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Fabrication and Surface Characterization of Poly(4-aminodiphenylamine) Film Modified Electrode and its Application for Lead and Cadmium Determination

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ABSTRACT: Poly(4-aminodiphenylamine), Padpa, film was synthesized electrochemically on a glassy carbon electrode by potentiodynamic repetitive cycling of 4-aminodiphenylamine (4-adpa) in 1.0 *M* HCl. The mechanistic steps involved the oxidation of the protonated monomer to diimine species followed by its dimerization to form the mono-charged radical intermediate, which was considered as the initiation step for the progress of polymerization. The electrochemical properties and surface morphology of the film modified electrode were characterized using electrochemical and various surface scanning techniques. The XPS data demonstrated the existence of =N– bonding responsible for polymer formation, while the AFM image revealed a uniform and symmetrical fiber structure with low energy dissipation. The modified electrode was primarily applied as an environmental sensor for the simultaneous and selective determination of Cd^{2+} and Pb^{2+} ions in water samples. The detection limit for Cd^{2+} and Pb^{2+} ions was 25 and 14 μg L^{-1}, respectively.

Keywords: Electropolymerization; 4-Aminodiphenylamine; Sensors; Cadmium; Lead.

تشييد وتقييم لغلاف رقيق من بوليمر (4 – أمينوا داي فنيل أمين) لقطب كهربائي معدل واستخداماته في تقدير أيونات الرصاص والكادميوم

محمد الهنائي، سالم الحارثي وعماد خديش

ملخص: تم تصنيع طبقة رقيقة من بوليمر (4 –أمينو داي فنيل أمين)على سطح قطب الكربون الزجاجي وذلك بإمرار جهد كهربائي متغير ومتسلسل لمادة (4 –أمينو داي فنيل أمين) المذابة في محلول حامض الهيدروكلوريك1 مولاري. تتضمن ميكانيكية التفاعل أكسدة الجزيء الأحادي الحامل لبروتون الى مادة داي ايمين والتي بدورها تمر بعملية تكاتف لجزيء ثنائي يدعى الأيون الموجب الجذري الذي يمثل الخطوة الاساسية لعملية البلمرة للوصول الى تحضير البوليمر النهائي. لقد تم دراسة الصفات الكهربائية والتركيب السطحي لطبقة البوليمر الرقيقة بواسطة الطرق الكهروكيميائية والطرق الفيزيائية لتوصيف السطوح. نتائج الوصف الفيزيائي والضوئي أوضحت وجود الرابطة (-N=) المسؤولة عن تكوين البوليمر الذي وصف بأنه من أنسجة منتظمة ومتماثلة ذات طاقة تشتت منخفضة. أن القطب الكهربائي المعدل تم استخدامه للتطبيقات البيئية المتصلة بالتقييم المتزامن والإختياري لكل من أيونات الرصاص والكادميوم في عينات المياه حيث وصلت حدود التقييم الى 14 و 25 جزء من البليون لكل من الرصاص والكادميوم على التوالي.

مفتاح الكلمات : البلمرة الكهروكيميائية، 4 – أمينوا داي فنيل أمين، أقطاب حساسة، كادميوم، رصاص.

1. Introduction

In recent years, electrochemical polymerization has received a great deal of attention as a unique method to construct and modify various electrode surfaces with certain polymeric films. The fabrication, characterization and application of polymer modified electrodes (PMEs) are important themes and a core area of research in chemistry. Electrochemical methods can effectively tailor the chemical and physical properties of the resulting polymer, including mechanical resistance, electrical conductivity, stability and high electron affinity [1]. They can also exert control over the parameters of the film thickness and homogeneity [2]. These novel PMEs may potentially find application in a wide range of technologies including, energy storage systems [3], membrane gas separation [4], electrocatalysis [5], and sensors [6]. The polymeric films can be further incorporated by some modifiers such as enzymes [7], nanoparticles [8] and polymer composite structures [9] to facilitate certain applications. Since the pioneering work of Diaz and coworkers in the late 70s [10,11], the fabrication of modified electrodes with highly stable and conductive polymeric films (polypyrrol, polyaniline, and polythiophene) has been a further developmental step towards their effective application in corrosion inhibition [12], light emitting diodes [13], electro-photosensitization [14] and biosensors [15].

The electrochemical polymerization of aromatic amines such as aniline (Ani) has been studied widely [16], exploring the reaction mechanism and the kinetics of polyaniline (Pani) growth on conducting substrates. The initial step is the formation of the Ani cationic radical followed by dimerization reactions, and then chain growth *via* the linkage of radical ions or the connection of the radical with the neutral monomer. The major intermediate product was characterized as the dimer-aniline like constituent called 4-aminodiphenylamine (4-adpa) [17]. Recently, Planes *et al.* [18] have identified 4-adpa as the Ani-dimer intermediate produced *via* head-to-tail coupling of Ani cation radicals using a spectroscopic method. The conductivity and molecular mass of poly(4-aminodiphenylamine) prepared in aqueous HCl solution [19] were found to be significantly less than those of Pani due to the formation of oligomeric products composed of four monomeric units. In another study, using *in situ* FTIR and UV-Vis methods, Zimmermann *et al*. [20] concluded that the main structure formed during the electrochemical polymerization of 4-adpa was the Ani-tetramer.

A composite conducting film was also constructed by electrochemical polymerization of 4-adpa at pH = 5.0 in the presence of Ani [21]. The incorporation of Ani was featured for two reasons: (i) due to the lack of homo-polymerization reaction of 4-adpa where its electrochemical oxidation is believed to be slow and inefficient, and (ii) to enhance the propagation reactions of the oxidized 4-adpa species. The resulting film showed a good catalytic reactivity towards a number of redox couples in a weakly acidic buffer solution. Another novel work of Cotarelo *et al*. [22] was devoted to characterizing the polymeric film produced by electrochemical oxidation of 4-adpa in a strongly acidic medium using a number of microscopic and spectroscopic techniques. It was concluded that the resulting polymer displayed electrochemical, morphological and spectroscopic characters similar to those shown by Pani.

Considerable attention has been given to environmental contamination with heavy metal ions for health and safety reasons. Therefore, a trace monitoring of these metal ions in the environment is an important but analytically challenging task. The maximum admissible limit for Pb^{2+} and Cd^{2+} ions for drinking water quality are 15 and 5 μg L^{-1}, respectively, as reported by the United States Environmental Protection Agency (USEPA) in 2008. Electrochemical stripping analysis was recognized as an efficient tool for simultaneous monitoring of heavy metals [23]. The scope of sensing tools has been developed significantly for simultaneous and selective trace quantification of heavy metals *via* appropriate surface modifications, for example by the incorporation of bismuth film [24], boron-doped diamond [25], polypyrrole [26], poly(3,4-diaminoterthiophene) [27] and polyaniline [28].

The present work is devoted to studying the nature of resulting Padpa film deposited at glassy carbon electrode (Padpa/GCE) and its application for trace determination of cadmium (Cd^{2+}) and lead (Pb^{2+}) ions. Surface modification with Padpa was selected due to the structural limitations and involvement of different intermediates in producing Pani, while the formation of Padpa is known to proceed *via* a single specific intermediate, as illustrated in Scheme 1 given below. Therefore, producing a thin and smooth polymeric film at lower oxidative applied potential and avoiding the polymer over-oxidation is another important major theme of the present work. Moreover, the presence of a surface modifier, such as a conducting polymer, is likely to increase the electrode surface area and its adsorption capacity.

2. Experimental

2.1 Reagents

Electrochemical measurements for metal analysis were carried out in an equimolar 0.1 *M* mixture of (KCl + HCl) solution (pH = 2.12) prepared in Millipore water. The electrolyte was degassed by purging oxygen-free nitrogen gas for 10 min, and blanketed throughout the experiment. A stock solution of the 4-adpa monomer (Aldrich) was prepared by dissolving a certain amount in 1.0 *M* HCl and sonicated for 5 min at 35 ^{o}C using (JAC Ultra Sonic, Korea). Standard solutions (1000 ppm, atomic absorption standard solutions) of Cd(II) and Pb(II) purchased from BDH Chemicals, UK, were diluted as required and used for simultaneous and selective determination. Also, Cu(II) and Hg(II) (BDH Chemicals, UK) were used for interference studies. All other chemicals were of analytical-reagent grade and used as received.

2.2 Electrochemical measurements

The electrochemical measurements including cyclic voltammetry (CV) and differential pulse anodic stripping voltammetry (DPASV) experiments were conducted using a BAS 50W work station. The measurements were performed in a 20 mL electrochemical cell using a glassy carbon electrode (GCE) with a geometric area of 0.071 cm^2 as the working electrode, a platinum coil with a geometric area of 1.90 cm^2 as the counter electrode, and an Ag/ AgCl/

$KCl_{(sat.)}$ as the reference electrode. The potentiostat and electrodes were from Bioanalytical System, West Lafayette, IN, USA.

Prior to each experiment, the working electrode was polished using a polishing cloth and alumina slurry (5.0 and 1.0 μm), washed with acetone, ultrasonicated for 5 min and finally rinsed thoroughly with distilled water. The electrode was then pre-treated electrochemically by scanning the potential repeatedly between -400 mV to +1000 mV for 25 cycles at a scan rate (v) of 100 mV s^{-1} and terminating at the anodic potential limit in the supporting electrolyte, in order to establish a reproducible electrode surface and avoid any previous fouling effect. Such a reversible potentiodynamic scan produces a surface composed of carbon-oxygen functional groups of phenol and quinol forms that increase the electrode reactivity and the grafting efficiency. The CV experiments were utilized mainly to study the progress of the electrochemical polymerization, and the stability and the sensitivity of the resulting polymeric film modified electrode. The typical parameters controlling the DPASV experiment were (i) deposition time = 120 s, (ii) deposition potential = –1200 mV (with stirring mode), (iii) final potential = +200 mV at scan rate of 40 mV s^{-1}, (iv) pulse amplitude = 50 mV, (v) sample width = 25 ms, (vi) pulse width = 50 ms, (vii) pulse period = 100 ms and (viii) quiet time = 10 s.

2.3 Characterization techniques

The structure and surface morphology of the polymer deposited at glassy carbon disks (5 mm × 100 μm) (from Hochtemperature-Werkstoffe, Gmbh, Germany) by repetitive potentiodynamic cycles were investigated by X-ray Photoelectron Spectroscopy (XPS) using an Omicron Nanotechnology XPS system, and by Atomic Force Microscopy (AFM) using a Nanoscope V Multimode microscope (Veeco Instrument, USA). The XPS spectra obtained were deconvoluted using CasaXPS program (Casa Software Ltd, UK), in which the background was simulated using Shirley function and the peaks were fitted using a Gaussian Lorentzian function. The AFM images were recorded ex situ using a tapping mode at a scan rate and imaging resolution of 0.5 Hz and 512 pixels, respectively.

Electrochemical Impedance Spectro scopy (EIS) was employed to further investigate the interfacial structure due to surface modification and extract important information about the rate of electron transfer, the double-layer capacitance and the diffusion limited process. The EIS was carried out on EIS 300 (GAMRY, USA) connected to a three-electrode cell composed of Ag/AgCl, $KCl_{(satd)}$ and platinum coil as reference and counter electrodes, respectively. The working electrode was either the bare GCE or Padpa/GCE modified electrode. The EIS measurements were conducted at an open circuit potential of 5.0 mM $[Fe(CN)_6]^{3-/4-}$ redox probe in the frequency range from 0.1 Hz to 100 kHz.

2.4 Treatment and preparation of the water sample

A treated waste water sample used for agricultural irrigation was collected from the botanical garden located inside the Sultan Qaboos University. The sample was collected in 100 mL polyvinyl bottles, filtered and acidified with 1.0 mL of 1.0 M HCl.

Prior to analysis, 5.0 mL of the sample was pipetted in a small vial and mixed with the required amounts of metal standard solutions. The standard addition method was applied to determine the concentration of both metal ions with reference to the metal-free water sample.

3. Results and discussion

3.1 Electrochemical polymerization of 4-adpa using CV method

Figure 1 shows typical cyclic voltammograms (CVs) corresponding to the electrochemical polymerization of Padpa at GCE using 5.0 m*M* 4-adpa in 1.0 *M* HCl solution. The polymeric film was obtained by repetitive potential scans (25 cycles) between -200 mV and +800 mV vs. Ag/ AgCl at 50 mV s^{-1}. A pair of redox peak currents was developed (anodic) at +425 mV and (cathodic) +197 mV which increased constantly upon subsequent cycling.

The reversible voltammetric waves describe the formation of reduced and oxidized oligomers called the leucoemeraldine and pernigraniline, respectively, which involves the transfer of two electrons and two protons [29]. The initiation step for the propagation of the polymer is the formation of a cationic intermediate called N-phenyl-quinonediimine (pqdi) [30] as shown in the mechanistic reaction presented in Scheme 1. This step is followed by a dimerization step of pqdi with the monomer to form the mono-charged radical intermediate responsible for the growth of the polymer. Petr *et al.* Have confirmed the formation of pqdi as the only product formed during the oxidation of 4-adpa by *in situ* UV-Vis electrochemical measurements [31].

Hence, in the reverse scan, the remaining surface amount of pqdi (not dimerized) may undergo a reduction reaction which gives rise to a smaller current response at 340 mV. It should be noted that the relative amount of both constituents (oxidized and reduced forms) depends on the acid concentration, the oxidative applied potential and the degree of polymerization (number of cycles).

The experimental data presented in Figure 1 can be expressed in consecutive steps initiated by the formation of radical intermediates, dimerization, oligo-merization and the deposition of less soluble oligomers (tetramers and/or octamers) at the electrode surface [19,20]. The formation of an adhering polymeric film at the electrode surface was confirmed by Petr *et al.* [33] using electrochemical and Electron Spin Resonance (ESR) methods. The electrochemical behavior of the modified electrode was examined by stepping the electrode potential between −400 mV to +900 mV vs. Ag/AgCl in a monomer-free aqueous solution of 0.10 *M* HCl.

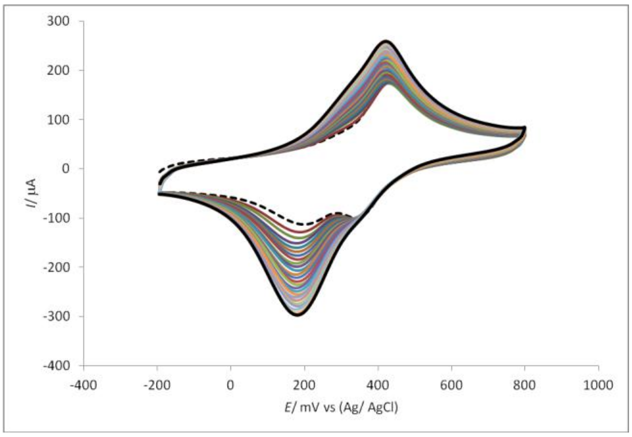
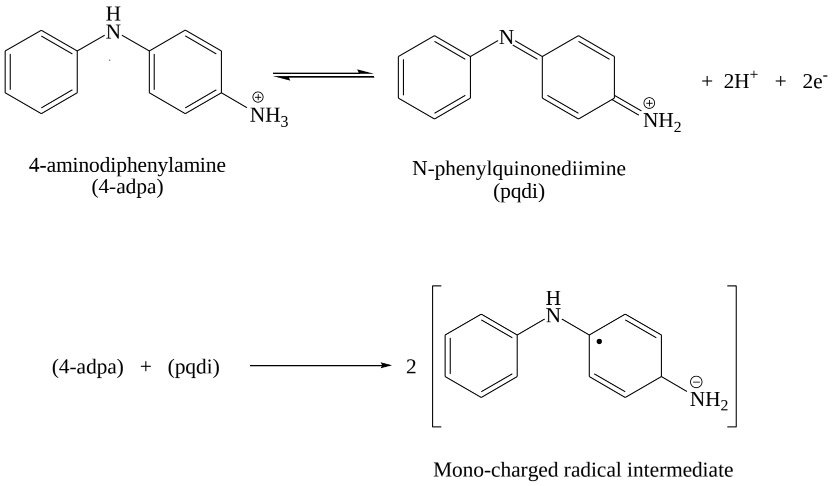


Figure 1. Typical CVs (25 cycles) depicting the electrochemical polymerization of Padpa onto GCE using 5.0 m*M* 4-adpa monomer in 1.0 *M* HCl (the first segment is indicated by the dotted line).



Scheme 1: The initiation steps for the electrochemical polymerization of Padpa.

Figure 2 depicts the electrode behavior as a function of scan rates in a monomer-free 0.10 *M* HCl solution. A redox surface type is developed that increased with increasing the scan rate from 25 to 300 mV s^{-1}. In the anodic scan, three peak currents arose at potentials +300, +350 and +440 mV, respectively (shown at the slowest potential scan rate). Apparently, a consecutive electron transfer process occurred due to a successive transition states of the surface material. In the reverse scan, the electron transfer also produces three cathodic peaks obtained at +435, +365 and +310 mV, respectively.

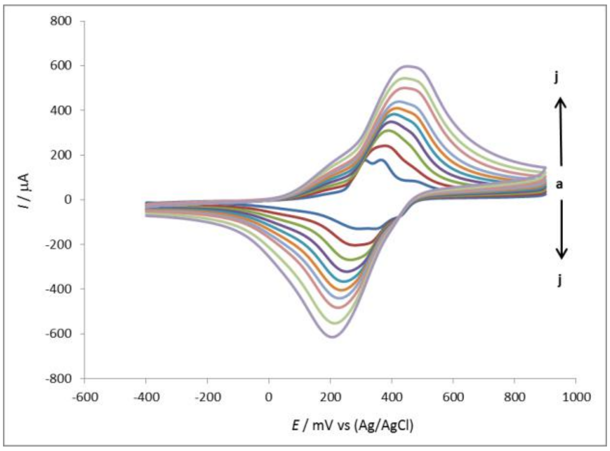


Figure 2. The development of redox surface-type behavior as a function of scan rates in mV s^{-1}; (a) 25, (b) 50, (c) 75, (d) 100, (e) 125, (f) 150, (g) 175, (h) 200, (i) 250 and (j) 300.

The first two peaks are shifted to more positive potential and increased with subsequent increase in the scan rate consistent with increasing the rate of electron transfer process. Furthermore, these anodic peaks are found to merge at scan rates higher than 200 mV s^{-1}. A similar trend was apparent for the cathodic peaks that merged and shifted to a more negative potential. The peak separation (ΔE) at the highest scan rate approached 216 mV suggesting the attachment of surface materials. The experimental data of the peak current as a function of scan rates (not shown) were further studied to calculate the surface coverage (Γ) of the deposited polymeric film in (mol cm^{-2}) applying Eq. (1) [34].

$$I_{\mathrm{p}} = \left(\frac{n^2 F^2 A \Gamma}{4RT} \right) v \tag{1}$$

The calculated surface concentration was 2.71×10^{-10} mol cm^{-2}, taking into consideration that $n = 2$ and A is the geometric area while other terms have their usual thermodynamic descriptions.

3.2 Surface morphological studies

XPS and AFM methods were used to characterize the elemental structure of the electrode surface and confirm the deposition of the polymer. Figure 3 demonstrates the XPS short scan of C 1s which is deconvoluted into three peaks at 283.9, 285.1 and 287.3 eV corresponding to C-C, C-N and C=O bonds, as anticipated from the original structure of the monomer [22]. Similarly, the N 1s short scan gave rise to three peaks at 398.8, 400.1 and 402.3 eV corresponding to the tertiary amine (=N–) bonding, neutral and protonated primary amines (NH_2) and (NH_3^+) respectively. The presence of =N– group is indicative of the fact that successive oxidation and deprotonation processes took place in the polymerization of the Padpa. AFM images reveal a uniform and symmetrical fiber structure with a lower energy dissipation factor. This could be attributed to reduction in the roughness factor of the film, having an average height of 35 nm and a cumulative surface area of 65 nm^2. It also shows a low and uniform Young’s modulus (~15 GPa) pertinent to the deposition of a pristine Padpa substance. The surface roughness of the polymer is expected to become much coarser by increasing the number of potentiodynamic cycles in which a new route of polymerization process may control the progress of film formation.

3.3 Electrochemical impedance studies

The AC impedance spectra presented by Nyquist plot in the presence of 0.5 M KNO_3 solution containing 5.0 mM $[Fe(CN)_6]^{3-/4-}$ are shown in Figure 4. Two characteristic parts are identified in the plot as a linear curve and a semi-circular shape, which occurred at low and high frequencies, respectively. The linear trend corresponds to the diffusion limited process while the arc shape represents the rate of electron transfer process. To understand the electrical properties of the electrode/solution interfaces, a modified Randle’s equivalent circuit (inset of Figure 4) was selected for fitting the impedance data [35]. The EIS data recorded at the bare GCE (inset) showed a charge transfer resistance (R_{ct}) with a given diameter of 147 Ω, compared to the Padpa/GCE modified electrode that revealed a larger value of 2670 Ω. This trend evidently demonstrates that Padpa was successfully assembled at the GCE.

3.4 Applications

3.4.1 Simultaneous determination of cadmium and lead ions

Figure 5 depicts the application of the modified electrode for simultaneous determination of Cd^{2+} and Pb^{2+} employing the DPASV method in which the anodic peak currents were recorded as a function of metal ion concentrations. The (I–E) curve illustrates the rising up of a couple of well-defined peaks at –825 mV and –535 mV, corresponding to the stripping of Cd^{2+} and Pb^{2+}, respectively. The peak separation (ΔE = 290 mV) is significantly large, indicating an excellent selectivity and catalytic activity of the present system. Moreover, the anodic peak currents of both ions are increasing linearly with the concentration as illustrated by the calibration curve given in the inset of Figure 5.

The sensitivity of the present system is evaluated by means of the slope difference of both ions obtained from the experimental data presented in Figure 5. The slope ratio of lead to cadmium ions $\left(\mathrm{S}_{\mathrm{Pb}^{2+}}/\mathrm{S}_{\mathrm{Cd}^{2+}}\right)$ is close to 2.75 indicating a higher sensitivity in determination of lead ions. The surface affinity of both ions was expected to be the same unless possible interaction forces occurred between them due to differences in their electronegativity values. Therefore, Pb^{2+} ions of higher electronegativity were reduced and formed a micro-structure of particles or coated film at cathodic potential lower than that of Cd^{2+} ions, which may have caused the formation of an intermetallic (Pb-Cd) structure [35]. The expected events occurred during deposition potential period when the preferential deposition of Pb was followed by a direct deposition of Cd at both the polymeric film and the Pb matrix already existing on the electrode surface.

During the anodic stripping mode, Cd deposited at the polymeric film will first dissolute at – 825 mV and the remaining Cd deposited on to Pb will be stripped with Pb at more positive potential. It should be noted that the positive potential shift in the stripping of both ions shown in Figure 5 with increasing the concentration is an indication of such energetic interaction.

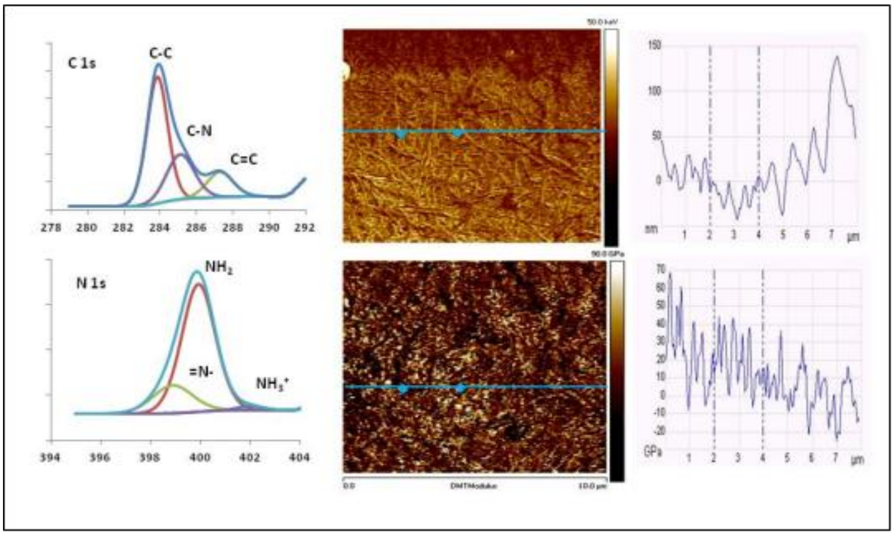


Figure 3. Surface topographic analysis represented by XPS short scans of C 1s and N 1s with AFM images of dissipation and DMT Modulus of the Padpa/GCE surface film.

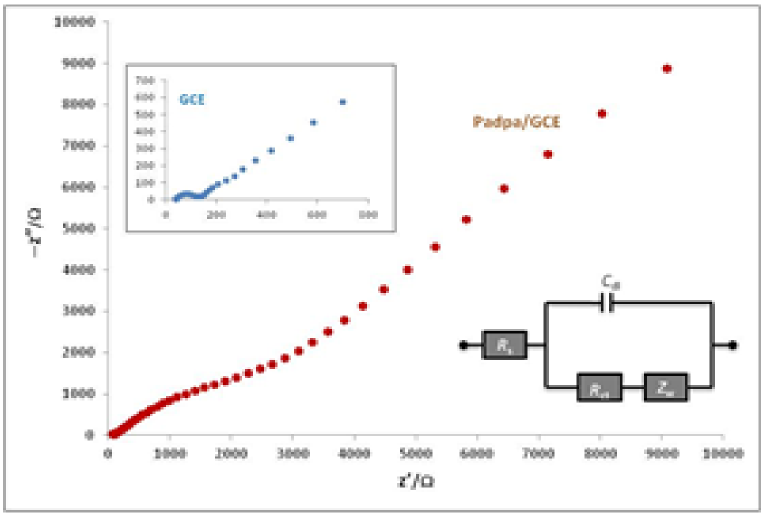


Figure 4. EIS data for Padpa/GCE and bare GCE (insert) with the modified Randle's equivalent circuit.

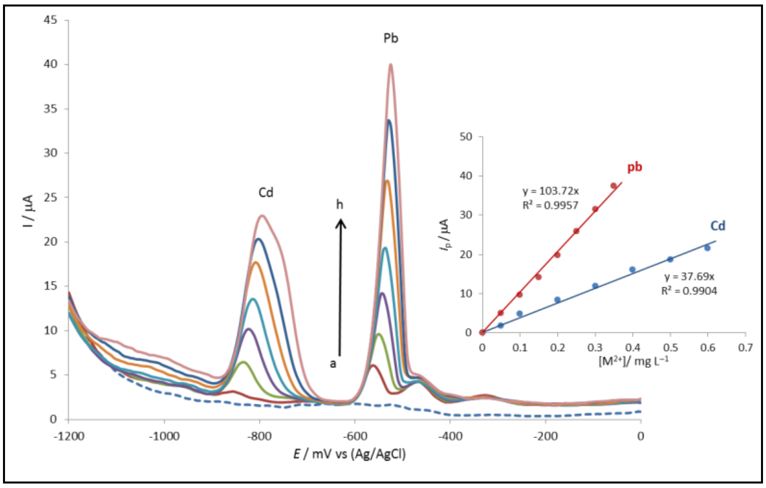


Figure 5. DPASV curves recorded at Padpa/GCE in acidified 0.1 *M* KCl solution (pH = 2.12) for the simultaneous determination of Cd^{2+} and Pb^{2+} ions. The range of [Cd^{2+}] and [Pb^{2+}] are indicated by the calibration curve (I_p vs [M^{2+}]) given in the inset.

Moreover, the limit of detection (LOD) was calculated using (3σ/S) where σ is the standard deviation obtained from 5 replicates of the blank. The LODs were 25 and 14 μg L^{-1} for Cd^{2+} and Pb^{2+}, respectively. The sensitivity of the present system given by the slope of the linear relationship of I_p vs $[M^{2+}]$ was compared with other electrochemical systems [36-42] and presented in Table 1.

The present work showed a good sensitivity for both metal ions suggesting the construction of a robust solid state sensor for environmental applications. It should be noted that the stripping analysis of each ion in the concentration range of 50 to 500 μg L^{-1} was conducted separately to evaluate the surface catalytic efficiency and the rational scenario of binary concentrations. Such primary analysis along with controlling the method parameters, in particular the deposition potential and accumulation period, enhance the separation facility and minimize possible suppression of the cadmium peak [43]. Therefore, the linear concentration range of Cd^{2+} ions presented in Figure 5 must have been relatively high to produce a significant change in the stripping peak current. Apparently, the binary solution of the above selected recipe allows a regular and steady deposition of both ions at the electrode surface, where only two symmetrical and well defined peaks arose regardless of the relative extent of surface capacitance due to the presence of the polymeric film.

Table 1. The sensitivity of various electrochemical systems in (μA/ μg L^{-1}) evaluated from the simultaneous determination data of both metal ions in their binary mixture.

Surface	Cadmium	Lead	Ref.
Bi/Pani	0.73	0.074	[36]
PEDOT	0.004	0.008	[37]
Pani	0.021	0.059	[38]
Bi/Nafion	0.027	0.019	[39]
PPMA	0.007	0.098	[40]
BDD	0.015	0.013	[41]
Bi/Poly(p-ABSA)	0.031	0.019	[42]
Padpa	0.038	0.104	this work

However, the estimated base peaks for the stripping of Cd and Pb at their highest concentrations shown above were found to be 175 and 100 mV, respectively.

The above important observations pertaining to analytical peak separation and low detection limits, suggest an excellent stability, sensitivity and adsorption capacity of the present electrocatalytic system. It is worthy to note that the above data were collected without intervening electrode conditioning between successive concentrations. The stability and the reproducibility of the modified electrode were examined by repeating the DPASV experiment 10 consecutive times in the presence of 250 μg L^{-1} (Pb) and 500 μg L^{-1} (Cd). The peak separation was successfully maintained, indicating a good stability of the modified electrode, while the current variation was 4.7% for Pb and 6.6% for Cd, suggesting that the electrode reactivity is not affected critically by the adsorption of analytes and can be used multiple times.

3.4.2 Selective determination of cadmium and lead ions

The electrode selectivity and hence the interference trend was tested for each metal ion by sequentially changing the concentration of one metal ion in the presence of a high and constant concentration of the second one. Figure 6 depicts the effect of 1000 μg L^{-1} of Pb^{2+} in the determination of Cd^{2+} ions using the DPASV method.

The stripping peak of Cd is well separated and occurred at –820 mV vs (Ag/ AgCl) and increased linearly with increasing $[Cd^{2+}]$ despite a possible interfering tendency that may be initiated by the presence of large $[Pb^{2+}]$. The calibration curve for the linear plot of I_p vs. $[Cd^{2+}]$ is shown in the inset of Figure 6, and the calculated LOD (3σ/S) was 23 μg L^{-1}. Nevertheless, the stripping peak of Pb (present in a large scale) obtained at –510 mV does not hinder or manipulate the stripping peak of Cd, indicating that Padpa active sites are capable of accommodating both metals during the accumulation period.

In a similar fashion, the data presented in Figure 7 illustrates that the presence of 2000 μg L^{-1} Cd does not alter the stripping peak position of Pb, which maintained its symmetrical shape and sharpness, and increased subsequently with increasing $[Pb^{2+}]$.

The calibration curve for the linear plot of I_p vs. $[Pb^{2+}]$ is shown in the inset of Figure 7, and the calculated LOD (3σ/S) was 13 μg L^{-1}. Accordingly, it can be concluded that the surface based material did not deteriorate due to deposition of both metals and sustained its structure during the stripping mode in the positive scan.

3.4.3 Interference studies

The presence of foreign metal ions in the water sample may change the nature and the morphology of the electrode surface and hence affect the electrochemical measurements of analytes under investigation. For this task, the simultaneous determination of 250 μg L^{-1} (Pb) and 500 μg L^{-1} (Cd) was investigated in the presence of 5000 μg L^{-1} of the foreign ion. Foreign ions such as Na^+, Mg^{2+}, Ni^{2+}, Co^{2+}, Al^{3+}, Fe^{3+}, VO_4^{3-}, MnO_4^-, Cl^-, and NO_3^- had no interference on the present system. The effect of Cu^{2+} and Hg^{2+} on the stripping voltammetry of Pb and Cd ions is presented in Figures 8(A) and (B), respectively.

The presence of 2500 μg L^{-1} Cu^{2+} (solid line) distorted the development of the Cd peak which appears very broad and unsymmetrical, while the peak potential of Pb was only shifted by +100 mV from its usual position (dotted line). The presence of 1000 μg L^{-1} Hg^{2+} (solid line) had a direct effect on the symmetry of the Cd peak current, which became much sharper and increased three fold the original value (dotted line), while it had no effect on the peak current of Pb. The above trend could be interpreted as due to the formation of a thin Hg layer that played a major role in the enhancement of the Cd voltammetric signal.

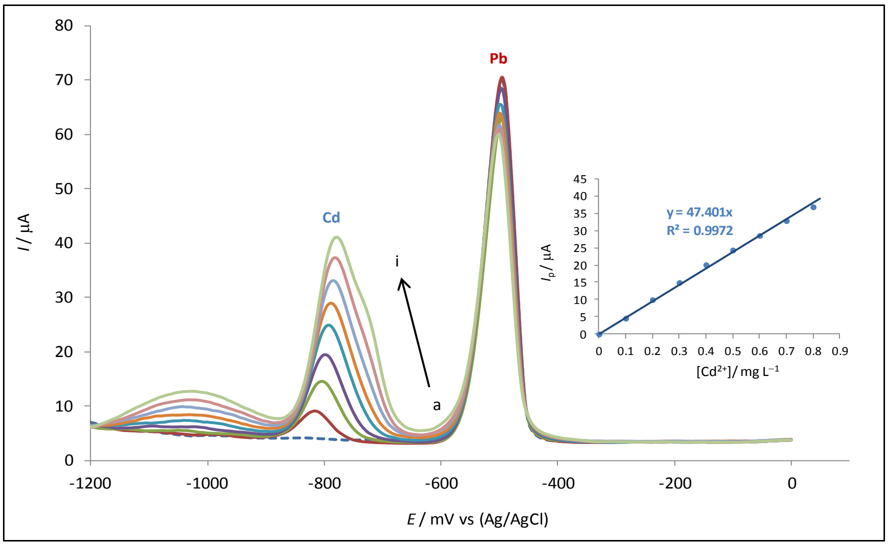


Figure 6. DPASV curves recorded at Padpa/GCE in acidified 0.1 *M* KCl solution (pH = 2.12) for the selective determination of Cd^{2+} in the presence of 1.0 mg L^{-1} Pb^{2+}. The range of $[Cd^{2+}]$ is (a) 0 increased by 0.1 mg L^{-1} each time to a final (i) 0.8 mg L^{-1} (inset is the calibration curve represented by I_p vs $[Cd^{2+}]$.

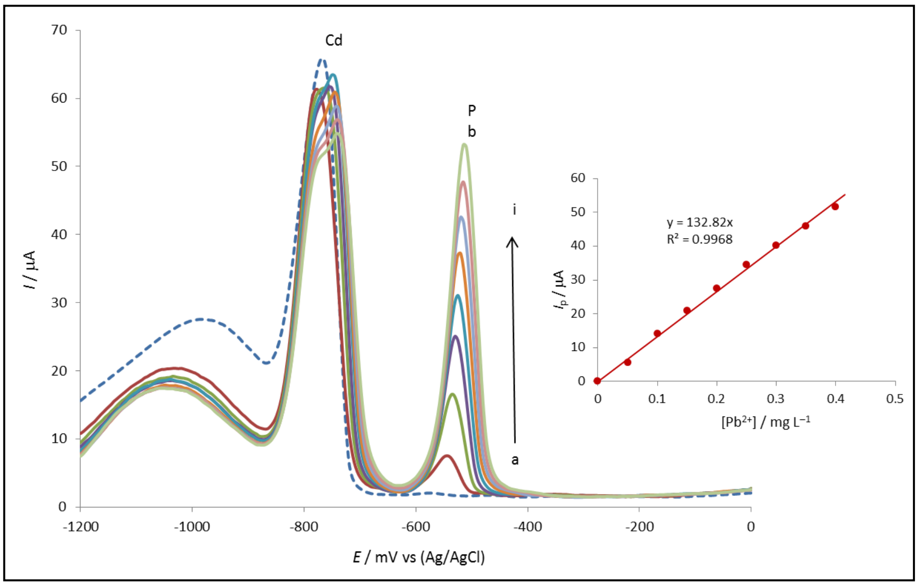


Figure 7. DPASV curves recorded at Padpa/GCE in acidified 0.1 *M* KCl solution (pH = 2.12) for the selective determination of Pb^{2+} in the presence of 2.0 mg L^{-1} Cd^{2+}. The range of $[Pb^{2+}]$ is (a) 0 increased by 0.05 mg L^{-1} each time to a final (i) 0.4 mg L^{-1} (inset is the calibration curve represented by I_p vs $[Pb^{2+}]$.

3.4.4 Analytical test to water sample

The proposed system was tested for the determination of both metal ions in a water sample treated and prepared as described above in section 2.4.

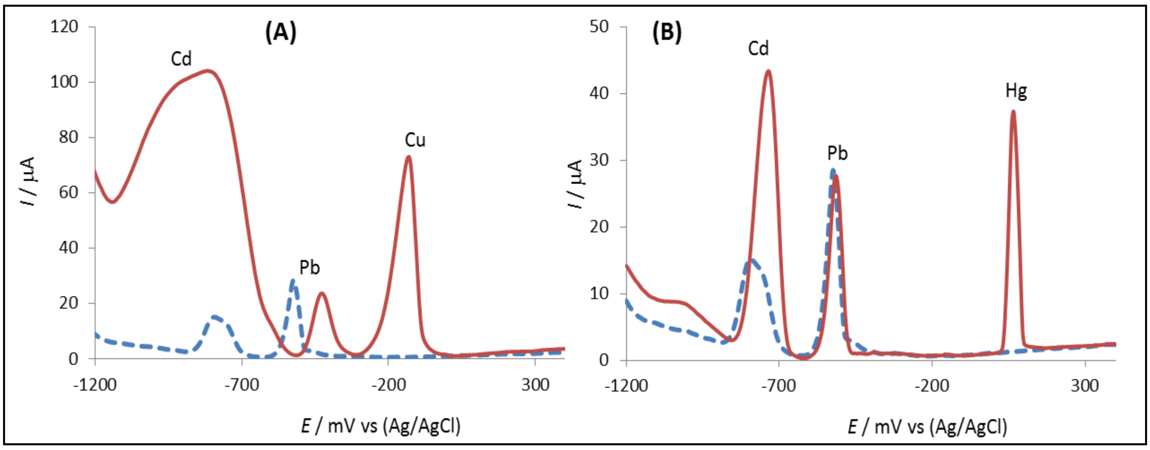


Figure 8. Interference study on the stripping peaks of 0.5 mg L^{-1} Cd^{2+} and 0.25 mg L^{-1} Pb^{2+} in the presence of (A) 2.5 mg L^{-1} of [Cu^{2+}] and (B) 1.0 mg L^{-1} of [Hg^{2+}] using acidified 0.1 *M* KCl solution (pH = 2.12).

The analytical results including the recovery percentage are given in Table 2. The recoveries were more than 97% (the calculated relative standard deviation values were less than 10%), and demonstrate that the present system can offer a sensitive and accurate method for the monitoring of trace metal ions.

Table 2. Analytical parameters and recovery percentage (n = 3) for Cd^{2+} and Pb^{2+} ions in water samples using standard addition method. The regression data obtained from Figure 5 were used to calculate their concentrations.

Metal ions	(I) (µA)	[Actual] (µg L^{-1})	[Found] (µg L^{-1})	Recovery (%)
(Cd^{2+})				
(1)	1.84	50	48.4	96.8
(2)	3.76	100	98.9	98.9
(3)	5.69	150	149.7	99.8
(Pb^{2+})				
(1)	2.45	25	24.4	97.7
(2)	5.21	50	50.1	100.2
(3)	7.88	75	75.8	101.0

4. Conclusions

A chemically modified electrode was fabricated *via* the electrochemical polymerization of Padpa at GCE in 1.0 *M* HCl solution. The surface coverage of the coated film was influenced by the applied anodic potential that initiated the progression of polymerization and defined the nature of the resulting polymer. The polymeric film modified electrode exhibited a reversible electrochemical behavior, demonstrated by the development of redox active sites. The estimated surface roughness and cumulative surface area of the modified electrode under the present working conditions is an index for possible doping process on the film matrix to improve its catalytic properties for certain analytical applications. The constructed modified electrode showed a potential capacity to be a reliable environmental sensor for the simultaneous determination of Cd^{2+} and Pb^{2+} ions. The incorporation of certain surface modifiers such as metal microfilms or metal nanoparticles on the Padpa moiety is another important area to investigate in developing solid-state sensors for environmental, biological and pharmaceutical applications.

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