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Investigation of sensor characteristics of Au and Cu modified PEDOT electrodes for dopamine

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Abstract: Hormones are important and necessary for the continuity of many vital functions in human body. Dopamine (DA) is a neurotransmitter affecting pain and pleasure perceptions, emotions, and movements. In the case of DA deficiency, severe discomforts such as Schizophrenia and Parkinsonism may happen. Thus, DA detection is an important subject. Electrochemical methods have been used in this work by developing a sensor for rapid and easy detection of DA. 3,4-Ethylenedioxythiophene (EDOT) monomer was polymerized on a platinum electrode using cyclic voltammetry method, and the film properties of the resultant polymer were investigated. Additionally, gold and copper coated PEDOT films, **Pt/PEDOT/Au** and **Pt/PEDOT/Cu**, respectively, were prepared to improve the sensitivity and stability of the films, compared to **Pt/PEDOT** electrode. The calibration curves were found to be linear in the concentration range of 50-1000 μM for DA in the presence of ascorbic acid (AA). The detection limits were determined as 18.46 μM, 13.33 μM and 6.80 μM for **Pt/PEDOT**, **Pt/PEDOT/Cu** and **Pt/PEDOT/Au** electrodes, respectively. Moreover, the electrodes demonstrated an electrochemical catalytic effect toward DA.

Keywords: EDOT; PEDOT; biosensor; electrochemical polymerization; dopamine.

1. Introduction

Conducting polymers are conjugated long chains made of repeating unsaturated monomer units. In order to make them conducting, they are doped with molecules to provide them with negative or positive charges (oxidizing or reducing operators), empowering current to move through the chains.[1] In recent years, conductive polymers have started to be integrated into the areas where metals are used. They have become more advantageous in some respect such as higher conductivity, low cost, flexibility, efficiency, and reversibility. Conductive polymers, especially based on thiophene, can be used for many purposes such as electrochromic screens, capacitors, batteries, biological sensors, anti-corrosion studies, and medical devices.[2,4]

Electrochemical polymerization is a method that has many advantages over other methods especially in sensor studies. This method provides an opportunity of working even with a small amount of monomer and the measurement can be completed in a very short time. By-products, which may occur, can be controlled by reducing the potential to an appropriate range. Moreover, the thickness and

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conductivity properties of the film can be improved by changing the scanning speed and potential range.[5,6]

PEDOT is one of the best known π-conjugated conductive polymers, which can easily be obtained through electrochemical polymerization of EDOT.[7] The polymerization can be achieved using a wide variety of electrode surfaces (Pt, Au, ITO etc.) and different electrolyte solutions (organic solvent and aqueous environments).[8] EDOT has a very low oxidation potential, high conductivity, and excellent stable structure due to the electron-releasing alkoxy groups in its structure. Depending on these features and diversity in polymerization system, PEDOT is studied intensively in recent years.[9]

Dopamine (DA), which has many functions in human body and is naturally synthesized in brain and kidneys, is responsible for the transport of electrical messages in brain. This neurotransmitter, which has an important share of data exchange in nerve cells, helps brain to function properly.[10] In order to develop a sensor compatible with human body, DA was reported to be adapted to the pH environment of human blood, and the measurements were performed in a buffer solution.[11] The DA molecule is synthesized in brain with the removal of a carboxyl group from the 3,4-dihydroxy-L-phenylalanine (L-DOPA) molecule by the help of an enzyme called decarboxylase (Figure 1).[12]

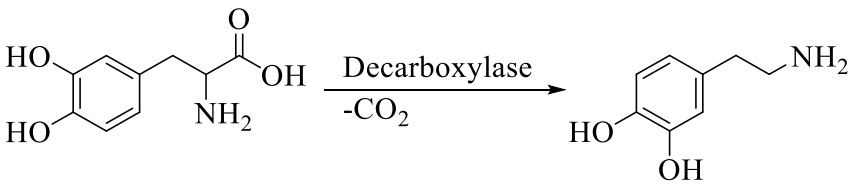


Figure 1. DA synthesis from L-DOPA molecule[12]

A biosensor is a device that measures biological or chemical reactions by generating signals proportional to the concentration of an analyte in the reaction.[13] Biosensors consisting of three components contain a selective recognition center (bio-agent) and converters to convert the physicochemical signals into electronic signals by interacting with this bio-agent. The signals are produced by the effect of mass change, release of various gases, changes in proton concentration, and absorption ratios.[14] There are certain static and dynamic attributes that every biosensor possesses. Optimization of these properties like selectivity, sensitivity, detection limit, response time, recovery time, and accuracy are reflected in the performance of a biosensor.[15]

PEDOT is considered to be useful in electrochemical sensor applications due to its electron transfer response, flexibility and low oxidation potential. Conducting polymers incorporating metallic or semiconducting nanoparticles provide an exciting system. Various PEDOT electrodes, modified using gold and copper nanoparticles, have been constructed for determination of DA, AA, and uric acid UA.[16-22] The detection limits of DA for these modified electrodes are in between 0.5-24 μM.[23-26] Although Au and Cu modified PEDOTs were reported for determination of DA and AA,[18] a comparative study by using both modified electrodes, to the best of our knowledge, is not available in the literature.

Thus, in this work, Pt/PEDOT electrodes modified with nano metals to improve electrode stability and increase sensing capabilities toward DA are reported. As copper is the cheapest conductive element, it was applied for the modification to prepare a commercial electrode. Additionally, Cu doped organic materials act as sensors electrode to determine o-diphenols in neutral solution. The formation of Cu(II)-o-quinolate complex occurs under the applied potential through DA electro-oxidation reaction.[18] The choice of Au nanoparticles supports the efficiently tunneling electrons and being "electron antennae" between electrode/polymer interface and electrolyte.[27]

Thus, the prepared Pt/PEDOT/Au and Pt/PEDOT/Cu modified electrodes are responsive to lower detection limits of DA with high peak currents.

2. Experimental

2.1. Chemical Material and Apparatus

All the solvents and reagents are commercially available and were used without further purification. 3,4-Ethylenedioxythiophene (EDOT), chlorauric acid ($HAuCl_4$), hydrochloric acid (H_2SO_4), copper(II) sulphate pentahydrate ($CuSO_4.5H_2O$), isopropyl alcohol (IPA), acetonitrile (ACN), DA and lithium perchlorate ($LiClO_4$) were purchased from Sigma-Aldrich. Monopotassium phosphate (KH_2PO_4) and disodium phosphate ($Na_2HPO_4.12H_2O$) were used for the preparation of phosphate buffer solution (pH:7) for DA sensing measurements.

Gamry Referans 600 potentiostat/galvansostat, interfaced to a computer, and Gamry Echem Analyst software were used for all electrochemical measurements. Working electrode was Pt button (0.022 cm^2), counter electrode was Pt and reference electrode was Ag. Polymerization of 0.01 M EDOT was performed applying potentiodynamic method in prophylene carbonate (PC) containing 0.1 M $LiClO_4$.

Scanning electron microscopy (SEM) studies were carried out using a Philips-FEI XL30 ESEM-FEG equipment.

2.2. Electrode Preparation

2.2.1. Cleaning procedure of Pt button electrode

Pt button electrode was first polished with alumina powder suspension applying circular motion, after which the electrodes sonically washed with distilled water for 5 minutes. Subsequently, the electrode was re-sonicated in IPA and ACN for 5 minutes and dried before use.

2.2.1. Electrochemical polymerization

Electrochemical polymerization was investigated with three electrode configuration system in a mixture of $5.0x10^{-3}$ M EDOT and 0.1 M $LiClO_4$/ACN as a supporting electrolyte. Pt button, Pt spiral and Ag electrodes were used as working, counter and pseudo-reference electrodes, respectively. The reference electrode was corrected with a standard ferrocene solution.

Optimum conditions were determined for the effect of various polymerization condition on the response of electrode. Electrochemical polymer was obtained on Pt button electrode surface by cyclic voltammetry (CV) method between -0.7-1.55 V with 50 mVs^{-1} scan rate.

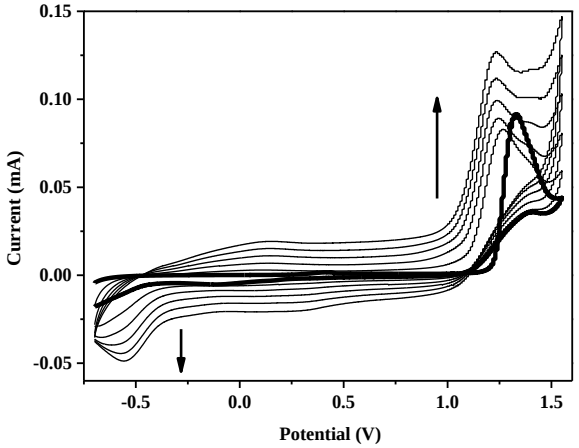


Figure 2. CV of the polymerization of EDOT in 0.1 M $LiClO_4$ solution at a scanning rate of 50 mVs^{-1}

2.2.2. Preparation of Cu and Au Modified Pt/PEDOT Electrodes

In order to improve the DA sensitivity of **Pt/PEDOT** electrode, PEDOT film was modified with Au and Cu nanoparticles due to the catalytic effects of these metals. One step method for preparation of Au and Cu nanocomposite films on Pt/PEDOT electrodes was performed by potentiodynamic method applying different cycle numbers, and an optimum condition was determined.

Au nanoparticles were electrochemically deposited on **Pt/PEDOT** surface by applying potential from -0.55 to 0.2 V in a mixture of 1 mM chloroauric acid and 0.1 M H_2SO_4 at a scan rate of 50 mVs^{-1} for 15 times (Figure 3a). The obtained EDOT film electrode modified by Au nanoparticles (Pt/PEDOT/Au) was washed with ultrapure water to remove disorders.

The Cu nanoparticles were also electrochemically deposited on **Pt/PEDOT** surface applying the same potential range, scan rate and cycle number in a mixture of 1 mM copper(II)sulphate pentahydrate and 0.1 M HCl (Figure 3b). The obtained **Pt/PEDOT/Cu** electrode was also washed with ultrapure water. All steps for the preparation of **Pt/PEDOT**, **Pt/PEDOT/Au** and **Pt/PEDOT/Cu** electrodes are given in Figure 4.

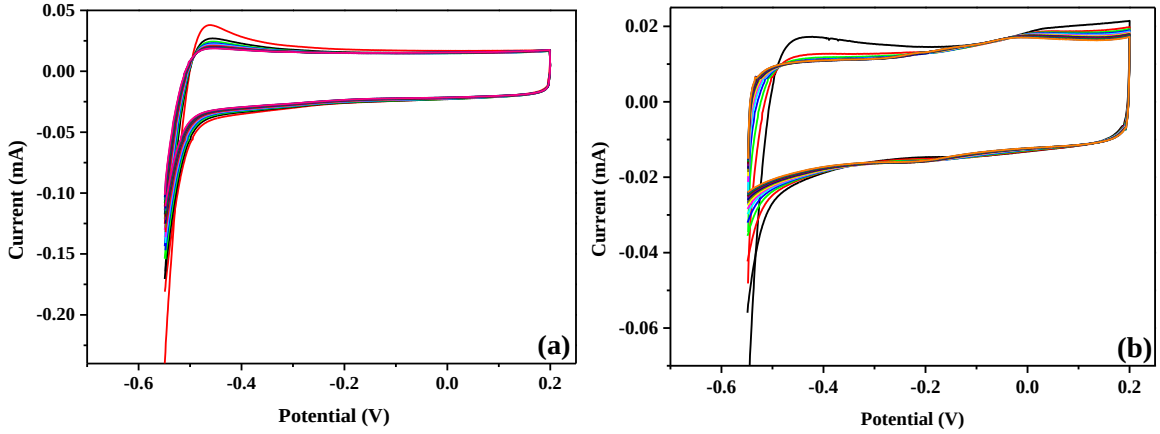


Figure 3. CVs obtained during the modification of PEDOT and formation of **Pt/PEDOT/Au (a)** and **Pt/PEDOT/Cu (b)** modified electrodes

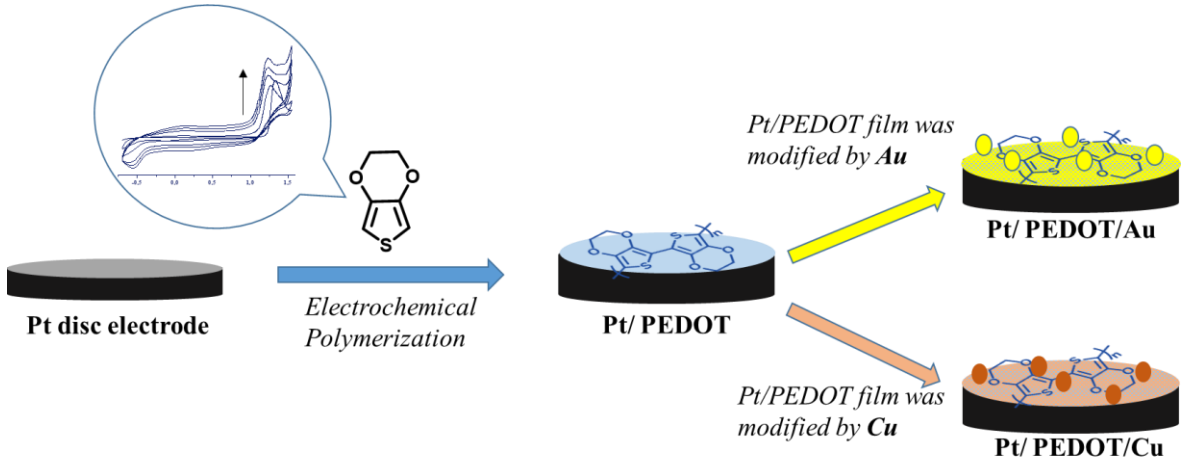


Figure 4. Preparation of **Pt/PEDOT**, **Pt/PEDOT/Au** and **Pt/PEDOT/Cu** electrodes

2.2.3. Redox Behaviour of Modified Electrodes

In order to examine the redox behavior of **Pt/PEDOT** electrode and to complete the polymerization of the oligomers on the surface, the CVs of the electrode in a monomer free 0.1 M $LiClO_4$ in ACN solution were performed (Figure 5). The measurements were carried out in the range of -0.7-1.0 V with the scan rates of 100, 200, 300, 400 and 500 mVs^{-1}. According to the Figure 5a, the peak currents increased steadily with the scan rates and it was observed that the PEDOT film was electroactive.

The redox behaviors of **Pt/PEDOT/Au** and **Pt/PEDOT/Cu** modified electrodes were also examined in monomer free 0.1 M H_2SO_4 and HCl solutions, respectively, with different scan rates (Figure 5b-c). The voltammograms showed that the peak currents of the electrodes increased regularly with the increasing scan rate due to their electroactivity.

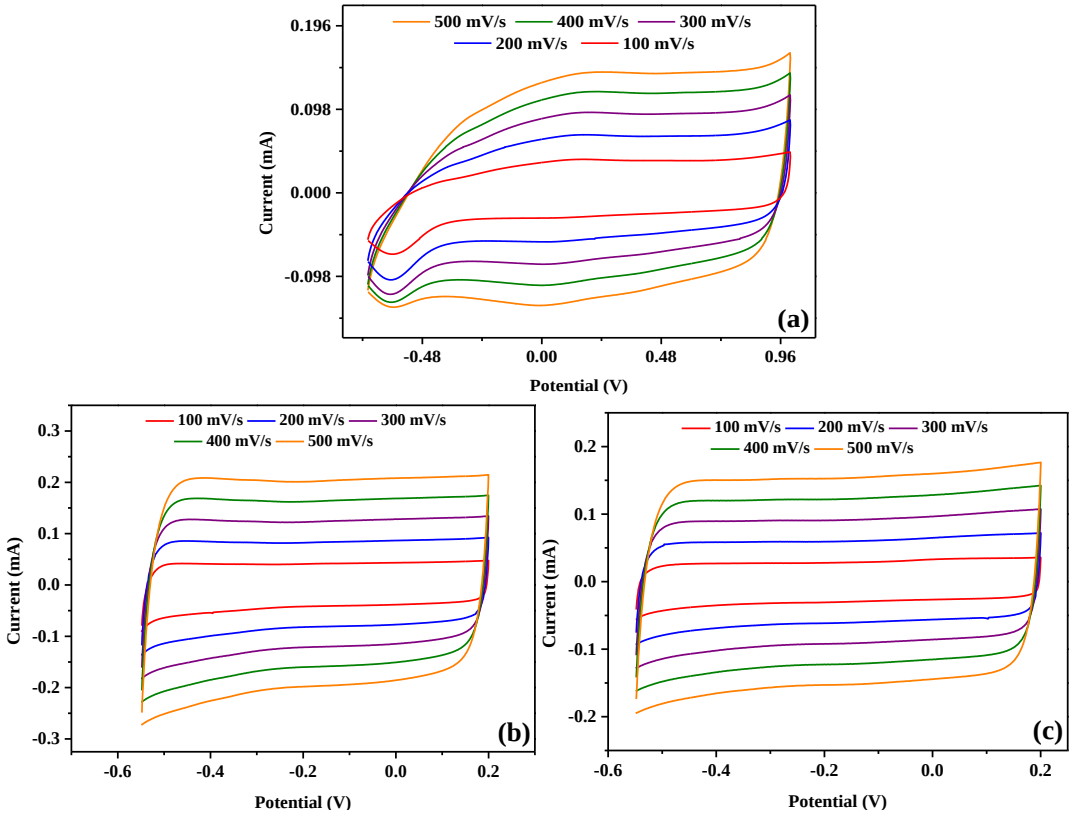
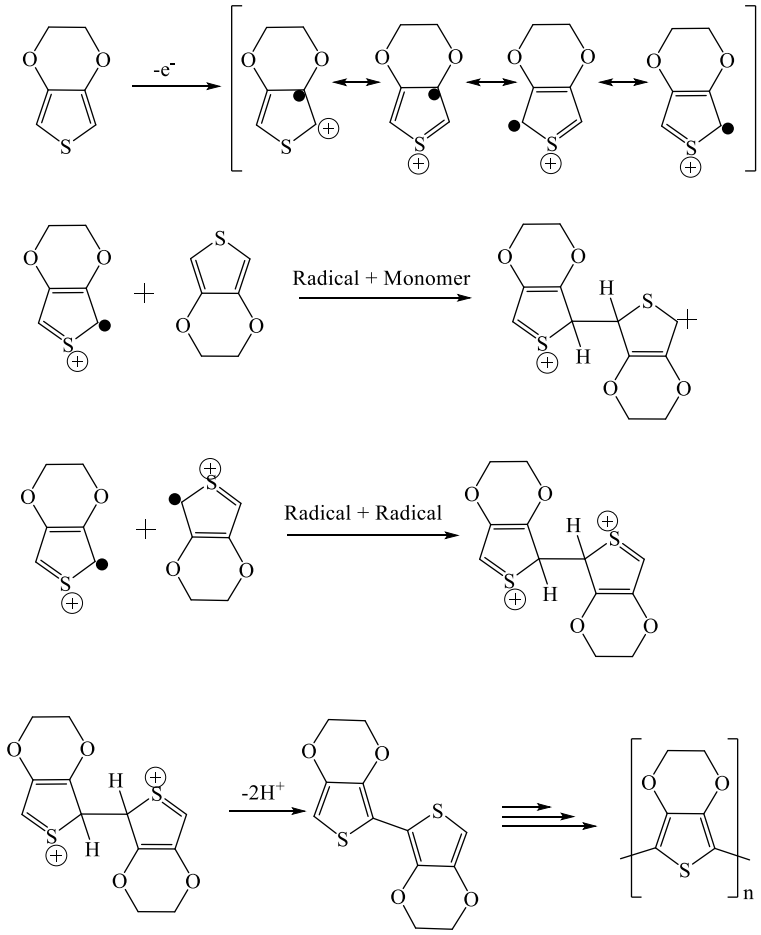


Figure 5. CVs of **Pt/PEDOT** in 0.1 M $LiClO_4$ in ACN solution **(a)**, **Pt/PEDOT/Au** in 0.1 M H_2SO_4 solution **(b)** and **Pt/PEDOT/Cu** in 0.1 M HCl solution **(c)**; electrodes obtained at different scan rates

3. Results and Discussion

A sensitive and easy-to-produce sensor study was conducted for the quantification of dopamine (DA). For this purpose, EDOT was polymerized and coated on a Pt button electrode. Oxidation of EDOT took place around 1.25 V in the first cycle (Figure 2, thick line). It is well explained in the literature that the formed and unstable cation radicals combine to form oligomers such as dimer, trimer and tetramer (Scheme 1).[28,29] In the following cycles, a new peak around 0.15 V of the oxidation of these oligomers forms and the peak currents increase regularly in each cycle due to the deposition of polymer film on the surface. These results support polymer formation on the electrode surface.

In order to improve sensitization of PEDOT, Au and Cu nanoparticles were integrated into the surface. Three different modified electrodes (**Pt/PEDOT**, **Pt/PEDOT/Au** and **Pt/PEDOT/Cu**) were obtained and used as working electrodes for detection of DA. CVs were performed at different concentrations of DA for qualitative and quantitative analysis of DA and the accuracy of the method was tested with reversible anodic and cathodic peaks. The detection limits were determined and compared for all the electrodes.



Scheme 1. Polymerization mechanism of EDOT

2.3.5. Determination of DA

DA determinations were performed in phosphate buffer solution at pH = 7 in order to be close to the pH value of human body. Before the measurement of DA, the behavior of **Pt/PEDOT** electrode in a buffer solution was examined applying two cycles in the range of -0.2V-0.6 V.

Solutions of DA in four different concentrations of $5.0x10^{-5}$, $1.0x10^{-4}$, $5.0x10^{-4}$ and $1.0x10^{-3}$ M were prepared in phosphate buffer. Then, CV measurements at a scan rate of 100 mVs^{-1} were performed. CVs of **Pt/PEDOT**, **Pt/PEDOT/Cu** and **Pt/PEDOT/Au** modified electrodes and $1x10^{-3}$ M DA, where **Pt/PEDOT/Au** additionally had ascorbic acid (AA), are given in Figure 6a-d.

Anodic peak current and concentration values of DA for **Pt/PEDOT**, **Pt/PEDOT/Au** and **Pt/PEDOT/Cu** electrodes are summarized in Table 1 and depicted in Figure 7. Increase in DA concentrations led to the increase in oxidation and reduction currents proportionally. The results indicated that **Pt/PEDOT/Au** and **Pt/PEDOT/Cu** electrodes were better compared to **Pt/PEDOT** toward DA determination. This might be due to the improved surface activity of PEDOT doped by metals.

Table 1. Anodic peak current and concentration values of DA for **Pt/PEDOT**, **Pt/PEDOT/Au** and **Pt/PEDOT/Cu** electrodes

	Anodic Peak Current (µA)		
Concentration (M)	**Pt/PEDOT**	**Pt/PEDOT/Cu**	**Pt/PEDOT/Au**
$5.0x10^{-5}$	13.02	30.82	33.16
$1.0x10^{-4}$	14.14	31.06	35.10
$5.0x10^{-4}$	28.07	40.46	55.59
$1.0x10^{-3}$	37.55	54.59	76.71

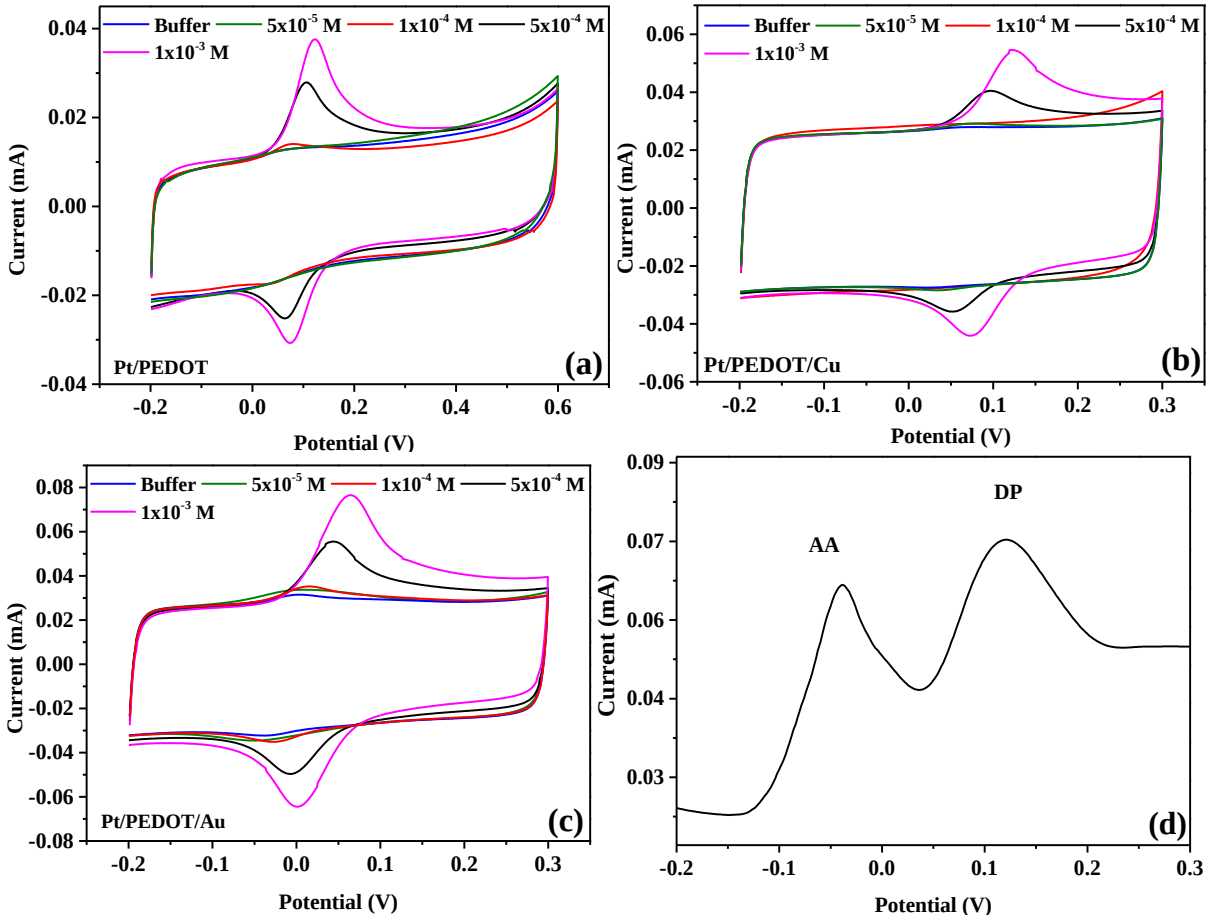


Figure 6. CV results at different concentration of DA with **(a) Pt/PEDOT**, **(b) Pt/PEDOT/Cu** and **(c) Pt/PEDOT/Au** modified electrodes, and **(d)** CV of 1x10^{-3} M DA in the presence of AA

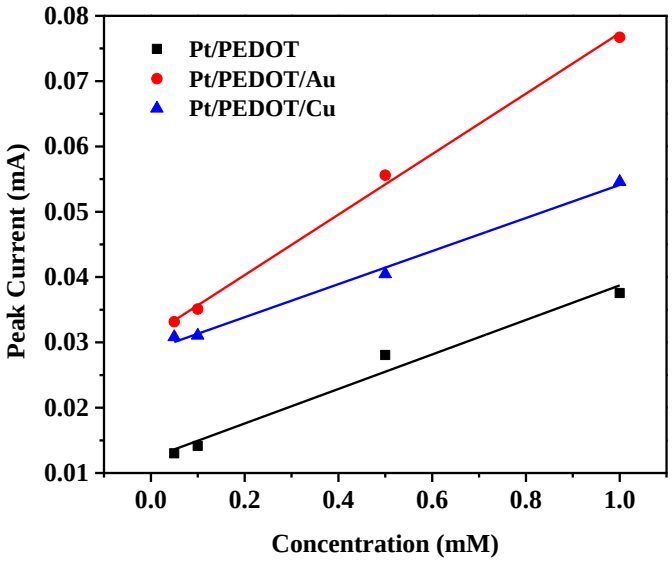


Figure 7. Pt/PEDOT, **Pt/PEDOT/Au** and **Pt/PEDOT/Cu** electrodes peak current values corresponding to different concentration values of DA

Comparison of the CVs of the electrodes in 1 mM DA solution showed that the peak intensity of **Pt/PEDOT/Au** higher than the rest of the electrodes (Figure 8) and **Pt/PEDOT/Au** modified electrode had the best electrochemical activity among the tested electrodes.

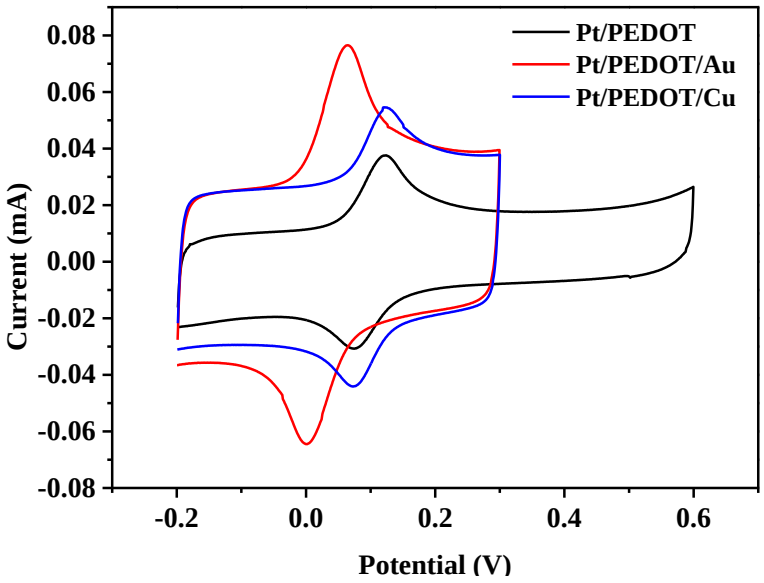


Figure 8. Comparison of the CVs of **Pt/PEDOT**, **Pt/PEDOT/Cu** and **Pt/PEDOT/Au** modified electrodes in 1 mM DA solution at 100 mVs^{-1} scan rate.

The detection limits (LOD) of DA were calculated using the equation below;

$$LOD = 3\ \sigma\ m^{-1}$$

Where σ symbolized the blank standard deviation and m the slope of the calibration curve. Anodic peak currents of DA sensing were plotted versus four different concentrations for each modified electrode, **Pt/PEDOT**, **Pt/PEDOT/Cu** and **Pt/PEDOT/Au**. The slope values of these plots were found to be 0.0260, 0.0252 and 0,463, respectively. Considering them, LODs were estimated at 18.46, 13.33 and 6.80 µM in the same order for a signal to noise ratio of 3 (Table 2).

Table 2. LODs of **Pt/PEDOT**, **Pt/PEDOT/Au** and **Pt/PEDOT/Cu** electrodes

	Pt/PEDOT	**Pt/PEDOT/Cu**	**Pt/PEDOT/Au**
LOD (µM)	18.46	13.33	6.80

The lowest detection limit was obtained with Au modified electrode (**Pt/PEDOT/Au**), and this result could be explained with a better adhesion of Au nanoparticles to the PEDOT electrode surface due to a good interaction between the sulfur atoms of PEDOT and Au nanoparticles.[27]

PEDOT contains hydrophobic and hydrophilic regions, namely reduced and oxidized states together as suggested in the literature.[27] Au nanoparticles tend to occupy inside of these hydrophobic part of PEDOT. As DA has a hydrophobic character, it interacts with these regions and the physical interactions become significant for the sensitivity and selectivity in determination of desired molecules.

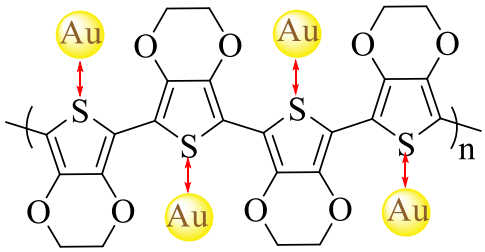


Figure 9. Interaction between PEDOT and Au nanoparticles

SEM images of **Pt/PEDOT**, **Pt/PEDOT/Au** and **Pt/PEDOT/Cu** electrodes are given in Figure 10a-c, respectively. **Pt/PEDOT/Au** electrode displayed a homogenous and more porous surface than the others, possibly due to a good interaction of Au nanoparticles with the PEDOT film. Additionally, the content of Au and Cu nanoparticles on the PEDOT films was found to be 5 and 2.5%, respectively. This result supported the lowest detection limits of Au modified PEDOT having a high conductive electroactive surface area.

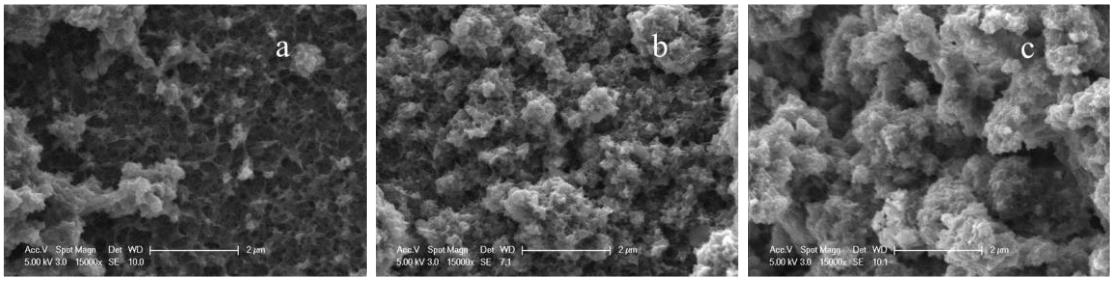


Figure 10. SEM images of **(a) Pt/PEDOT**, **(b) Pt/PEDOT/Au** and **(c) Pt/PEDOT/Cu**

Stability of **Pt/PEDOT/Au** and **Pt/PEDOT/Cu** electrodes were tested in time and the CVs obtained for **Pt/PEDOT** electrodes after four days and one week in 1 mM DA solution are given in Figure 11a and b. This result indicated that **Pt/PEDOT/Au** was more stable than **Pt/PEDOT/Cu** due to a better interaction of PEDOT with Au particles compared to Cu particles.

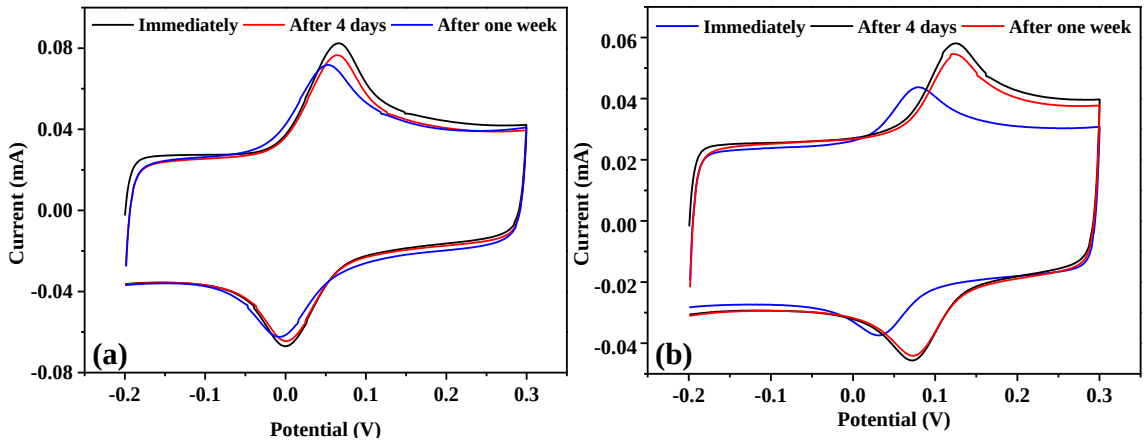


Figure 11. Comparison of stability CV's of **(a) Pt/PEDOT/Au**, **(b) Pt/PEDOT/Cu** modified electrodes pristine, after four days and after one week in 1 mM DA

4. Conclusion

In order to obtain a sensitive DA detection electrode, **Pt/PEDOT**, **Pt/PEDOT/Au** and **Pt/PEDOT/Cu** modified electrodes were obtained electrochemically. As metal doping improves the surface activity by increasing active sites on the surface of an electrode, and also due to an increased conductivity, Au and Cu modified PEDOT electrodes displayed better sensitivity than PEDOT alone. Based on the CV and SEM measurements, **Pt/PEDOT/Au** had the best result compared to **Pt/PEDOT/Cu** and **Pt/PEDOT** electrodes, which could be explained with an interaction between sulfur atoms of PEDOT and Au atoms. Under the optimized experimental conditions, detection of DA in a concentration range of $5x10^{-5}$ - $1x10^{-3}$ M was obtained with detection limits of 6.80, 13.33 and 18.46 µM for **Pt/PEDOT/Au**, **Pt/PEDOT/Cu**, and **Pt/PEDOT**, respectively.

In conclusion, among the synthesized electrodes, **Pt/PEDOT/Au** could be a promising candidate for a practical and sensitive DA sensor.

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Supporting Information

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