Polymer Bulletin 56, 201–210 (2006)
DOI 10.1007/s00289-005-0485-z

Polymer Bulletin

Electrochemical synthesis and characterization of poly(*2,2'* -dithiodianiline) thin films loaded with copper microparticles. Application to the amperometric analysis of γ- aminobutyric acid

G. Alfonso[a], M. A. del Valle[a] (✉), G. M. Soto[a], M. A. Cotarelo[b], C. Quijada[c], J. L. Vázquez [b]

[a] Facultad de Química, P. Universidad Católica de Chile, Av. Vicuña Mackenna 4860, Santiago, Chile
[b] Departamento de Química Física, Universidad de Alicante, Apartado n99; E-03080, Alicante, España
[c] Departamento de Ingeniería Textil y Papelera, Universidad Politécnica de Valencia, Paseo Viaducto1, 03801, Alcoy (Alicante), España

Received: 17 October 2005 / Accepted: 7 December 2005

Summary

Modified electrodes with poly(*2,2'*-dithiodianiline*)*,PDTDA, were prepared from the corresponding monomer by cyclic voltammetry between 0.0 V and 1.5-1.6 V on gold or stainless steel respectively. The potentiodynamic method proved to bring about good quality and adherent thin films. The wide potential window shown by this modified electrode allowed attempting the insertion of copper in the polymeric matrix using several strategies. The response of this modified electrode copper was checked in the presence of γ-aminobutyric acid (GABA). Copper loaded on PDTDA/Au electrodes showed the highest sensitivity along with a stable and reproducible response for the detection of GABA. The surface morphology and composition analysis by SEM and XPS shows that copper is deposited in the polymeric matrix as uniformly scattered microparticles. The surface of these particles is mainly composed of Cu(I) species.

Keywords: *2,2'*-dithiodianiline, γ-aminobutyric acid, polymer- modified electrode

Introduction

The electrochemical synthesis of polymers has recently become a very attractive route in the field of conducting polymers. A great number of these compounds have been prepared by electro-oxidation of the corresponding monomers on an adequate electrode and characterized by different methods and techniques. The electrical conduction mechanism of these polymeric materials has also been elucidated. It has been shown that the doping of these polymers with certain elements causes a change in properties such as magnetic susceptibility, morphology, kinetic parameters, charge transfer coefficients, etc. to an extent which depends on the nature and size of the dopant, hence determining their potential applications [1-3].

The explotation of the use of conducting polymers in electrocatalysis has become a fast growing area of research in applied electrochemistry [4]. Conducting-polymer modified electrodes are known to possess intrinsic catalytic activity for the redox transformation of a number of organic and inorganic species [4-8]. Also, polymer thin films can be used as an organic matrix to host active metal particles in order to develop new hybrid materials with enhanced electrocatalytic properties [4, 9-12]. In these metal-polymer composites, the conducting organic matrix allows electrons to be shuttled between the electrode surface and the dispersed active metal sites. Many reports can be found in the literature accounting for the use of these materials as conductimetric, potentiometric, colorimetric and fluorimetric sensors [13].

For some time our group has been working on the modification of electrodes by dispersion of metals in a polymeric matrix in order to use them for the electro-oxidation of formic acid [9] and the analytical determination of aminoacids like γ–aminobutyric acid (GABA) [10]. In the latter case, copper was dispersed on a polymeric matrix of poly-*o*-phenylenediamine and its response to GABA was checked observing that the sensitivity actually increased. However, this modified electrode is useful only for a small number of measurements because the metal gets oxidized as a consequence of the applied potential and it is removed from the polymeric matrix [10]. The immobilization into the polymer material of small molecules bearing complexing sites for copper ions (i.e. benzoquinone) can help solve this problem. In this case quinone groups were found to keep metal ions bound within the polymer in such a way that the catalytically active particles could be regenerated by reduction after each measurement [11].

A step ahead within this strategy is that the polymer chain itself is composed of monomeric units with the ability to complex copper ions. It has been reported that the monomer 2,2'-dithiodianiline (DTDA) forms reversible 1:1 Cu(II)/ionophore complexes [13] and therefore it can be a promising candidate to build polymers with complexing properties. This monomer can be chemically or electrochemically oxidized to yield a conducting polymer, which has been characterized by using electrochemical and spectroscopic methods [14-19].

This work is aimed to the study of the electropolymerization of DTDA on several metal substrates to obtain polymeric thin films and their further modification by the loading of copper particles. The surface morphology of the modified electrodes will be examined by SEM and the surface elemental composition determined by XPS. The capability of the resulting metal-polymer composite to detect γ-aminobutyric acid (GABA) will be also evaluated.

Experimental

Conventional three electrode electrochemical cells were used. The reference electrode was Ag/AgCl immersed in tetraethylammonium chloride solution with a concentration adjusted to the potential of a SCE. The auxiliary electrode was a platinum wire and the working electrodes were discs of gold or AISI 316 stainless steel. The disc electrodes employed in electrochemical measurements had a geometric surface area of 0.07 cm^2. Larger electrode discs (8 mm in diameter) were utilized for surface analysis. All discs were polished on a piece of cloth using an alumina slurry 0.3 μm particle size and finally rinsed with distilled water and acetone.

All solutions were daily prepared from analytical-reagent grade chemicals without further purification using deionized water. Chemicals were purchased from Aldrich Chem. Co. Experiments were performed at room temperature and all solutions were protected from oxygen by purging with high-purity argon. Also, an argon atmosphere was maintained on the solutions during electrochemical measurements.

The modification of the electrode substrates with a deposit of poly (2,2'-dithiodianiline), PDTDA, was carried out from 30 mM DTDA + 60 mM tetraethyl-ammmonium hexafluorophosphate (TEAHFP) dissolved in 1:1 water:acetonitrile solution. The potential was cycled between 0.0 V and either 1.5 V or 1.6 V for gold and stainless steel respectively. The polymer film thickness was varied by the number of potentiodynamic cycles. The corresponding data were acquired with a VoltaLab PGZ 100 system.

Two methodologies were attempted for the loading of Cu particles in PDTDA thin films. In the first one, PDTDA-modified electrodes were immersed for 5 min in a 0.1 M $CuSO_4$ solution at open circuit potential (this period was found to give a maximum electrode response toward GABA [10]) and then the potential was stepped to -0.3 V for 3 min to reduce Cu(II) ions that might diffuse into the bulk of the matrix. In the second procedure, PDTDA-modified electrodes were immersed in a 3.0 $g \cdot L^{-1}$ $CuCl_2$ + 0.02 M HCl solution and a linear sweep potential scan was applied between 0.0 V and 0.8 V *vs* SCE. Then a negative potential of -0.3 V *vs* SCE was applied for 3 min. After the anodic limit has been reached the application of the reduction potential generates copper metal particles on the surface. According to earlier authors [20,21], chloride-containing solutions allow the deposition of Cu(I) species, while cathodic reduction from $CuSO_4$ favors the formation of Cu(0).

For the determination of GABA, calibration curves for the response of Cu-dispersed modified electrodes were derived from the measurement of the charge under i-t transients recorded in 5 to 10 mg/L GABA solutions while a potential step of 0.8 V *vs* SCE was applied.

X-ray photoelectron analyses were carried out in a VG-Microtech Multilab electron spectrometer at a base pressure routinely maintained at the 10^{-9} mbar level and a temperature of about 173 K. The samples were irradiated with unmonochromatized MgKα (1256.3 eV) radiation from a twin anode source operated at 300 W (20 mA, 15 kV). Photoelectrons were collected into a hemispherical analyser working in the constant energy mode at a pass energy of 50 eV. The Au4f7/2 line at 84.0 eV was used for binding energy (BE) an Auger kinetic energy scale referencing. Survey and high-resolution scans were taken with 1 eV- and 0.1 eV/energy step intervals respectively. Surface charging corrections seemed not necessary. Peak BEs were given with an accuracy of ±0.2 eV. Peak synthesis was done with mixed 70/30 Gaussian/Lorentzian function lineshapes. Copper chemical states were distinguished with the aid of the modified Auger parameter, which is the sum of the BE of the Cu $2p_{3/2}$ core level and the kinetic energy of the Cu L_3VV Auger line ($\alpha' = E_b(\text{Cu } 2p_{3/2}) + E_K(\text{Cu } L_3VV)$). Peak area ratios were given after correction with proper sensitivity factors. SEM micrographs were obtained with a Hitachi S-3000N scanning microscope. The electrode specimens were mounted on Al stubs with double-sided conducting adhesive tape.

Results and discussion

Both potentiostatic and potentiodynamic methods were tested for the coating of stainless steel or gold electrodes with electrosynthesized films of PDTDA. Cyclic potential sweeping was always found to be the most suitable way to obtain good quality films. Instead, those coatings formed under potentiostatic control unevenly covered the electrode surface and showed poor adherence.

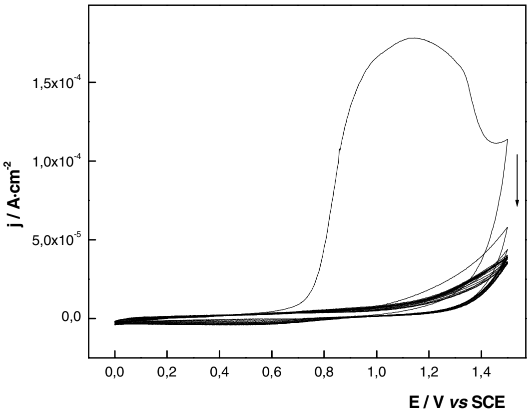

Fig. 1 Cyclic voltammogams during the oxidative polymerization of 30 mM DTDA + 60 mM TEAHFP in 1:1 water/acetonitrile solution on a gold disc electrode; v = 50 mV·s^{-1}. Arrow indicates the evolution of the current with the increasing number of voltammetric cycles.

Figure 1 shows cyclic voltammograms recorded during the oxidation of 30 mM DTDA on a gold electrode in a 60 mM TEAHFP + 1:1 water/acetonitrile solution. The electrode was immersed at 0.0 V *vs* SCE and the potential was swept repeatedly in the range 0.0-1.5 V. During the first forward scan a very broad wave of the irreversible oxidation of the monomer is observed. The absence of any cathodic peak in the reverse sweep suggests a fast consumption of the oxidized monomer by a follow-up chemical coupling reaction. In the following sweeps, the current density decreases gradually until significant inhibition of the DTDA oxidation is attained, which is characteristic of the growth of an electroinactive polymer film. Indeed, the electrode surface was covered by a pale yellowish thin film. When stainless steel is used as the substrate, the same yellowish thin film was develop during cyclic voltammograms of DTDA solutions between 0.0 and 1.6 V *vs* SCE.

After the synthesis of the polymer film, copper particles were dispersed on PDTDA-modified electrodes by following the procedures outlined in the experimental section. In the case of stainless steel, Cu particles could only be deposited from $CuSO_4$ solutions by following the first dispersion protocol. The second procedure caused serious damage of the substrate surface and a loss of adherence of the polymer. This behavior is likely to be due to pitting processes of the steel passive layer which occurs in chloride-containing acidic media.

Cu/PDTDA electrodes were immersed in GABA-containing 0.1 M NaOH solutions and the j-t transients at 0.8 V were recorded. The response of the hybrid metal-polymer composite to GABA was assessed from the charge under the current transients. Figure 2a-d show the current transients recorded in 0.1 M NaOH (blank transients) and GABA + 0.1 M NaOH (test transients) solutions. The charge under the blank transient amounts to 635.1 mC·cm^{-2} for the Cu-PDTDA/SS electrode (Fig. 2a) and it increases up to 1493.5 mC·cm^{-2} in the presence of 47 mg·L^{-1} GABA (Fig. 2b). These results indicate that Cu-PDTDA thin films provide sufficient sensitivity to GABA so to be considered as materials with potential applicability to the development of GABA amperometric sensors. However, the j-t transient plots obtained for Cu-PDTDA on steel does not level off in a smooth fashion, but appear to have a fairly erratic or noisy character. This behavior can be explained by assuming that the polymeric deposit has a porous morphology when formed on stainless steel. Hence, the electrolyte can permeate through and reach the polymer-steel interface. Then, the erratic response should be attributed to the substrate response. The chronoamperometric response of bare stainless steel electrodes in NaOH 0.1 M solutions (not shown) exhibited similar erratic current decays, thus confirming the aforementioned assumption.

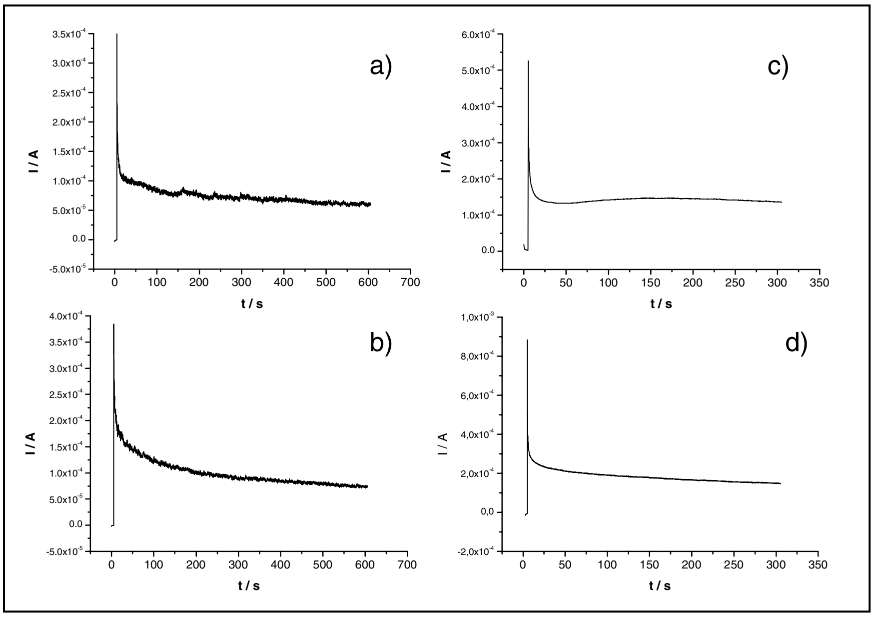

Fig. 2 Constant-potential (E = 0.8 V *vs* SCE) chronoamperometric response of Cu-PDTDA thin films on a) stainless steel in 0.1M NaOH, b) stainless steel in 47 mg·L^{-1} GABA + 0.1 M NaOH, c) gold in 0.1M NaOH, and d) gold in 10 mg·L^{-1} GABA + 0.1 M NaOH.

Current transients obtained on Cu-PDTDA/Au electrodes for a total running time of 5 min are shown in Fig. 2c-d. The test transients were obtained at a GABA concentration of 10 mg:L^{-1}. In this case, the transferred charge changes from 613.3 to 1362.5 mC·cm^{-2}. Note that this charge increment occurred at half the time and at a GABA concentration of about 5 times as low as that employed in stainless steel modified electrodes. Therefore, it can be inferred that the composite films deposited on gold exhibit better sensitivity to GABA. In addition, the profile of the current decay is much smoother than that recorded in the case of steel substrates, which is important to propose it use as amperometric sensor, because it allows predict a most stable response with time. In summary, Cu-PDTDA films deposited on Au possess an overall better response to GABA than those formed on steel substrates, which will be no longer treated in this work.

In figure 3, SEM microphotographs of pristine and copper-modified PDTDA thin films formed on Au by repeated potential cycling are shown. Pristine films (Fig. 3a) present a rather smooth surface texture with some aggregate regions. After copper loading (Fig. 3b), a deposit of well-distributed micron-sized crystal particles is observed on top of the polymer surface. A wide-scan X-ray photoelectronic spectrum (Fig. 4a) displays lines originating from C1s, N1s and S2p photoelectrons, which are the elemental components of the organic film. The [S]/[N] and the [S]/[C] peak area ratios are 0.98 and 0.148, i.e, very close to the theoretical ones expected for a polymer

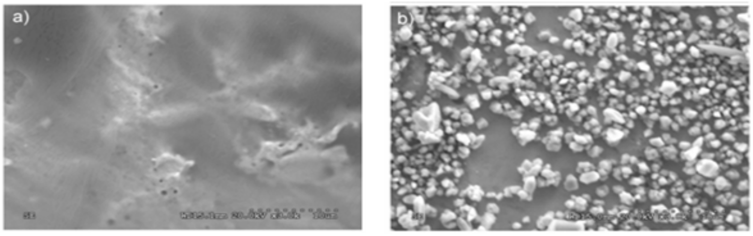

Fig. 3 SEM microphotographs of a) pristine PDTDA/Au, and b) Cu-PDTDA/Au. Magnification ×3000.

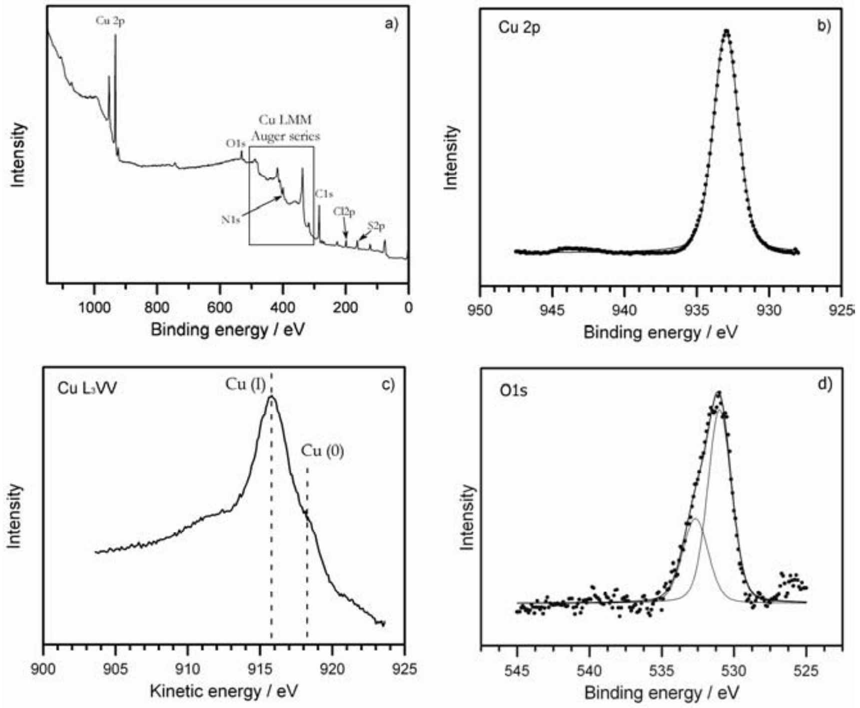

Fig. 4 Photoelectronic spectra of Cu-PDTDA/Au. a) wide scan spectrum, b) high-resolution Cu $2p_{3/2}$ core-level spectrum, c) Cu L_3VV Auger spectrum and d) high-resolution O1s spectrum.

Table 1. Summary of the BEs of the core-level XPS lines of Cu-PDTDA hybrid films and their assignments.

Spectral region	Peak center (eV)	Assignment
C1s	284.6	-C=C-/ >C-S
	285.5	>C-N
	286.5	oxidized carbon (either C-OH or C=O)
N1s	399.7	-NH-
$S2p_{3/2}$	164.0	-S-S-
O1s	531.0	Cu_2O
	532.7	oxidized carbon
$Cu2p_{3/2}$	933.0	Cu(I) particles
Cu L_3VV	915.7	
	918.2	

backbone with a ladder structure consisting of two parallel PANI-like chains bridged by S–S bonds [18,19]. These results are in excellent agreement with our previous XPS studies on chemically synthesized PDTDA [14]. Strong Cu 2p core-level lines and Cu LMM Auger series features are observed, thus confirming the incorporation of copper species. The O1s and Cl 2p signals are also related to this Cu species as will be discussed below. The positions of the various relevant photoelectron peaks and their assignments are summarized in Table 1.

For an accurate determination of the chemical state of Cu particles to be gained, high resolution scans were acquired in the energy range of the Cu 2p core level and the Cu L_3VV Auger line (Fig. 5b-c). The main Cu $2p_{3/2}$ peak appears at 933.0 eV, which points that Cu is not present in a single oxidation state. Nevertheless, the absence of a high BE asymmetry and the narrow peak linewidth allows to discard the presence of Cu(II) species. In addition, the multiplet splitting satellite at ~ 944 eV, typical of paramagnetic transition metal elements like Cu(II), is negligible. The Cu L_3VV Auger region (Fig. 4c) shows a main peak at a kinetic energy of 915.8 eV and a shoulder at 918.2 eV. The corresponding Auger parameters (1848.8 and 1851.2 eV) are within the areas reported for Cu(I) and Cu(0) species [22]. It should then be concluded that the copper deposit is mainly formed by Cu(I) species along with minor metallic Cu. Moreover, the $Cl2p_{3/2}$ line at 198.8 eV and the O1s line at 531.0 eV are compatible with the occurrence of mixed Cu(I) chloride-Cu(I) oxide clusters [21]. A careful inspection of the O1s spectral region (fig. 4d) shows a broad peak which is best fitted with two lines, O_1 and O_2, at 531.0 and 532.7 eV respectively. The first contribution can be assigned to Cu_2O species, whereas the second one is ascribable to oxidized carbon from the polymer matrix. The $[Cl+2O_1]/[Cu]$ peak area ratio exceeds 1, which confirms that grains observed in SEM micrographs (fig 3b) are chiefly composed of Cu(I) species, at least at the outermost layers probed by XPS. Copper (I) clusters were also identified as the major species in Cu-Ppy, Cu-PANI and Cu-PMT composites obtained by pulsed potentiostatic deposition from Cu(II) solutions [21,23,24]. Copper (I) particles dispersed onto polymeric matrices have shown to possess excellent electrocatalytic properties for the constant-potential amperometric detection of polyhydroxyl compounds and amino acids in alkaline media [23,24]. Therefore, the electrochemical response of the Cu-PDTDA hybrid films to GABA should be related to the presence of active Cu(I) particles.

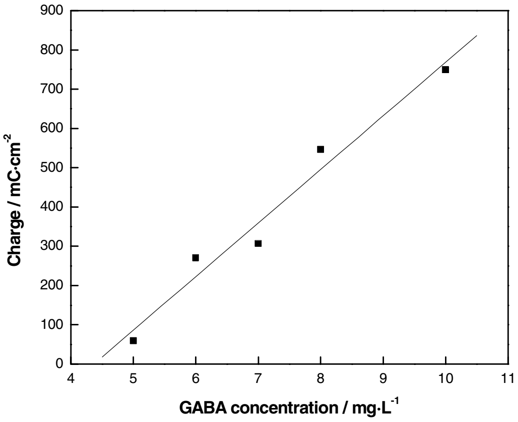

Fig. 5 Calibration curve for the determination of GABA at Cu-PDTDA/Au electrodes in 0.1 M NaOH solution. The charges were obtained from potentiostatic chronoamperograms at 0.8 V *vs* SCE, after subtraction from blank transients.

Finally, considering that the better response to GABA was obtained with Cu-PDTDA/Au electrodes, GABA analyses were carried out on Cu-PDTDA/Au electrodes in 0.1 M NaOH solutions. The Cu loading on the polymer-modified gold electrode was done from $CuCl_2$ hydrochloric solutions according to the method described in the experimental section. A five-point calibration curve was obtained from the integrated charge under the current transients recorded in GABA standard solutions after a potential step of 0.8 V. The concentration of the GABA standards ranged from 5 to 10 mg·L^{-1}. The potentiostatic method was preferred over the potentiodynamic runs because current transients gave rise to more stable and reproducible readings. By contrast, repeated potential cycling up to 0.8 V led to a gradual decrease in the GABA oxidation current, which was ascribed to a copper loss in the PDTDA matrix, as it has been observed earlier for other polymeric thin films [10]. Another obvious advantage of the potentiostatic method is that the charge is easily obtained from the current transient and data analysis is made straightforward. The results are shown in Table 2. The calibration curve (fig. 5) shows a reasonably good linear dependence (correlation coefficient= 0.985) between charge and concentration within the concentration range explored. This result is promising for a future development of a Cu-PDTDA-based amperometric sensor for GABA. Further analytical investigation (detection limits, linearity ranges, response time, etc) is under way, but it can be advanced that the studied materials show excellent reproducibility and stability.

Table 2. Charges under j-t transients for the oxidation of GABA as a function of the concentration in the 5-10 mg·L^{-1} range.

GABA concentration (mg·L^{-1})	Charge (mC·cm^{-2})
5	59.43
6	270.44
7	307.08
8	546.08
10	749.18

Conclusions

Polymeric thin films derived from 2,2'-dithiodianiline (DTDA) can be deposited on gold and stainless steel electrodes by electrochemical oxidation in 1:1 water/acetonitrile solutions with tetraethylammonium hexafluorophosphate as the supporting electrolyte. Uniform, adherent, pale yellowish coatings are grown by cyclic voltammetry between 0.0 V and 1.5-1.6 V vs. SCE. Those films show a wide potential window that encourages attempting the insertion of active metal particles for analytical purposes.

Copper is loaded into the polymer film by cathodic deposition from $CuSO_4$ (on PDTDA/SS) or hydrochloric $CuCl_2$ solutions (on PDTDA/Au). This latter procedure yields a hybrid metal-polymer composite with the best amperometric response toward γ-aminobutyric acid (GABA) in 0.1 M NaOH. Scanning electron micrographs reveal the formation of well-distributed copper microparticles on the polymer surface. Photoelectron spectroscopy studies suggest that Cu(I) is the prevalent surface oxidation state. Moreover, it is put forward that Cu(I) occurs as a mixture of CuCl and Cu_2O. Also, XPS data are consistent with a ladder structure for the polymer backbone. Finally, calibration curves (Q *vs* GABA concentration) shows good linearity in the range 5-10 $mg{\cdot}L^{-1}$. A detailed analytical study is in progress to assess the feasibility of this material as a GABA amperometric sensor.

Acknowledgements. The authors would like to thank the financial support of projects 3020033 and 1020520 from FONDECYT (Chile) and project MAT2004-01479 from Ministerio de Educación y Ciencia (Spain).

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