalized source film for making several electrodes with the same material.

The DLT method was applied to different functionalized polyanilines. The voltammogram of the transferred functionalized polyanilines, show the typical behavior of PANI doped form (Fig. 6). It is possible to observe that the typical anodic peak at 240 mV present in PANI shifts to a more anodic potential in the functionalized PANI likely due to the steric effect of the attached groups [2]. It is noteworthy that the cathodic current varied for different polymers. This is likely to be due to the fact that the same potential window is used for all the polymers while the peak potential is different. For a non-ideal thin layer electrochemical response, as it is the case in polyaniline, the amount of charge injected is different for each polymer and this affects the reduction current.

The successful application of DLT to modified PANI, demonstrates that it is possible to apply the method not only to pristine polymer but also to modified polymers even when the pendant

group incorporated is attached by a thermally labile group such as the azo bound. In that way, active electrodes with different electrochemical behavior could be made.

3.2.4. DLT as a physical method to build multilayers

In principle, applying the DLT method several times on the same target spot, but using different spots of the source film, should be able to produce multilayers. However, this would be the case if the transfer of the successive layers does not degrade previously transferred layers and all the layers have good adhesion between themselves. To test if DLT is able to build multilayers, the procedure was applied several times using a conductive transparent electrode (Indium Tin Oxide film on glass, ITO) as target substrate to be able to study the electrochemical and electronic properties of the film.

In Fig. 7a are shown the UV-vis spectra of doped PANI-T form onto ITO in a doped state after several consecutive depositions (1–4) of the polymer. All the characteristic bands are present in the spectra. It is clear that the absorption of the substrate is enhanced in each successive process of transference.

As it can be seen in Fig. 7, both the spectra and cyclic voltammograms of the successive layers are quite similar. However, it can be seen that peak potentials for the first layer are slightly different to those of the following layers. This can be due to specific interactions between the polymer layer and the underlying conductive substrate. Similar cyclic voltammograms are observed when the layers are deposited on gold (not shown). The insert in Fig. 7 shows the linear relationship between the current maxima and the number of transferred layers.

These data indicate that the DLT method generates layers in a very reproducible fashion and the amount of charge stored increases linearly with the number of transfer, strongly suggesting the incorporation of the same quantity of material in each transference step. The successful application of DLT to create PANI multilayers on ITO makes the method suitable to build electrochromic devices, [23] with tuned transmittance.

The most usual method to produce multilayers is the layer by layer self assembly, which was pioneered by Decher [24]. It involves the adsorption of water soluble and charged polymers by successive adsorption in solutions of opposite charge. Besides its widespread use to build technological devices (sensors, electrochromics, supercapacitors, etc.), the ability to build multilayers with controlled addition of new layers is especially suitable to investigate the dependence of electrochemical phenomena (e.g. diffusion) on the amount of materials. The method described here could be used for

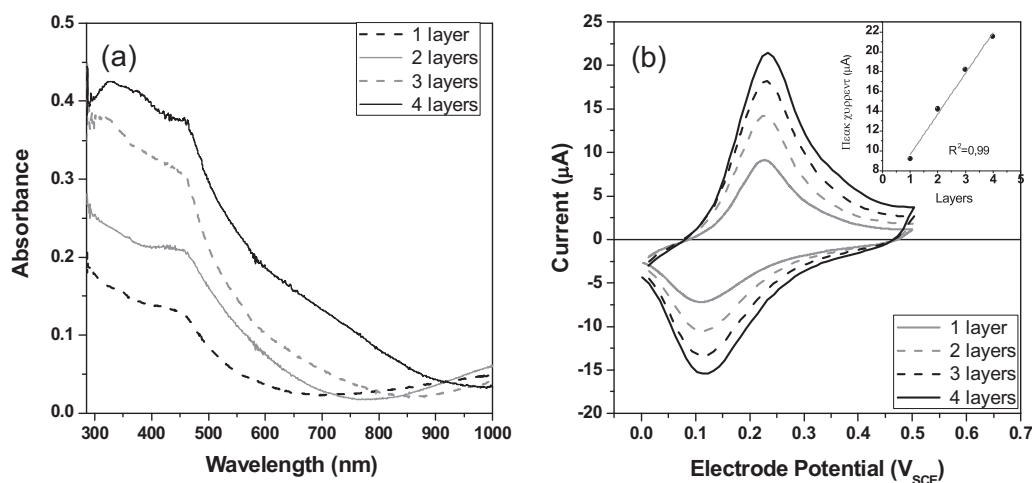


Fig. 7. (a) UV-vis spectra of multilayers made of different number of transferred PANI (emeraldine salt) layers onto ITO. Electrolyte = 1 M HCl, scan rate = 50 mV/s. (b) Cyclic voltammograms of multilayers made of different number of transferred PANI (emeraldine salt) layers onto ITO. Electrolyte = 1 M HCl, scan rate = 50 mV/s. The insert show the peak current maxima (extracted from the CVs) of doped PANI multilayers, as a function of the number of layers deposited.

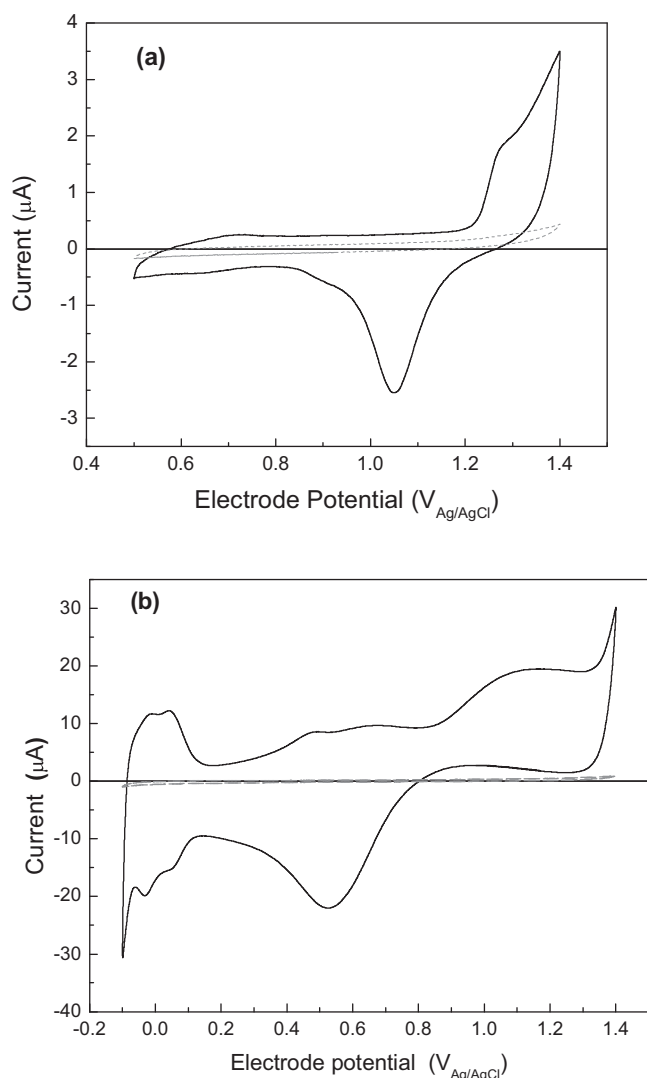


Fig. 8. Cyclic voltammograms of: (a) Au transferred onto an ITO electrode (full line) and a base ITO electrode (dashed line). Electrolyte = 0.1 M H₂SO₄, scan rate = 50 mV/s. (b) Pt transferred onto an ITO electrode (full line) and a base ITO electrode (dashed line). Electrolyte = 0.1 M H₂SO₄, scan rate = 50 mV/s.

the same purposes but with the advantage of being able to deposit insoluble or not charged polymers and being able to build the multilayer with the same or different polymers.

Both single layers and multilayers of polyanilines can be used to build electrochemical sensors where the conductive polymer acts as a catalytic layer [25]. Additionally, the conducting polymer can act as an active layer in microbatteries [26], or supercapacitors [27].

3.3. Transference of electrocatalytic metals

3.3.1. Electrochemical behavior

The DLT method was also applied to transfer gold and platinum from thin films on glass and using ITO as target substrate.

In Fig. 8a shows a voltammogram of transferred gold, while in Fig. 8b it is shown the voltammogram of transferred platinum. The transferred Au exhibited a sharp reduction peak at ca. +1.1 V vs. SCE and a broad oxidation peak at ca. 1.3 V vs. SCE, (Fig. 8a) characteristics of the reduction and formation of gold oxides, respectively [28,29]. Thus, we can conclude that the gold deposit is in good contact with the ITO electrode. The voltammogram of the deposited platinum metal shows the typical profile for Pt in deaerated H₂SO₄ solution (Fig. 8b). The fine structure of the hydrogen

absorption/desorption peaks clearly appeared (Fig. 8b). A reduction peak centered at 0.45 V can be observed during the negative-going potential sweep. This reduction peak can be attributed to the reduction of platinum oxide. This feature of the curve is consistent with those previously reported cyclic voltammogram for Pt electrodes [30]. The true surface area of the electrode, determined from the charge for the desorption of hydrogen by assuming 210 µC cm⁻² for monolayer, is 0.193 cm² [30], while the geometrical area of the electrode measured using optical microscopy was 0.015 cm². Therefore the roughness of the DLT Pt is of 12.86, which is in agreement with a non-flat deposit. The shape of the CV suggests that the platinum is transferred as a clean and well connected metal surface.

3.3.2. Morphology of the transferred metal layers

The SEM images of transferred metals are shown in Fig. 9. As it can be seen in Fig. 9a and b gold is transferred as plates about 20 µm, which are interconnected. Also, it is possible to observe small particles of gold onto these plates (Fig. 9b). On the other hand the images of the transferred platinum (Fig. 9c and d) show a more compact and uniform surface which is formed by microparticles of platinum onto the uniform surface.

In Fig. 10, it is possible to visualize the AFM images of transferred metals. In the images of transferred gold can be observed rectangular plates with areas of several µm² (Fig. 10a and b). The tilted image (Fig. 10b) reveals that the plates have nanometric thicknesses. On the other hand, the images of the platinum deposit (Fig. 10c and d) contain mostly plates with areas of only some nm². The tilted image (Fig. 10d) reveals that the plates have nanometric thicknesses. These results suggest that metals are vaporized and/or sputtered by the laser heating and then condensate onto the target surface with nucleation and growth of nano/micro plates at the target substrate surface. It seems that gold particles grow into larger particles than platinum. It is likely that the lower heat of vaporization of gold (324.4 kJ/mol) than platinum (510.5 kJ/mol) means that gold vapor has less latent heat and condensate in a slower fashion than platinum, leading to larger particles.

Fig. 11 shows the UV–visible spectrum of gold transferred on quartz. A clear band at ca. 550 nm is observed due to the plasmon absorbance of Au nanoparticles. This result suggests that the Au deposit contains a significant amount of nanoparticles.

To test the capability of the deposited metals to build active electrodes, we measured the activity of platinum and gold layers in electrochemical reactions which are known occur at slow rate on the base electrode.

3.3.3. Electrochemical oxidation of methanol on ITO electrodes modified with DLT platinum

The cyclic voltammogram for methanol oxidation on DLT transferred platinum is shown in Fig. 12. The current from methanol oxidation becomes apparent as the potential rises above 0.50 V. It is noteworthy that no current signal is observed at those potentials when plain ITO is used. In the forward scan, methanol oxidation produced a prominent symmetric anodic peak around 0.80 V. In the reverse scan, an anodic peak appeared at around 0.65 V. This anodic peak in the reverse scan could be attributed to the removal of the incompletely oxidized carbonaceous species formed in the forward scan. The reaction mechanism of methanol electro-oxidation on the surface of platinum is a complex one which involves many carbonaceous species as intermediates. It is generally agreed that the most abundant surface intermediate is chemisorbed carbon monoxide [31]. The ratio of the forward anodic peak current (I_f) to the reverse anodic peak current (I_b) can be used to describe the catalyst tolerance to carbonaceous species accumulation [32,33]. A high I_f/I_b ratio involves nearly complete oxidation of methanol to CO₂. The ratio is estimated to be 1.34 for the electrode. Such value indicates that most of the intermediate carbonaceous species were

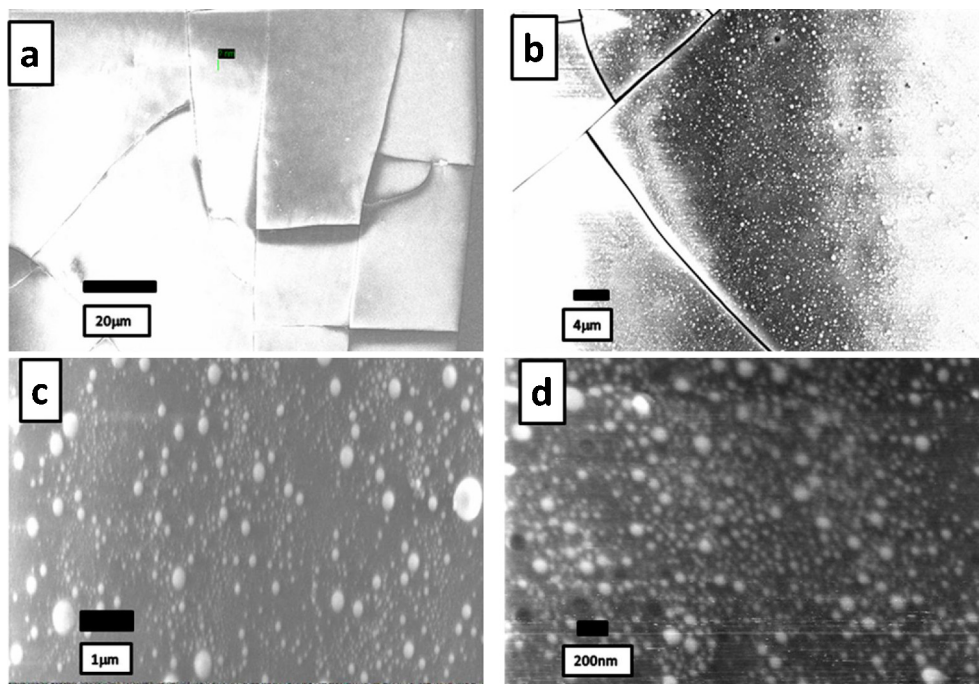


Fig. 9. SEM images of gold (a and b) and platinum (c and d) transferred on glass.

oxidized to CO_2 in the forward scan. These experimental results involve that the major deficiency of all Pt catalysts, that is, the accumulation of intermediate carbonaceous species on the catalysts' surface leading to "catalyst poisoning", can be partly overcome by using DLT to prepare the platinum deposit. While more extensive studies are required, such as those previously performed with other Pt based supported nanoparticle electrodes [34], this behavior is likely to be related to the fact that the metal deposit is made

of micro/nanoparticles. It can be seen (Fig. 12) that the methanol oxidation current increases when multiple DLT transfers are used, compared with the electrode made by one pulse. This result suggests that additional metal is deposited during each DLT pulse into a rough surface, since addition of successive flat metal layers will not change the electrochemical area. On the other hand, the shape of the electrochemical response is independent on the number of layers, suggesting that the electrocatalytic activity is maintained.

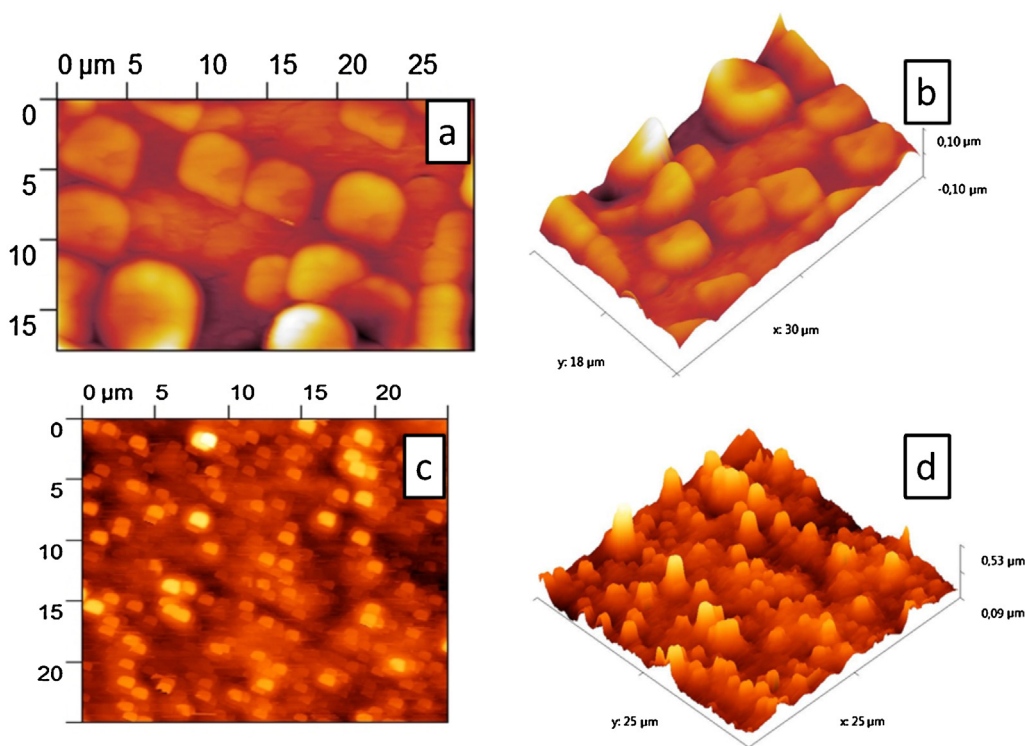


Fig. 10. AFM images of gold (a and b) and platinum (c and d) transferred on glass.

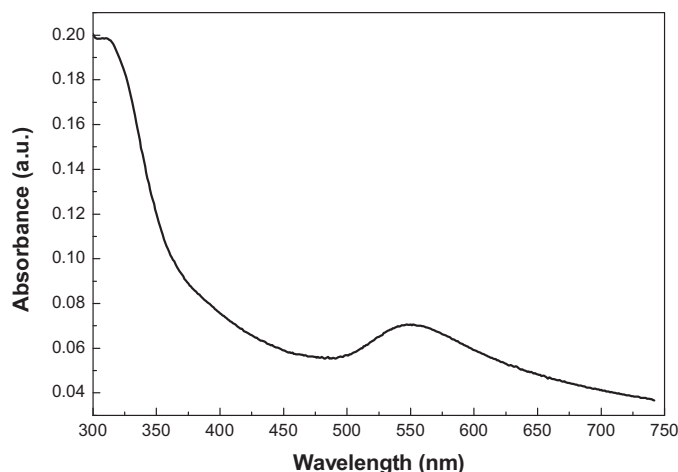


Fig. 11. UV-Vis transmission spectrum of gold transferred on quartz.

Moreover, it is possible to transfer platinum using an optical mask to limit the laser beam and to produce small Pt spots to generate ultramicroelectrodes. Such electrodes can be used in micro fuel cells [35].

3.3.4. Electrochemical oxidation of ferrocyanide on electrodes modified with DLT gold

In Fig. 13 is possible to observe the voltammetric response of potassium ferricyanide on an ITO electrode modified with transferred gold. The oxidation peak is observed at ca. 0.4 V and the reduction peak is observed at ca. 0.27 V vs. SCE. The peak separation ($\Delta E_p = 150$ mV) suggests a quasireversible electron transfer mechanism. Moreover, the peak separation increases with the scan rate, as expected for such mechanism. However, the same couple shows an irreversible behavior ($\Delta E_p > 300$ mV) on plain ITO. The result suggests that the gold transferred onto the ITO electrode maintains its electrocatalytic activity. It is noteworthy that, besides been extensively used as redox probe for electrodes, ferricyanide is also used as redox shuttle in enzymatic electrochemical biosensors [36]. Therefore, the electrodes modified with gold by DLT could be used to fabricate electrodes of electrochemical biosensors.

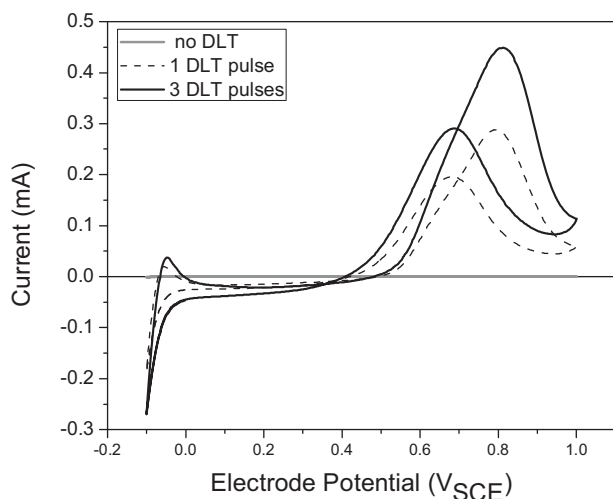


Fig. 12. Cyclic voltammograms for the oxidation of CH_3OH (1 M) on Pt transferred by DLT in one pulse (dashed black line), three pulses (full black line) and base ITO (gray line). Scan rate = 20 mV/s, electrolyte = H_2SO_4 0.1 M

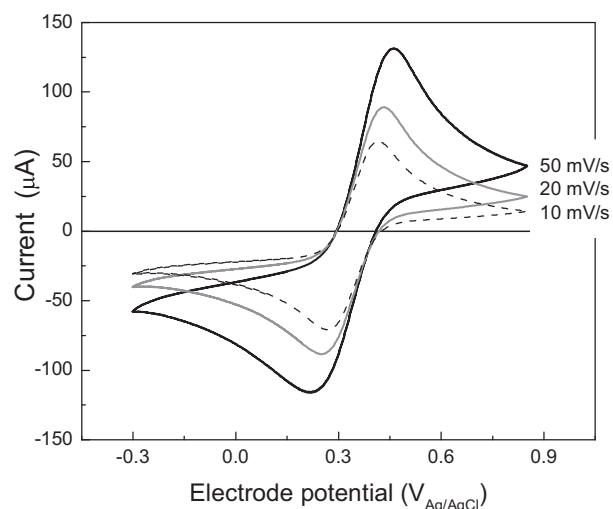


Fig. 13. Cyclic voltammograms of $\text{K}_3[\text{Fe}(\text{CN})_6]$ 0.01 M in KCl 0.1 M on ITO modified by DLT transfer of Au. The scan rates are depicted in the figure.

4. Conclusions

The Direct Laser Transference (DLT) is used to generate active electrodes modified with conducting polymers, or electrocatalytic metals. It is demonstrated that the technique can be applied to produce modified electrodes with different conducting polymer, even those containing labile group such as the azo-group. The polymers are transferred with negligible alteration of the chemical structure or the electronic and electrochemical properties.

Additionally, it is shown that it is possible to generate polymer multilayers which show UV-visible spectra and electrochemical response that scale up with the number of layer deposited. The method is a physical alternative to the well known layer by layer method of multilayer formation.

Using the same method it is possible to transfer electrocatalytic metals such as gold and platinum. The characterization of the modified electrodes shows that when the metal is transferred nano/microparticles are formed on the surface. The UV-visible spectrum of transferred gold shows a band at ca. 550 nm characteristic of the Plasmon absorbance of Au nanoparticles.

The gold modified electrodes show electroactivity toward the electrochemical reduction of ferricyanide ion. The platinum modified electrodes show electrocatalytic activity toward methanol oxidation. The DLT method can be used to produce ultramicroelectrode arrays for sensing applications.

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