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Electropolymerization of diaminofluorene and its electrochemical properties



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KEYWORDS

Electrochemical polymerization; Cyclic voltammetry; Conducting polymer Abstract Poly 2,7-diaminofluorene (PDAF)/Au modified electrode was prepared using 2,7-diamino fluorene (DAF) dissolved in acetonitrile (ACN) containing 0.1 M LiClO₄ using consecutive multisweep cyclic voltammetry (CV) and controlled potential electrolysis (CPE) techniques. Factors affecting the film formation, such as limits of potential cycling, sweep rate, number of sweeping cycles, monomer concentration, and also polymerization techniques were examined in detail. It was found that the optimum conditions, using a potentiodynamic technique on Au electrode as the working electrode, are by sweeping the potential between -200 mV and 800 mV at a sweep rate of 50 mV/s for 10 cycles using 5 mM DAF monomer solution. The obtained modified electrode was active only in acidic aqueous solutions (pH range from 0 to 2) and its activity was found to be pH dependent. PDAF was isolated and characterized using UV-vis, ¹HNMR and SEM analyses. The electrical conductivity was found to be 1.5×10^{-5} S cm⁻¹. An electropolymerization mechanism was proposed and discussed based on the obtained experimental data and molecular orbital calculations. The obtained modified electrode has been found to improve the electrochemical reversibility and decrease the overpotential of hydroquinone. PDAF/Au was stable chemically and electrochemically both in aqueous and organic solutions, making it an excellent candidate for sensing and/ or electrocatalytic applications.

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1. Introduction

The study and the synthesis of conducting organic polymers have been of great interest since the last few years. Thus, the first chemical synthesis of such compounds dates from 1973 $(SN)_x$ by walatka. Since this discovery several other polymers have been synthesized: the $(CH)_x$ by McDiarmid and poly.p.phenylene by Miller in 1979. At that time, Diaz and coworkers reported the first electrochemical synthesis of a conducting polymer in organic medium: the polypyrrole (Rault-Berthelot and Simonet, 1986; Rault-Berthelot et al., 1988, 1995a,b).

The polymers obtained by anodic oxidation of fluorene and their monosubstituted or 9,9-disubstituted parents have been already described as materials whose reversible electroactivity lies in a high potential range when compared with other conducting polymers such as polypyrrole or polythiophene (Bidan, 1985; Rault-Berthelot and Raoult, 2001; Rault-Berthelot et al., 1997). The reversible oxidation of the polyfluorenic matrices occurs between 0.8 and 1.2 V (reference Ag/ Ag⁺NO₃) 0.1 M in CH₃CN. Because of this rather positive potential, the polymers cannot be synthesized, studied and, therefore, used as electrode modifiers in aqueous media.

Anodic oxidation of aromatic amines has been extensively studied in both aqueous and nonaqueous solutions, and some general rules for reaction pathways have been obtained for mononuclear aromatic amines. For polynuclear aromatic amines (Rault-Berthelot and Roze, 1998; Ferraris et al., 1995; Leclerc, 2001; Cimrova et al., 1996; Groenendaal et al., 2003), however, little is known about the oxidation pathway. This is partially because in many cases the oxidation products film the electrode surface and no product could be isolated.

Since 1985, interest was shown in the anodic polymerization of fluorene derivatives. At the beginning, we demonstrated that polymers derived from fluorene, 9-substituted or 9,9-disubstituted fluorenes are electroactive materials possessing p- and n-doping processes. Their uses as electrochromic materials, electrode modifiers, in bi- or trilayer devices or as complexing materials were developed (Berkenkotter and Nelson, 1973; Nelson, 1974; Rault-Berthelot and Granger, 1999; Malitesta et al., 1990; Dong and Li, 1990). When the substitution was performed by cyano group, these matrices were demonstrated to present affinity towards metallic cations and metal-polymer composites were used as efficient electrode modifiers for electrocatalytic reactions (Imamoglu and Onal, 2004; Johansson et al., 2001; Millard, 2000; Yousef et al., 2001).

In this paper, electropolymerization of 2,7-DAF and characterization of its polymers were studied. PDAF films were easily prepared by the anodic oxidation of DAF monomer in acetonitrile. The electrochemical properties, conductivity and electroactivity of the resulting PDAF films were studied. PDAF was isolated and characterized using UV–vis, FT-IR and SEM analyses. The electrical conductivity was found to be 1.5×10^{-5} S cm⁻¹.

2. Experimental

2,7-Diaminofluorene (DAF), from Sigma and Fluka (97% pure), acetonitrile (99%), Lithium perchlorate (97%) and hydroquinone (90%) were obtained from Aldrich Co., and

used without further purification. The acidic aqueous solutions used were prepared using freshly distiled water to avoid contamination with atmospheric CO_2 and sulphuric acid (BDH).

Electrochemical measurements were carried out with a BAS (CV50w) (West Lafayette, IN, USA) potentiostat and Voltalab potentiostat 006. The electrodes consisted of a gold disk electrode (BAS, area: 0.03 cm^2) as the working electrode, Ag/Ag⁺ as the reference electrode and platinum wire as the counter electrode. Before each use, the gold disk electrode was mechanically polished using alumina slurries (particle size $0.3 \mu m$). The electrode was then washed thoroughly and dried in air. The electrode was then dipped in acetonitrile solution containing 0.1 M LiClO₄ and 5×10^{-3} M of DAF for electropolymerization by potential cycling between -0.2 V and 0.8 V for 10 cycles at a scan rate of 50 mV/s. The modified electrode obtained was denoted as poly diaminofluorene/gold film-electrode and symbolized as PDAF/Au.

2.1. pH metre

A type model 810-pH metre (Fischer Co) was used for measuring the pH values of the acidic aqueous solutions.

2.2. Controlled potential electrolysis (CBE)

The polymeric films were deposited on a platinum plate (9 cm^2) by controlled-potential electrolysis at 0.8 V vs. Ag/Ag⁺ of an acetonitrile solution containing 0.1 M LiClO₄ and 0.05 M of the monomer. The resulting polymer was collected, washed several times with acetonitrile and dried under vacuum.

2.2.1. UV-vis spectra

UV-vis Spectra were recorded using a Guided Wave Model (4802 UV/vis Double Beam) spectrophotometre.

2.2.2. ¹H NMR spectroscopy

The ¹H NMR spectra of the monomer and the resulting polymer (in DMSO as a solvent) were measured on mercury-300BB "NMR300".

2.2.3. Electrical conductivity

The electrical conductivity of the pressed film was measured utilizing 4.5 Digit true RMS Multimetre (model 2833), BK Precision.

2.3. Scanning electron microscope (SEM)

Measurements by SEM Model Philips XL 30 attached with EDX Unit, with accelerating voltage 30 kV, magnification $10 \times$ up to 400,000× were carried out on polymeric films deposited on a platinum surface by using controlled-potential electrolysis at 0.8 V in acetonitrile solution containing 0.1 M LiClO₄ and 0.05 M of the monomer.

3. Results and discussion

3.1. Electropolymerization studies

Fig. 1 shows a typical cyclic voltammogram of the electrochemical growth of poly DAF on a gold disk electrode in an



Figure 1 Cyclic voltammograms of DAF/Au disk electrode in an acetonitrile solution containing 5×10^{-3} M of DAF and 0.1 M LiClO₄, 10cycles, scan rate, 50 mV/s.

acetonitrile solution containing 5×10^{-3} M of DAF and 0.1 M LiClO₄. The monomer electrochemically oxidized in two reversible peaks at 230 mV and 580 mV (peaks I and II). Also, reduction peaks for the products formed during the first anodic sweep are observed at 450 mV and 100 mV (peaks III and IV). The first peak (peak I) could be attributed to the oxidation of the amino group to the corresponding radical cation NH₂.⁺ (Imamoglu and Önal, 2004; Yasukouchi et al., 1979; Rault-Berthelot and Granger, 1999). The presence of strongly electron donating amino groups in the fluorene ring will stabilize the radical cation, giving rise to a two-peak reversible redox reaction. Continuous sweeping lead to the improvement of the currents of the two redox systems which was considered as great evidence about the accumulation of an electroactive polymer film on the electrode surface. This growth behaviour



Figure 2 Cyclic voltammograms response of PDAF/Au modified electrode in 0.01 M H_2SO_4 aquoeus solution at a sweep rate 50 mV/s.



Figure 3 Cyclic voltammograms of DAF/Au electrode in an acetonitrile solution/0.1 M LiClO₄ at 1×10^{-3} M (a), 5×10^{-3} M (b), 1×10^{-2} M (c), 5×10^{-2} M (d), scan rate 50 mV/s.

is in close agreement with that reported previously for the electropolymerization of 2-aminofluorene in dichloromethane in the presence of $(Bu)_4NBF_4$ as the supporting electrolyte and other fluorene derivatives (Rault-Berthelot and Granger, 1999; Rault-Berthelot and Simonet, 1985; Abdel-Azzem et al., 1996). After 10 cycles, the prepared modified electrode was removed from electrolysis medium, rinsed with acetonitrile to remove any monomer traces and then transferred to a pure aqueous 0.01 M H₂SO₄ solution and cycling between potential limits from -200 mV to 500 mV (cf. Fig. 2).

3.2. Effect of monomer concentration

The electrochemical activity of the prepared modified electrode was found to be dependent on monomer concentration in the electrolytic medium during the film formation. This study was carried out on films prepared by cycling the electrode potential from -200 mV to 800 mV at a sweep rate of 50 mV/s for 10 cycles in an acetonitrile solution containing 0.1 M LiClO₄

and different monomer concentrations in the range from 1×10^{-3} M to 5×10^{-2} M. It was found that the oxidation behaviour of DAF and the electrochemical activity of the resulting film modified electrode depends significantly on the monomer concentration. Cyclic voltammograms shown in Fig. 3(a–d) indicate that increasing DAF concentration from 1×10^{-3} M to 5×10^{-3} M (Fig. 3a and b) lead to the appearance of two reversible systems. Increasing the monomer concentration up to 5×10^{-2} M causes the disappearance of reversible peaks (cf.Fig. 3c and d).

3.3. Electroactivity of the prepared film

After cycling the gold electrode in the monomer solution for several scans, its surface was observed to be coated with a very thin and transparent film. The electrochemical activity of the resulting polymeric film was examined in both non aqueous and acidic media. The modified film electrode was found greatly active in acid aqueous medium traced by observing of the redox peaks that were not seen in non aqueous media. To identify the most suitable conditions for obtaining a stable and reactive film electrode, the following factors were tested.

3.3.1. Effect of film relative thickness

Effect of film thickness determined by the number of polymerization scans, on the electroactivity and stability of PDAF/Au



Figure 4 Plot a curve between different number of cycles and the peak currents (*I*pa,c) of the film-electrode.

Table	1	Effect	of	different	number	of	cycles	on	its
electro	acti	vity.							

	-				
No. of cycles	I _{pa} , μA	<i>I</i> _{pc} , μΑ	$\Delta E_{\rm p},{\rm mV}$	% Drop of <i>I</i> _{pc}	% Drop of <i>I</i> _{pa}
10	-3.1	3	51	27	10
20	-1.9	2.5	60	44	28
30	-1.7	1.95	65	30	29
40	-1.6	1.8	71	39	31



Figure 5 Cyclic voltammograms response of PDAF/Au modified electrodes in 0.01 M H_2SO_4 at different sweep rates in the range from 10 to 200 mV/s.

modified electrode was examined on film/electrodes prepared in an acetonitrile solution containing 5×10^{-3} M DAF and 0.1 M LiClO₄ by performing different numbers of scans in the range from 10 to 40. Fig. 4 indicates that the current intensities of the redox systems of the obtained films decrease gradually as the number of cycles increases. This behaviour could be attributed to the increase of the resistivity of the film which prevents the progress of electrochemical polymerization process. On the other hand, the percentage drop of the anodic current of the film redox response caused by repeating the scan to

3.3.2. Effect of potential sweep rate

age drop also increases (Table. 1).

Fig. 5 shows the cyclic voltammograms of PDAF/Au modified electrode at different scan rates ranging from 10 mV/s to 200 mV/s. It was clear that the cyclic voltammograms of PDAF/Au modified electrodes are almost symmetrical and the redox peak currents increased linearly with the scan rate between 10 and 200 mV/s as expected for the thin-layer electrochemical behaviour. It could be observed that the cathodic

eigth sweeps, as the number of cycles increases as the percent-



Figure 6 Cyclic voltammograms of DAF in an acetonitrile solution containing 5×10^{-2} M of DAF and 0.1 M LiClO₄ on Pt (a) GCE (b) electrodes.

and anodic peak currents (I_p) of the PDAF increased with the increase of the scan rate (v), at the same time the cathodic and anodic peak potentials exhibited a small shift and the peak-to-peak separation also increased (Yang et al., 2006).

3.3.3. Effect of acid concentration

PDAF/Au modified electrode prepared in an acetonitrile containing 0.1 M LiClO₄ and 5×10^{-3} M of monomer. The electroactivity of these films was studied in 0.01 M of H₂SO₄. The effect of acid concentration in the aqueous medium solution on the film electroactivity was examined by using different concentrations of sulphuric acid in the range from 0.01 M to 0.08 M (cf. Table 2) shows the increase in the acid concentration from 0.01 M to 0.08 M and is accompanied by decrease of

Table 2 Effect of different concentrations of H_2SO_4 on activity of the film formed.

[H ₂ SO ₄], M	$I_{\rm pc}~(\times 10^{-6})$	I _{pa} (×10 ⁻⁶)	$E_{\rm pc}$	$E_{\rm pa}$	ΔE
0.01	3.01	-2.98	211	267	56
0.03	2.66	-2.61	208	268	60
0.06	1.8	-2.08	212	279	67
0.08	0.81	-1.8	228	307	79



Figure 7 Cyclic voltammograms response of PDAF in 0.01 M H_2SO_4 using 5×10^{-2} M of DAF on Pt (a) and GCE (b) electrodes.

the current. The potential separation between the anodic and cathodic peak potentials (ΔE_p) increases by increasing the acid concentrations.

3.4. Effect of types of electrodes

Films prepared on three different electrodes (1) Au electrode (2) Pt electrode (3) GC electrode in acetonitrile containing 0.1 M LiClO₄. Comparison between different electrodes by (1) film formation (2) the electroactivity of these films studied in H₂SO₄. These films on different electrodes show the behaviour of film formation on different surfaces of electrodes and show the film formed was less stable than gold electrodes (Figs. 6 and 7).

4. Physicochemical analyses of the polymers

4.1. UV-visible spectra

The UV–vis spectra of both DAF and PDAF in DMF solution are shown in Fig. 8. The monomer showed an absorption peak at 445 nm while the polymer exhibited two peaks at 450 (which can be ascribed to the π – π * transition) and 685 nm which is due to polaronic transitions (Poriel et al., 2005).

4.2. ¹H NMR spectra

Fig. 9 shows the 1H NMR spectra of DAF (a) and its resulting polymer (b) in deuterated DMSO. In the monomer spectrum (Fig. 9a) the aromatic protons signals appear at $\delta = 7.26$ (d, J = 10.8 Hz, 2H), 6.69 (s, 2H) and 6.48 (dd, J = 2.8, 10.8 Hz, 2H) assigned for H-4, H-1 and H-3 respectively. The exchangeable protons appear as a broad singlet at $\delta = 4.87$ ppm and the non aromatic protons resonate at $\delta = 3.56$ ppm. The polymer spectrum (Fig. 9b) shows that the change of the position of the exchangeable protons from 4.87 ppm to 3.34 ppm and the non aromatic protons from 3.56 ppm to 3.80. The chemical shifts of the aromatic protons



Figure 8 UV-vis spectra of (A) DAF monomer and (B) PDAF polymer in DMSO solutions.



Figure 9 ¹H NMR spectra of monomer (a) and PDAF (b), solvent: d₆ DMSO (a, b)



Figure 10 SEM of PDAF film deposited on the Platinum surface. The films were synthesized electrochemically in acetonitrile containing 0.1 M LiClO₄ at a constant applied potential of 0.8 V.

have been changed from 7.26, 6.48 and 6.69 to 7.60, 6.88 and 7.09, respectively.

4.3. Morphology

The surface morphology of polydiaminofluorene on the Platinum surface obtained potentiostatically in $LiClO_4$ was observed by SEM (Fig. 10). Films of PDAF were prepared in an acetonitrile solution containing 0.05 M of monomer and 0.1 M $LiClO_4$ at a constant applied potential of 0.8 V by using CBE. The scanning electron micrographs of these

films show particles of equal shape. Microscopically, the polymer resembled a growth of tubes shaped growths. The growth of the nuclei was in the form of tubes. The conductivity of 2,7-DAF was measured to be 1.5×10^{-5} S cm⁻¹, which was higher than the conductivity of poly(1-naphthylamine) 10^{-6} S cm⁻¹ and lower than of unsubstituted polyfluorene film obtained from BFEE (0.25 S cm⁻¹) (Nie et al., 2008), which indicated that the side groups affected polymerization of DAF, the conductivity of PDAF decreased. These results were in accordance with fluorene and bromofluorene (5.4×10^{-2} S cm⁻¹).



Figure 11 Cyclic voltammograms of 10^{-3} M HQ at Au bare electrode and PDAF/Au modified electrode in 0.01 M H₂SO₄ on different number of cycles.

4.4. Application of film formed

Cyclic voltammetry of 10^{-3} M of HQ/0.01 M H₂SO₄ was studied. The effect of film thickness on the electrocatalytic ability of the prepared modified electrodes was investigated by using the formed modified electrodes. Films of PDAF were deposited electrochemically onto the Au electrode by using different number of cycles from 1 to 10 cycles (cf. Fig. 11). Then cyclic voltammetry was carried out after each deposition for 10^{-3} M hydroquinone in 0.01 M H₂SO₄ at these modified electrodes. In the oxidation peak currents I_{pa} of HQ increases as the number of cycles increases from 1 to 10 cycles. The separation of peak potential E_{pa} decreases as the number of cycles increase the decrease in overpotential E_{pa} means that there is less background current and interference from other dissolved species. From these data, PDAF films having a catalytic behaviour on the oxidation reduction processes for hydroquinone at a polymeric film prepared at successive number of cycles.

5. Conclusions

PDAF films could be prepared at Au electrode by potential sweep electrolysis. It was found that the optimum conditions for the preparation of PDAF/Au are 50 mV/s in the potential range between -200 mV and 800 mV for 10 cycles using 5 mM of DAF in CH₃CN/0.1 M LiClO₄. The resulting film electrodes are electroactive in aqueous 0.01 M H₂SO₄ solution and no response was observed in non-aqueous. CPE technique was used to separate the polymer. PDAF was characterized using UV–vis, ¹HNMR and SEM analyses. The electrical conductivity was found to be 1.5×10^{-5} S cm⁻¹.

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