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Immobilization of salophen derivative Schiff base cobalt(II) complex on a copolymer coated platinum electrode and electrocatalytic investigations

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In this study, o-amino-benzylalcohol (pBA) and o-anisidine (pA) homopolymers and their copolymer (o-amino-benzylalcohol-co-o-anisidine) (Cp) were synthesized on the platinum electrode in 0.5 M H_2SO_4 as a supporting electrolyte medium by electrochemical methods. Then, Co(II) complex of salophen type Schiff base (CoL) was immobilized on these polymer coated electrode surfaces in acetonitrile containing 0.15 M $LiClO_4$. The prepared modified surfaces were characterized by Cyclic Voltammetry, UV-Vis, SEM-EDAX and ICP-MS techniques. The electrocatalytic activity of modified electrodes was investigated on electrooxidation of Dopamine (DA) as biosensor application. One of the prepared modified electrodes showed good electrocatalytic effect on the oxidation of DA using Square Wave Voltammetry method (SWV). The oxidation peak current of DA increased linearly in the range of 0.2 μM - 2 mM in pH 7 phosphate buffer solution at [CoL] immobilized pA modified Platinum electrode. Limit of Detection (LOD) was calculated as 0.1 μM for DA determination.

Keywords: o-amino-benzyl alcohol, electropolymerization, Schiff Base metal complex, immobilization, electrocatalytic investigation.

INTRODUCTION

Electrode materials that used in electrochemical studies are mainly limited commercial species like carbon, mercury, gold, platinum, so researches are significantly restricted in this area [1].

Electrochemical work areas can be expanded by modifying of electrode surfaces with organic-inorganic compounds in order to improve their properties of selectivity, sensitivity and catalytic activity [2-4]. Conductive polymers have also attracted much attention largely at modification of conventional electrode materials as supporting material [5,6]. Because they have been allowed to immobilization, adsorption and covalent attachment for different species due to its porous structure and functional groups.

Common approach of biosensor applications, with immobilization of enzyme to conducting polymer coated electrode surface have been designed as sensors that have selectivity and catalytic activity [7-9]. In this area, alternative solutions have been gained attention against to enzyme immobilization due to decreased of enzyme activities during immobilization, high-cost, their easily degradation and hard isolation.

Recently, inorganic metal complexes that have active metal centre and functional groups are becoming attractive materials as alternatively in this research area because of their catalytic activity and stability [10,11]. Recently prepared new electrode materials studies by using directly electropolymerization of metal complexes of inorganic compounds that have various functional groups and to be linked to an electropolymerizable monomer, their characterization and catalytic activity have been attracted much interest research area in scientific literature [12-15].

The previous studies have been shown that, the electocatalytic properties of modified electrodes containing metal complexes were related with metal species and functional groups of complexes [16].

This study is focused on the preparation of modified electrodes with immobilization of Schiff base metal complex onto new electroactive polymeric supporting materials and also investigation of electocatalytic activity of these electrodes towards determination of dopamine.

EXPERIMENTAL

Materials and methods

A CHI 604E model electrochemical analyzer was used for SWV and cyclic voltammetry (CV) measurements. All the electrochemical studies were carried out by using of conventional three electrode system. A 1 cm^2 Pt plate, Pt wire and saturated Ag/AgCl (3M NaCl) were used as working, counter and reference electrodes, respectively.

Schiff base (H_2L) and metal complex (CoL) were synthesized according to the literature [17]. The proposed structures of H_2L and [CoL] are given in figure 1.

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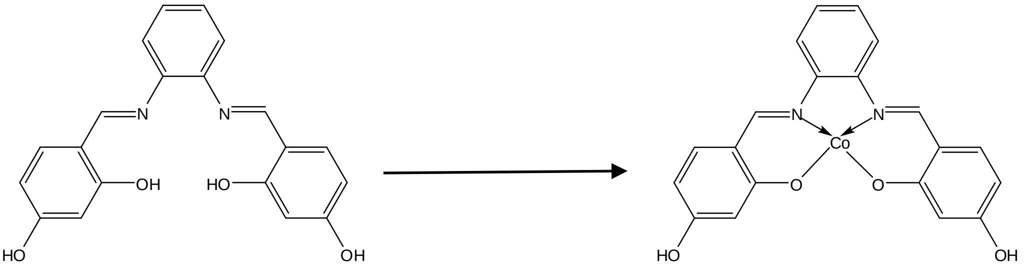

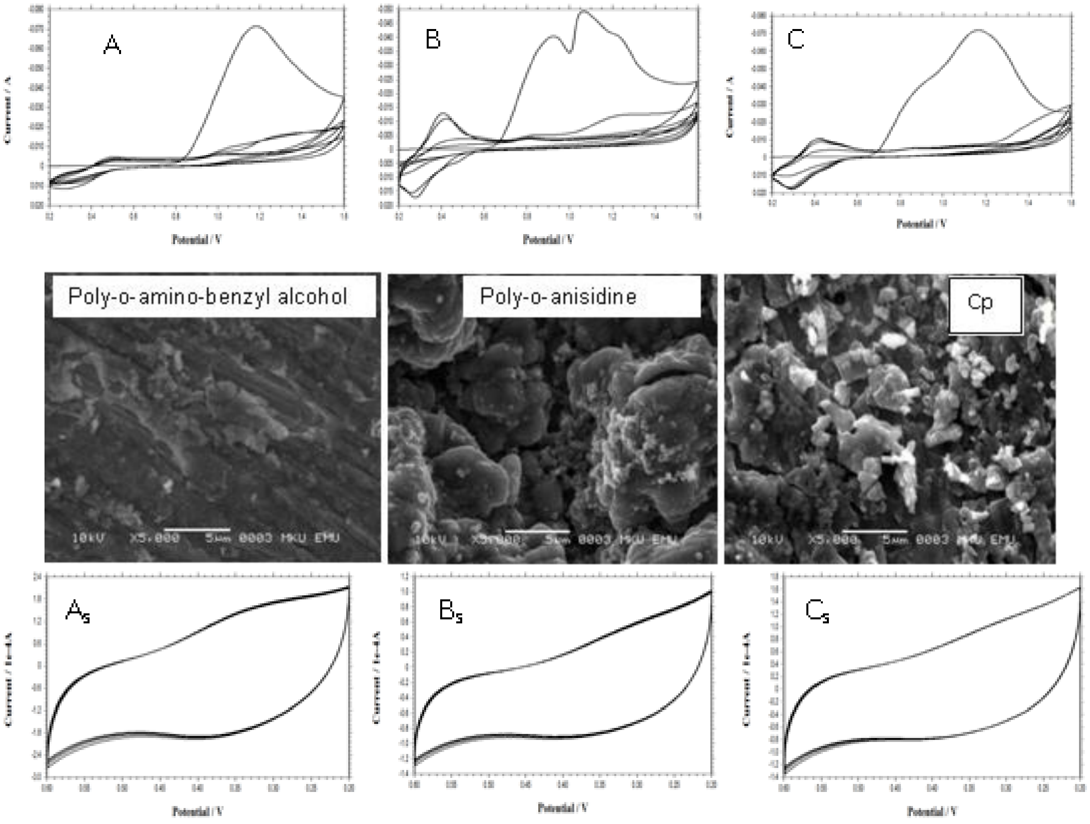

Fig.1. Multicycle voltammograms of o-amino benzyl alcohol (A); o-anisidine (B) and Cp in 0.5 M H_2SO_4 solution as supporting electrolyte at Pt electrode; The SEM images of homopolymer and copolymer coatings on Pt electrode and Successive CVs of poly-o-amino benzyl alcohol (As), poly-o-anisidine (Bs) and poly(o-anisidine-co-o-aminobenzyl alcohol) (Cs) films in 0.3 M KCl solution at 0.2-0.6 V potential range.

Electropolymerization procedure was performed by CV with scanning from 0.2 V to 1.6 V at a sweep rate of 100 mV s^{-1} for 25 cycles in 0.5 M H_2SO_4 solution containing homopolymers. Copolymer (Cp) was also synthesized in 0.5 M H_2SO_4 solution containing 0.05 M o-anisidine and 0.05 M o-amino benzyl alcohol. Immobilization procedure was performed by CV with scanning from -0.2 to 2.0 V at a sweep rate of 50 mV s^{-1} for 25 cycles in 1 mM [CoL] solution in acetonitrile containing 0.15 M $LiClO_4$. For electrocatalytic activity studies, Phosphate buffer solution (PBS) pH 7 was used as supporting electrolyte. Solutions of DA (1mM), ascorbic acid (AA, 1mM) and uric acid (UA, 1mM) were prepared daily by dissolving them in water.

RESULTS AND DISCUSSION

A typical multicycle CV voltammograms for electropolymerizations of o-anisidine, o-aminobenzyl alcohol and its copolymer on Pt electrode were given in Fig.1. While one oxidation peak was observed for o-amino benzyl alcohol at 1.2 V, two oxidation peaks were observed for anisidine at 0.9 V and 1.1 V belongs to monomer oxidation. On the other hand, at the voltammogram of copolymer were seen an overlapped oxidation peak arising from two monomer oxidation. Polymer film of pBA was obtained dark blue color, whereas pA was obtained black color. The color of coating has shifted from dark blue to black color, as the ratio of anisidine increases in the copolymer. The SEM images and electrochemical stability voltammograms (successive CVs) were also given in Fig.1. SEM images of homopolymer and copolymer films were recorded in order to investigate the surface morphology and structure. It can be easily seen from SEM images that the surface morphologies of homopolymers and copolymer were different from each other. Also, these images were shown that the pA coating have more porous structure than the pBA coating. Stability voltammograms have given to get the information about the stability and electroactivity of the polymer and copolymer films obtained on Pt electrode with investigating of electrochemical behavior during successive cycles. The oxidation of the film was observed in the forward scan and the reduction was obtained at the reverse scan. Current values of the polymer film were highly stable and regularly changed between its redox states during these successive cycles. It could be concluded that the polymer film was both stable and extremely electroactive [18].

FT-IR spectra of homopolymer and copolymer films are shown in Fig.2. In the spectra of polymer and copolymer films, the bands are broader than the bands belongs to monomers of pA and pBA as described in the literature [19]. It is clear that after polymerization, due to either increasing molecular weight or the molecular weight distribution of the polymers, the signals of polymers become broader than their monomers. This result is significant evident for polymer formation in this study. The peaks which were come from $–NH_2$ groups, were observed at 3458 cm^{-1} and 3368 cm^{-1} for o-anisidine monomer and at 3390 cm^{-1} and 3300 cm^{-1} for o-amino benzyl alcohol, whereas these peaks disappeared after polymerization. Disappearance of $-NH_2$ group peak indicates that the polymerization occurs through the -NH group. This situation has confirmed the proposed structures of the homopolymers and copolymer.

Electropolymerization voltammograms of [CoL] on both the bare and the homopolymer- copolymer coated Pt electrode were given in Fig.3. Oxidation peak potential of [CoL] which was observed around 1.7 V at bare Pt, shifted to lower potential values at copolymer coated Pt electrode (Cp-Pt) and peak current decreased with successive cycles during immobilization. Film was very stable during the successive cycles according to stability voltammograms. The SEM micrographs were indicating to significant differences among coating morphologies of Cp and Cp-[CoL]. This difference confirmed the immobilization of metal complex onto the copolymer.

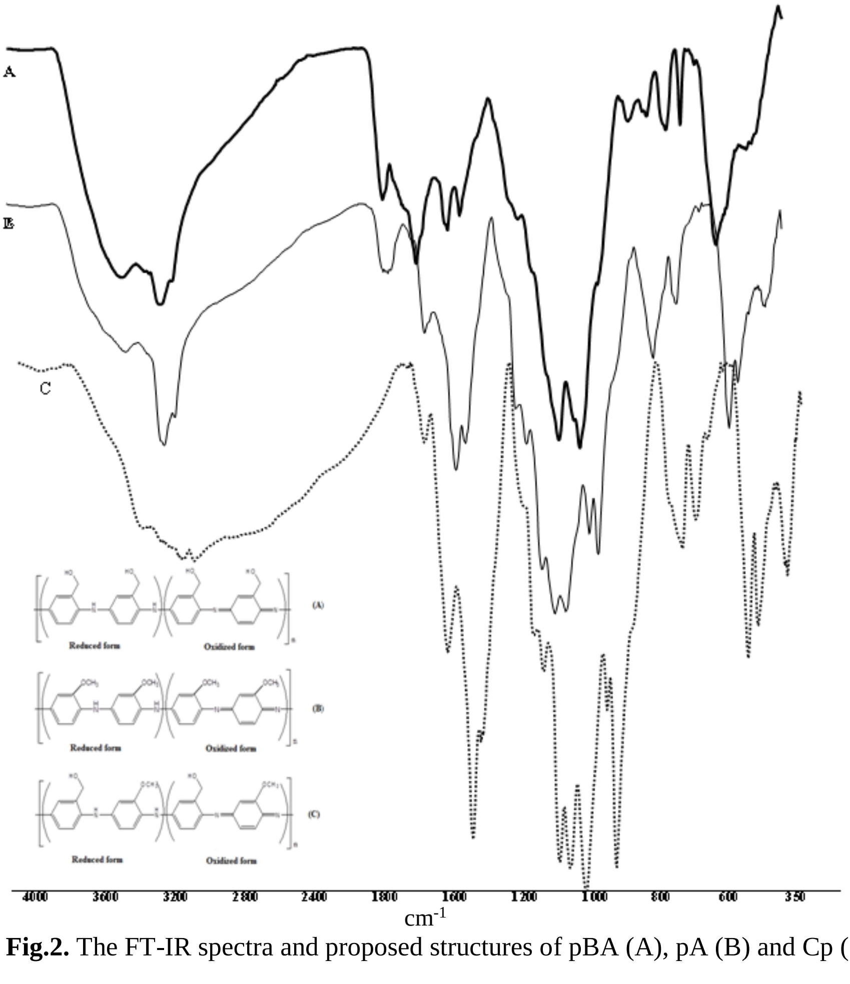

Fig.2. The FT-IR spectra and proposed structures of pBA (A), pA (B) and Cp (C).

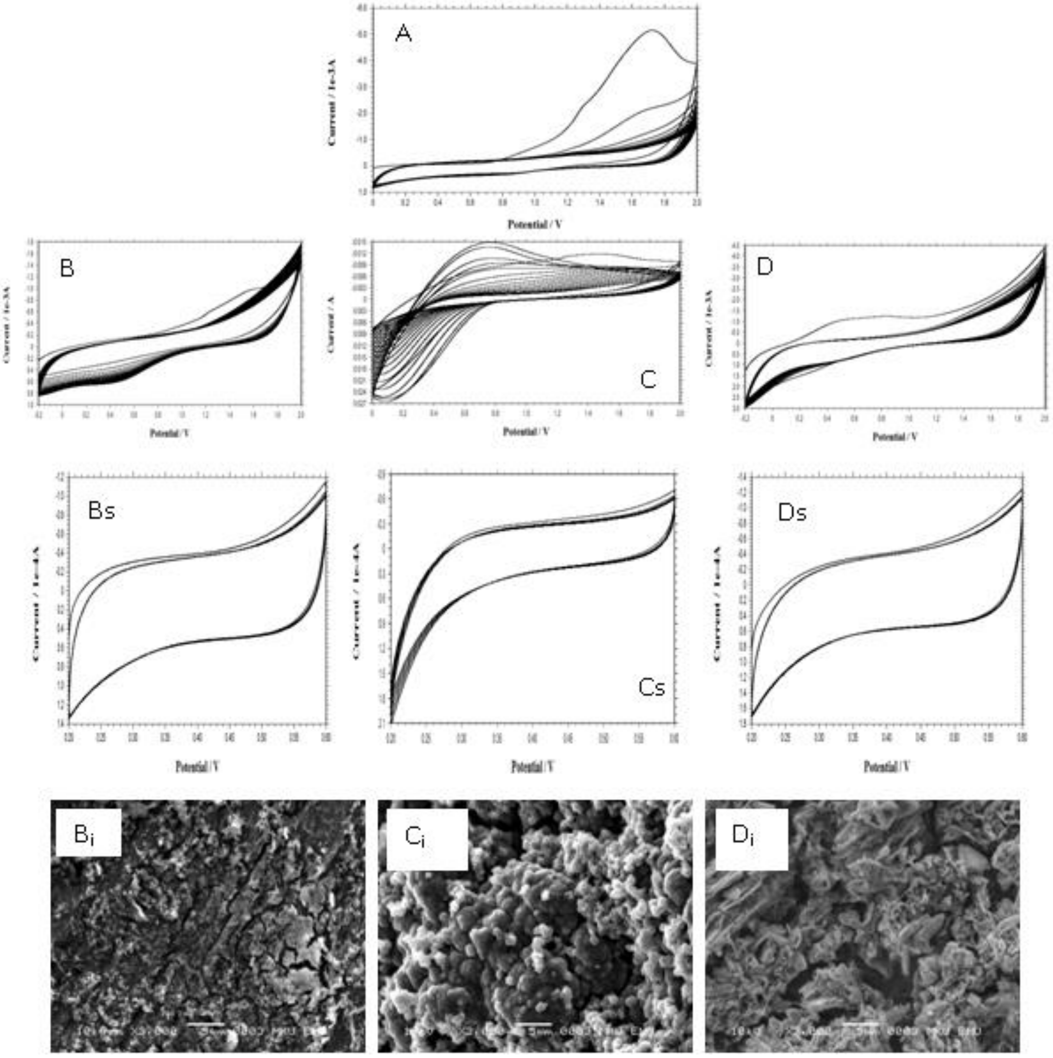

Fig.3. Electropolymerization voltammograms of [CoL] on the bare Pt (A), on the pBA-Pt (B), on the pA-Pt (C) and on the Cp-Pt (D) in acetonitrile containing 0.15 M $LiClO_4$ with 25 cycles. Successive CVs (Bs, Cs, Ds) and SEM images (Bi, Ci, Di) of pBA-Pt, pA-Pt and Cp-Pt, after immobilization of [CoL], respectively.

In the UV spectrum of the copolymer film after immobilization of [CoL], the band was observed at range of 330–450 nm were attributed to the n–π* transition of the non-bonding electrons present on the nitrogen of the azomethine group of the Schiff base moiety [20]. In addition, the weak bands observed in the 500–700 nm region can be attributed to d–d transitions of the metal ions [21]. Cobalt ion distribution at Cp-[CoL] modified surface was illustrated as red points at spectrum of SEM-EDAX mapping analysis (Fig.4.). According to the ICP-MS analysis, quantities of cobalt ion on modified electrodes were determined as 3.96 ppm, 1.96 ppm and 1.92 ppm for pBA-[CoL]-Pt, pAns-[CoL]-Pt and Cp-[CoL]-Pt, respectively. These results have also give an important evidence about the immobilization of [CoL] onto polymer coating.

Catalytic activity studies for DA were investigated in different supporting electrolyte medium like Britton Robinson buffer solution, acetic acid/acetate buffer solution and phosphate buffer solution at modified electrodes. As a result of these studies, the best electrocatalytic activity for DA oxidation was observed at pA-[CoL]-Pt electrode in pH 7 PBS. CV and SWVs were recorded in this medium for DA at bare Pt and pA-[CoL]-Pt (Fig.5.). In comparison with the bare platinum electrode, at this modified electrode, anodic peak current belongs to DA oxidation has increased for six times. Also, as can be seen in Fig.5., anodic peak currents belongs to DA have proportionally increased with changing DA concentration from 0,2 µM to 2 mM. As a result of these studies a linear calibration curve was obtained for DA in the range of 0,2 µM-2 mM and LOD was calculated as 0,1 µM.

When electro-oxidation of DA was investigated in the presence of UA and AA, oxidation peak potential of DA was observed at 0.2 V by using of pA-[CoL]-Pt modified electrode and at 0.3 V was observed by using of bare Pt electrode. The oxidation peak potential of DA appeared on more negative value at modified electrode than bare Pt electrode and peak shape was sharper at modified electrode than bare electrode. In order to investigate the applicability and selectivity of electrocatalytic effect on the DA oxidation, SWVs were recorded for different concentrations of DA in the presence of 1mM AA and 1 mM UA. Anodic peak currents for DA have proportionally increased with changing DA concentration. Therefore, linear calibration plots were obtained for DA in the presence of UA and AA, in the region between 1.6 µM and 8 µM and LOD was calculated as 0,65 µM.

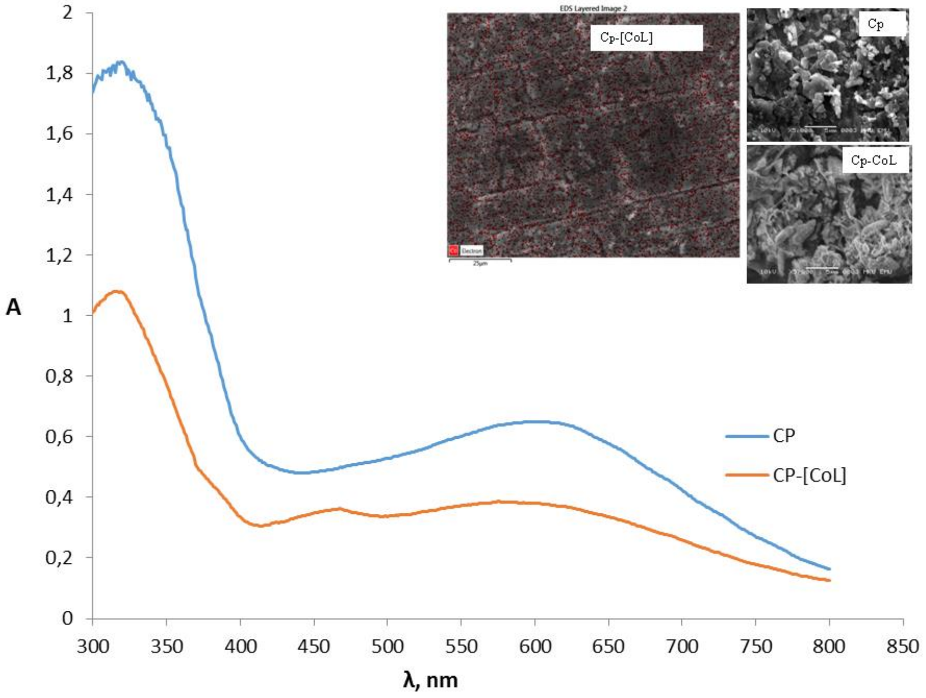

Fig.4. UV-Vis spectra, SEM-EDAX mapping analysis and SEM micrographs for Cp after and before immobilization of [CoL].

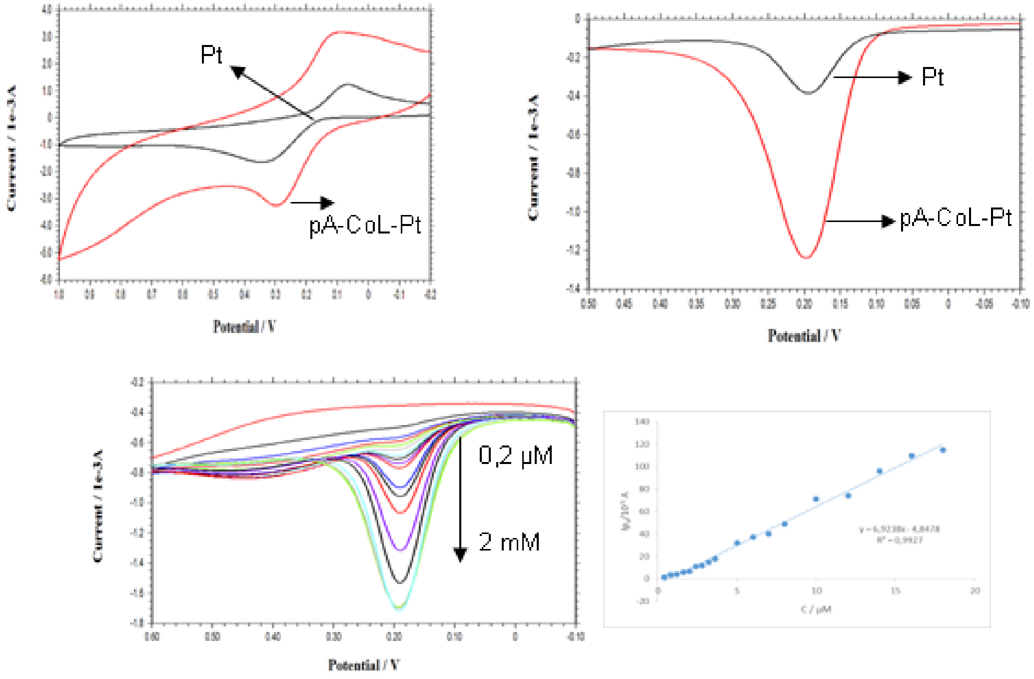

Fig.5. CVs and SWVs of DA at bare Pt and modified electrode , SWVs of various concentrations of DA in pH 7 PBS and calibration plot for DA.

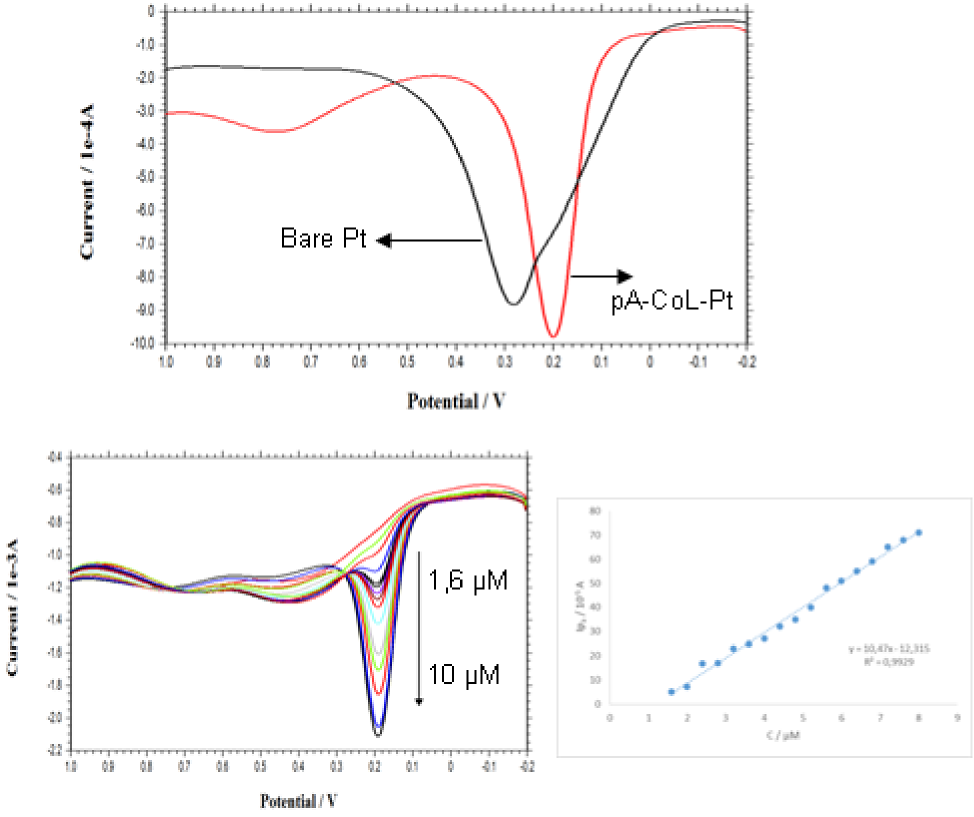

Fig.6. SWVs of DA in the presence of UA and AA at bare Pt and modified electrode in pH 7 PBS; SWVs of DA for various concentrations in pH 7 PBS and calibration plot for DA.

CONCLUSIONS

This study shows that metal complexes have been successfully immobilized onto the electroactive polymeric supporting material by using electrochemical methods. In this way, alternative systems can be developed to enzyme immobilization at biosensor applications. Modified surfaces were characterized by electrochemical, spectroscopic and microscopic techniques. The results of the characterization studies have shown that the films are homogeneous, very stable and extremely electroactive. Modified electrodes exhibited catalytic activity towards the oxidation of DA. Furthermore, they have potential use for other bioanalytical species at further applications.

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