Development of sol-gel based carbon ceramic electrode modified by graphene oxide - polypyrrole nanocomposite for simultaneous determination of uric acid and dopamine in presence of ascorbic acid

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Abstract

In this paper a sensitive carbon ceramic electrode (CCE) based on Methyltrimethoxy Silane (MTMOS) was prepared simply by three step sol-gel process. The surface of CCE was modified with polypyrrole -electrochemically reduced graphene oxide (ERGO-PPy) nanocomposite by electro polymerization. Scanning electron microscopy, electrochemical impedance spectroscopy, XRD, FT-IR and electrochemical techniques were used to characterize the composite electrode. The cyclic voltammetry and differential pulse voltammetry results suggested that the modified electrode exhibited enhanced sensitivity and selectivity towards the oxidation of dopamine and uric acid. Differential pulse voltammetry results show that simultaneous determination of DA and UA in presence of ascorbic acid could be performed selectively and sensitively at ERGO/PPy modified sol-gel based CCE. The oxidation peak currents of DA and UA in presence of AA, presented a good linear relationship with the concentrations in the range from 0.05 to 65 μM and 0.1 to 120μM respectively with a detection limit of 0.002 μM for DA and 0.08 μM for UA. The good performance of the modified electrode provided a promising modified electrode in electrochemical determination of DA in human blood serum and urine samples.

Keywords: Sol-gel, Graphene oxide, Polypyrrole, dopamine, uric acid.

1. Introduction

The Sol-gel technology is a three-step process which includes the low temperature hydrolysis of a monomeric precursor of organometallic alkoxide and its condensation followed by poly-condensation to yield a polymeric oxo-bridged network [1]. The mid-1800s was the beginning of interest in sol-gel process with Ebelmanl and Graham's studies on silica gels [2]. For a period of time (last 1800 to 1920) sol-gel technology was one of the major field of activity among the researchers [3]. According to Dislich, at the beginning of the 80s of the 20th century, the number of publication shows the exponential growth of this claim [4]. In the permanent demand for ceramic and glasses with better properties and greater purity, three method of processing have proposed to have important roles. These are preparation of ultrafine powder of controllable size, ceramic from metal-organic polymers and the sol-gel process [3]. Low preparation temperatures and inorganic supports offer some advantages to sol-gel process over other methods, among which are chemical inertness, physical strength, and good surface renewability [5]. Additional advantages come from the fact that sol–gel derived materials are porous and thus mass transport is relatively easy through pores [6].

This advantageous cause sol-gel process to be one of the most used synthetic method in material science and nanotechnology [3] as the protective coatings, thin films, Nanoscale powders and Opto-mechanical materials [7]. Carbon-ceramic composite electrodes (CCEs) are comprised of a dispersion of carbon powder that is held together by sol-gel derived ceramic binder [8]. This composite material can be used in a wide range of application such as electrode in rechargeable batteries [9], supercapacitors [10] solar cells [11], fuel cells [12], Electrochemical sensors [5,6,8,13-18] and opto-plasmonic sensory devices. Since the CCEs in the first stage of preparation is a paste like material, so it is easy to shape and form it in any arbitrary structures and be used in a wide range of applications. However bare carbon ceramic electrodes as sensor have some drawbacks such as low detection sensitivity and poor resolution to specific analytes, therefore their modification is needed. Bulk modification of carbon-ceramic electrodes is an effective route which has been utilized by numerous authors [8,13-16], but this procedure is time consuming, expensive and difficult, where surface modification is not. However, some modifiers suffer from the weak adhesion and low physical stability on surface of this substrates but in presence of an immobilizing material, this procedure is the best way of modification [5]. In recent years, electrically conductive polymer (ECP) attracted great interest because of its hybrid properties of having metal-liked conductivity and polymeric characteristics [25] such as flexibility, low density, and ease of structural modification at the same times [26], leading to an enormous range of potential applications [27]. Among the ECPs, polypyrrole is popular due to its strong electrical properties, ease of synthesize and good environmental and mechanical stability [28], which rise to its

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wide application in electronic devices, electrodes for rechargeable batteries [29], solid electrolytes for capacitors [30], sensors [31] and corrosion protection materials [28].

On the other hand, graphene, the building block of carbon allotropes, was theoretically established in 1940 [19]. Boehm and coworkers separated thin lamellae of carbon by heating and chemical reduction of graphite oxide in 1962 [20]. This discovery was a revolution in the fields of physics, chemistry, biotechnology, and materials science [21]. The ''thinnest'' known material graphene exhibits excellent electrical conductivity, mechanical flexibility optical transparency, thermal conductivity, and low coefficient of thermal expansion (CTE) behavior [22]. But most of this properties are only associated with individual sheets [23]. Among the graphene synthesis methods including mechanical and chemical exfoliations [23], epitaxial growth via chemical vapor deposition (CVD) [19] and unzipping of carbon nanotubes (CNT) [24], the oxidation of graphite by modified Hummers method, followed by chemical and electrochemical reduction, is the common method due to its simplicity and scalability [21,23].

Up to our knowledge, DA, UA and AA are always coexisted in the extra cellular fluids of central nervous system and serum in mammals [32], which play very important roles in human metabolism system [6]. DA, as one of the important neurotransmitters, belongs to the catecholamine group which belongs to the family of excitatory chemical neurotransmitters [5] and has very important role in the central nervous, renal, hormonal and cardiovascular systems [33]. Low level of DA may cause neurological disorders such as schizophrenia and Parkinson's disease [34]. Meanwhile, UA is the primary final product of purine metabolism [35]. Abnormal concentration of UA has a relation with several diseases such as hyperuricemia, gout and pneumonia [36]. AA is a common anti-oxidant, which plays a great role in the metabolic process of human bodies [36]. As the AA concentration is much higher (100–1000 times) than that of DA in body fluids, therefore selective detection of DA and UA, and even their simultaneous detection in the presence of large amount of AA have received tremendous attention in biomedical chemistry and diagnostic and pathological research owing to their similar properties [37]. As these molecules are electroactive, electrochemical methods are promising advantageous such as rapid response, high sensitivity, easy operation, and low cost [38]. However, the key challenge in determination of DA and UA, is the interference of coexisted AA with high concentrations, because AA can also be oxidized and its peak currents are overlapped with those of DA and UA at conventional electrodes [31]. Thus, a variety of modified electrodes were recently realized to either reduce the over-potential of AA oxidation or prevent the approach of AA to the electrode surface [32]. To deal with this problem, there is lots of modifiers materials which can facilitates determination of DA and UA even simultaneously by eliminating of AA reaction onto the electrode surfaces [32].

In this research (which is a part of the other project in which the presented electrochemical sensors will be coupled to a plasmonic and solitonic sensor), a CCE was fabricated by sol-gel process and graphene nano-sheets was immobilized on surface of CCE by electro-polymerization of pyrrole to enhance its electrochemical activity toward oxidation of DA and UA. This modified electrode was successfully used for simultaneous determination of DA and UA in the presence of high levels of AA in human blood serum and urine samples.

2. Experimental methods
2.1. Apparatus

Electrochemical experiment was carried out by AUTOLAB PGSTAT 30 electrochemical analysis system and GPES 4.9 software package (Eco Chemie, The Netherlands) consisting of three electrodes: bare or modified carbon ceramic electrode (CCE) as working electrode, Ag/AgCl as auxiliary electrode and a Pt wire as counter electrode. The FTIR spectroscopy was conducted on FT-IR Tensor 27 Bruker, over a frequency range of 4000- 500 cm^{-1}. Crystallographic structure of graphene oxide and pure graphite were performed using a D/Max 2500V/PC diffractometer (Siemens-Germany). The scanning electron microscopy (SEM) experiment was made on a Hitachi Japan S4160 SEM.

2.2. Reagents and chemicals

Methyltrimethoxy Silane (MTMOS), DA and graphite (GR) powder were purchased from Merck and were of analytical grade from Merck. Pyrrole monomer was purchased from Merck and distilled prior to use. Dopamine, ascorbic acid, uric acid and other reagents were of analytical grade from Merck. The human blood serum and urine samples were obtained from Drug Applied Research Center, Tabriz University of Medical Sciences-Iran. The pH of solutions was adjusted to 7.0 with phosphate buffer. Distilled, deionized and sterilized water was used in all solution preparations.

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2.3. Preparation of graphene oxide

Modified Hummers method was used in preparation of graphene oxide [23]. Mixture of sulfuric acid (46 mL, 98 wt. %) and phosphoric acid (6 mL 85 wt. % in H2O) was poured to a mixture of graphite powder (2.0 g) and sodium nitrate (1.0 g) and cooled to 5 ºC in ice bath. Potassium permanganate (6.0 g) was slowly added to prevent the temperature exceeding from 20 ºC. The ice bath was removed and temperature was increased to 35±4 ºC and kept for 12 hr. Deionized water (92 mL) was gradually added to the vessel and the temperature of vessel increased to 98 ºC for 30 min. The heat was removed and reaction cooled by water bath for 10 min. The resultant brown-yellow suspension was diluted by additional of deionized water (280 mL) and treated with H2O2 (20%, 50 mL) to remove the remained oxidizing agents. The suspension was washed repeatedly with 5% HCl and deionized water respectively. The resultant solid on the filter was dried at 60 ºC (48 hr.) obtaining 2.7 g of GO.

2.4. Preparation of modified Carbon Ceramic Electrode

The carbon-ceramic electrode prepared as follows. The silica sol solution was prepared by mixing 0.6 mL of MTMOS, 0.9 mL methanol and 0.1 mL hydrochloric acid (0.1 M) and stirred for 5 min to afford a homogeneous gel solution. This ormosil was mixed well with 300 mg graphite powder for 5 min. The mixture was added to a Teflon tube (with 3 mm id and 3 cm length, and the length of composite in the tube was about 8 mm) and dried for 48 h at room temperature. The surface of all electrodes was removed by mechanical polishing with 800, 2000, 2500 and 3000 grit polishing papers, respectively. The electrodes were rinsed thoroughly with water to yield shiny surfaces. Copper wire contacted to the other end, provided the electrical contact. To modifying the surface of CCE, a mixture solution containing 1 mg/ml graphene oxide and 0.1M pyrrole monomer in phosphate buffer solution (pH=7) was prepared. Cyclic voltammetry (CV) methods was chosen to electro-polymerization of pyrrole monomer and subsequently electrodeposition of graphene oxide nano-sheets by sweeping the potential from 0 to 0.8 V for 5 scan (scan rate of 0.01 V/s). To reduction of graphene oxide in composite, CV method was used as an efficient tool. The reduction was performed in 0.1 M KCl solution and by double scanning of the potential from 0 to -1.2 V (scan rate of 0.05 V/s).

3. Results and discussion
3.1. Surface morphology of modified electrode

Scanning electron microscopy was used to characterize the surface of modified and bare electrodes. As shown in Fig. 1(c, d) on bare carbon ceramic electrodes a dense, scaly and porous surface but in the case of modified nanocomposite electrode a crispy, wrinkled and layer liked structure was observed. According to the Fig.1 (a,b), a thin layer of PPy was electrodeposited onto the surface of GO, that immobilizes the sheets on electrodes surface by hydrogen bonding between oxygenated functionality of GO and N-H of pyrrole ring that increases physical stability of modified electrode.
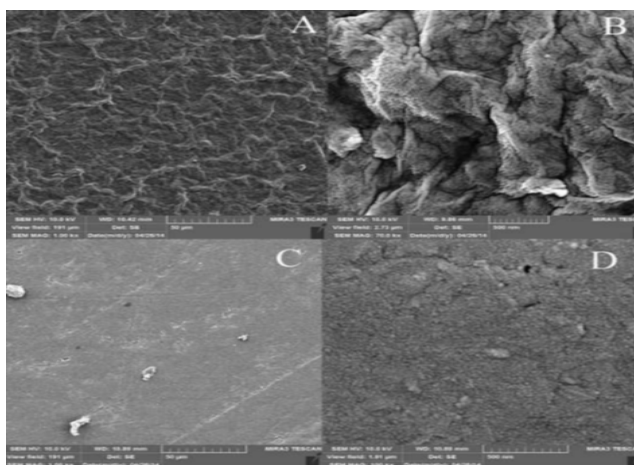

Figure 1. SEM images of (a, b) ERGO/CCE, (c, d) bare electrode with two different magnifications.

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3.2. Characteristics of the modified electrodes by electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy can provide information about the impedance changes of the electrode surface by using $[Fe(CN)6]^{3-/4-}$ redox couples as the electrochemical probe during the modification process. The Nyquist plots of modified and bare electrodes are shown in Fig. 2. The terms R_s, CPE1, R_{ct} and W1 in the inset of Fig.2 refer to solution resistance, double layer capacity, charge transfer resistance and specific electrochemical element of diffusion or Warburg element, respectively. On the bare carbon-ceramic electrode, the charge transfers resistance (R_{ct}), which was derived from the semicircle domains of impedance spectra, can be estimated to be 1227.3 Ω (curve a). On the ERGO/CCE (by casting of 20 μl, GO with concentration of 1mg/ml and electrochemical reduction) this value decreased to 147 Ω (curve b) which was attributed to high conductivity of ERGO on the surface of electrode. After electro-polymerization of polypyrrole and deposition of nanocomposite on the surface of carbon ceramic electrode, the R_{ct} value was increased to 234 Ω (curve c), that proves immobilization of nanocomposite on electrode surface. This decrease in conductivity was acceptable because, by introducing the PPy, the mechanical stability of ERGO on surface of carbon ceramic electrode was dramatically increased.
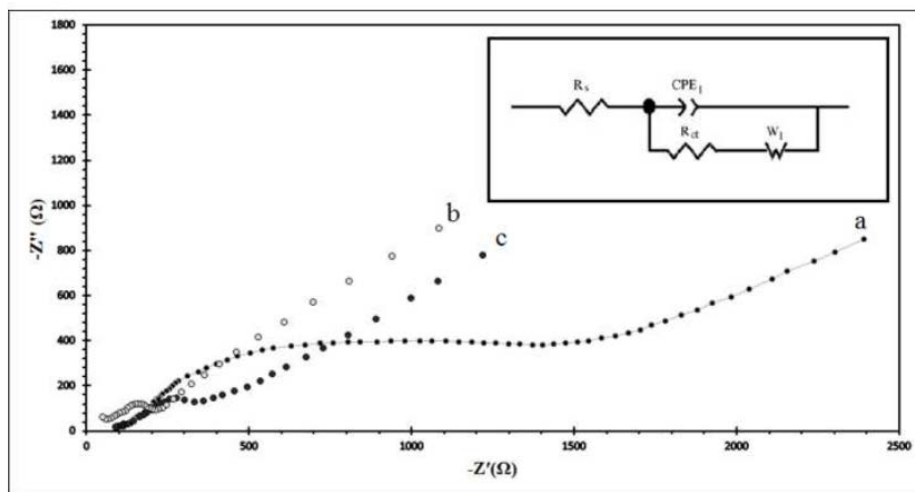

Figure 2. EIS for (a) bare carbon-ceramic electrode, (b) ERGO/ carbon ceramic electrode and (c) ERGOPPy/carbon ceramic electrode in a mixture solution of 10.0 mM [Fe(CN)6]3-/4- and 0.1M KCl with the frequencies swept from 2×106 to 0.1 Hz under an open circuit potential condition.

3.3. XRD study

Although XRD is not a perfect tool for identifying single-layer graphene, but it is very informative. This analysis was used to verify the formation of the synthesized GO. According to Fig.3 the XRD pattern of pristine graphite shows that, after oxidation by modified Hummers' method, the peak around 26.38° corresponding to 002 reflections peak [19], shifts to the lower angles (11.36°). After oxidation of graphite, the interlayer distance of the sheets, increases from 0.377 nm (GR) to 0.772 nm (GO), proving oxidation of graphite. It reveals that the space of the sheets in GR increases by introducing the water molecules and generation of highly oxygenated functional group between the interlayer galleries. Generation of oxygen functionality attenuate π-π interaction of the sheets and helps to better exfoliation of graphite oxide into graphene oxide.

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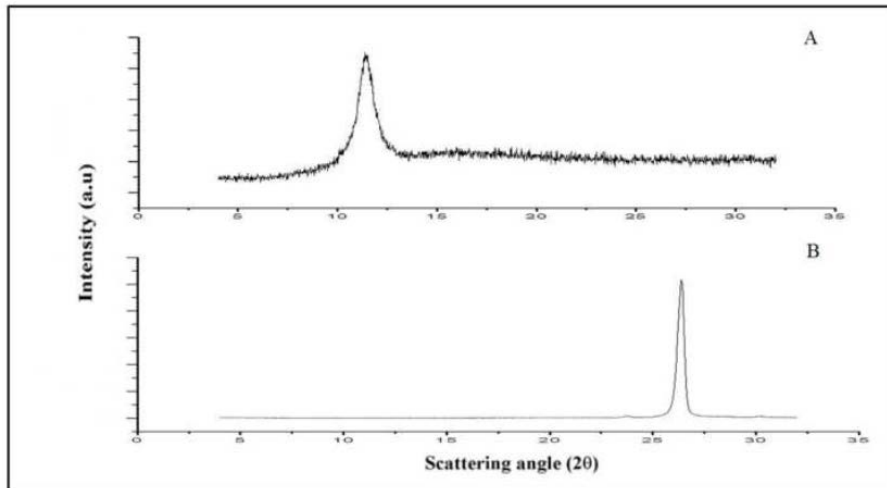*ISSN: 2395-3470*
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Figure 3. XRD structure of Graphite (A) and Graphene oxide synthesized by modified Hummers' method (B).

3.4. FT-IR spectroscopy

FT-IR spectroscopy is known to be an important tool to characterize the graphene based hybrid materials. From the Fig.4, the peaks at 3076 and 2882 cm^{-1} are attributed to the asymmetric stretching and symmetric vibrations of CH2 [26]. The broad peak at 3432 and 1720 cm^{-1} are designated to O-H stretching vibration and the carbonyl (C=O) stretching respectively. Peak at 1059 cm^{-1} proves the existence of epoxide group on GO sheets representing C-O stretching vibrations [39]. The peak appeared at 1620 cm^{-1} is responsible for residual C=C sp2 carbons and peak at 1179cm^{-1} attributed to C-C stretching vibrations [29].
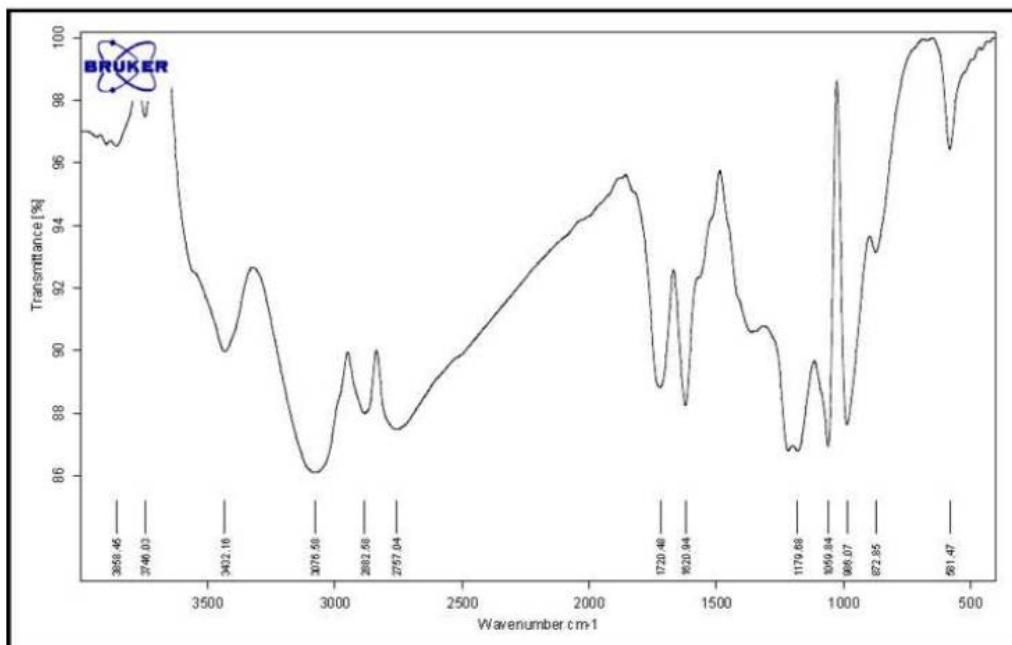

Figure 4. FT-IR analysis of Graphene oxide, synthesized by modified Hummers' method.

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3.5. Cyclic voltammetry

Since Cyclic voltammetry (CV) has become an important and widely used electroanalytical technique in many areas of chemistry, it was selected for the assessing the ability of ERGO-PPy nanocomposite modified CCE toward catalytic oxidation of DA and UA in presence of AA. The cyclic voltammograms of bare and modified CCE are shown in Fig.5 (A). On the bare CCE DA, UA and AA shows broad anodic peak with the anodic peak potential of 229, 263 and 376 mV (Vs. Ag/AgCl) respectively. It is obvious that electron transfer kinetics in oxidation of these three species on bare CCE is sluggish and irreversible. In contrast modified CCE can effectively eliminate AA electrochemical reaction and separate overlapped oxidation peaks of DA and UA. For DA on bare CCE oxidation and reduction peaks appears at 239 and 150 mV ($\Delta E=89$ mV), while in case of ERGO/PPy/CCE (Fig.5 (B)) it appears at 228 and 180 mV ($\Delta E=48$ mV) respectively. Oxidation current of DA on ERGO/PPy/CCE is 3.88 times higher than that of bare CCE which suggesting electro-catalytic activity of ERGO/PPy toward DA oxidation. In case of UA on bare and modified CCE oxidation peaks appears at the same potential but oxidation currents of modified CCE toward UA is 6 times higher than that of unmodified which suggest ERGO/PPy can increase in access surface area of bare CCE and as a result, increase the sensitivity of electrode. Cyclic voltammograms of bare and modified CCE in a ternary system containing 1mM of DA UA and AA in phosphate buffer solution are shown in Fig.5 A and B (curves d). Results shows that on bare CCE there is no enough resolution to determine DA and UA in presence of AA, but in case if modified CCE by eliminating the AA responses, resolution of electrode improves and makes simultaneous determination of DA and UA possible.

To evaluate the reproducibility of the modified electrode in simultaneous detection of DA and UA, a ternary solution of 1 mM DA, 1mM UA and 1mM AA was detected through an operation of 50 cycles in a potential ranging from -0.2 to 0.9 V. The absence of any remarkable change of the voltammetric current response on modified electrode revealed that it has excellent electrochemical stability. The related standard deviation (RSD) of the oxidation peak currents of DA and UA are used to assess the reproducibility of the detection. The RSDs of the peak currents of 50 successive runs are 2.23% and 3.11% for DA and UA, respectively, which are both lower than 4%, showing excellent reproducibility of the ERGO/PPy/CCE. We believe the porous nature of the carbon ceramic electrode allows ERGO-PPy be adsorbed by CCE and this prevents its tubing from the surface of CCE.

The electrochemical behavior of DA and UA toward ERGO- PPy/CCE was investigated in phosphate buffer (0.1M) with different pH using cyclic voltammetry. The catalytic oxidation peak of DA and UA shifted to less positive potential by increasing the pH values with linear slope of 53 and 56 mV/pH, which proves the proton involvement in the overall mechanism of electron transfer. As the anodic current has maximum value at pH 7. This pH was chosen as the optimum value for later experiments.
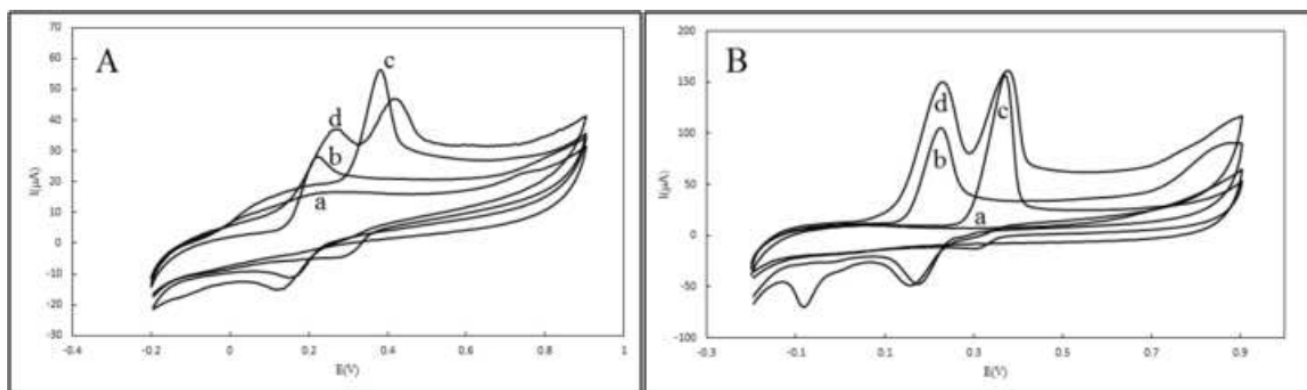

Figure 5. A: Cyclic voltammograms of bare CCE (a) in presence of 1mM AA, (b) 1mM AA and DA, (c) 1mM AA and 1mM UA and (d) 1mM AA,1mM DA and 1mM UA. B: cyclic voltammograms of ERGO/PPy modified CCE in presence of (a) in presence of 1mM AA, (b) 1mM AA and DA, (c) 1mM AA and 1mM UA and (d) 1mM AA,1mM DA and 1mM UA.

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3.6. Differential pulse voltammetry study

Pulse voltammetric techniques, such as differential pulse voltammetry, have been recognized as useful tools in the rapid and sensitive detection in electroanalytical chemistry. Simultaneous detection of DA and UA was performed on the ERGO/PPy/CCE in 0.1 M phosphate solutions containing 1.0 mM AA. As shown in Fig. 6A, with the increase of the DA concentrations in the presence of 1.0 mM AA and 0.1 mM UA, the anodic peak currents of DA are linearly increased ranging from 0.05 to 65 µM. For DA the regression equation is y = 0.4396C + 1.2109. Similar trends are observed by increasing the UA concentrations (Fig.6B) from 0.1 to 120.0 µM (regression equation is y = 0.2921C + 0.9021) in the solution containing 1.0 mM AA and 0.1 mM DA. The detection limits for DA and UA are evaluated to be about 0.002 and 0.08 µM at 3 folds of the signal to noise ratio (S/N = 3), respectively.

Fig.6C shows simultaneous determination of DA and UA in presence of 1mM AA. By increasing the concentration of DA and UA simultaneously, oxidation peak currents linearly increase accordingly. The linear range is from 0.4 to 80µM for DA (y = 0.8809C - 0.0986) and from 0.4 to 50 µM for UA (y = 0.9221x - 0.0787), respectively. The detection limits are found to be 0.12 µM for DA and 0.16 µM for UA at three folds of the signal-to-noise ratio (S/N = 3).
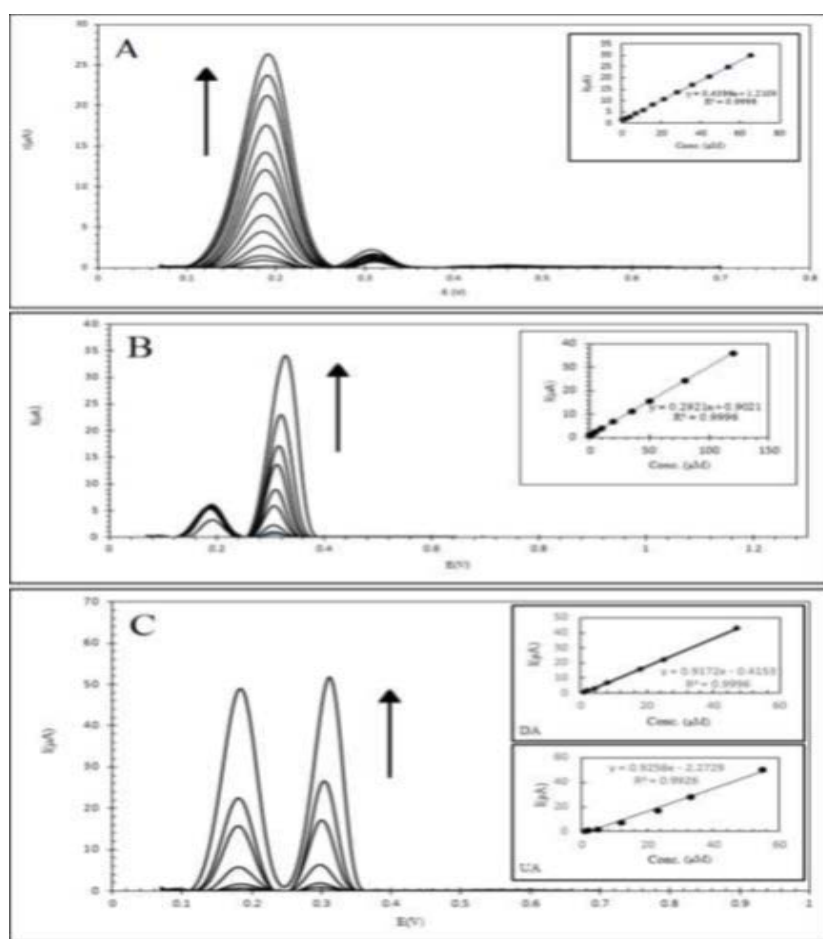

Figure 6. A: DPV of the ERGO/PPy/CCE in 0.1 M phosphate solutions (pH 7.0) containing1.0 mM AA and 0.1 mM UA in the presence of different concentrations of DA: 0.1, 1.0, 1.9, 3.9, 6.8, 10.7, 15.6, 21.4, 28.1, 35.7, 44.2, 53.6 and 65.8 µM. (B) DPV of the ERGO/PPy/CCE in 0.1 M phosphate solutions (pH 7.0) containing 1.0 mM AA and 0.1 mM DA in the presence of different concentrations of UA: 0.2, 1.0, 2.0, 5.0, 10.0, 20.0, 35.0, 50.0, 80.0 and 120 µM. (C) DPV of the ERGO/PPy/CCE in 0.1 M phosphate solutions (pH 7.0) containing 1. mM AA in the presence of different concentrations of DA: 0.4, 2.0, 4.0, 8.0, 18.0, 25.0 and 47.0 µM and UA 0.4, 2.0, 5.0, 12.0, 23.0, 33.0 and 55.0 µM. Insets show the calibration curves of the DA and UA concentration vs. the anodic peak currents. Experimental conditions: step potential: 0.005 V, modulation amplitude: 0.025 V, scan rate: 0.01 V s-1.

Table 1 compares the response characteristics for simultaneous determination of DA and UA at various modified electrodes. In comparison with other modified electrodes [35-38,40], the proposed modified electrode possesses unique properties. Firstly, it has all the advantages of CCE and benefited from the advantages comes from mechanical properties of PPy and electrical properties of ERGO. The proposed modified electrode can be easily constructed in a simple procedure, and the surface of electrode is also easily renewable. Also the modified electrode shows high conductivity and promotion of fast electron transfer. Secondly, the ERGO-PPy/CCE eliminates the interference of AA in DA and UA determination due to proposed interaction mentioned above. Furthermore, sensitivity, detection limit and linear range of the proposed electrode are comparable with other methods.

Table 1. Response properties of determination of DA at various modified electrodes

Electrode	Method	Linear range (µM) DA UA	Detection limit (µM)	Refs.
layer-by-layer graphene and chitosan assembled multilayer/GCE	DPV	0.1 - 140.0	0.050	[37]
		1.0 - 125.0	0.100	
pretreated pencil graphite electrode/GCE	DPV	0.15 - 15.0	0.033	[38]
		0.30 - 150.0	0.120	
poly(L-methionine)/gold nanoparticle GCE	DPV	0.05 - 5.0	0.037	[35]
		0.07 - 7.0	0.045	
poly (naphthol green B)-film modified/CPE	DPV	5.0 - 270.0	0.250	[40]
		12.5 - 750.0	5.0	
Pt nanoparticles supported on reduced graphene oxide/GCE	DPV	10.0 - 170.0	0.250	[36]
		10.0 - 130.0	0.450	
Electrochemically reduced graphene oxide/polypyrrole/CCE	DPV	0.05 - 65.0	0.002	This work
		0.1 - 120.0	0.08	

3.7. Application

The ERGO-PPy modified carbon ceramic electrode was used for the determination of DA and UA in human blood serum and urine samples (Table 2). 1.0 mL human blood serum sample was deproteinized by adding 2.0 mL of acetonitrile. After centrifugation at 12000 rpm for 20 min, the supernatant was transferred into another centrifuge tube and dried with an N2 stream. The residue was dissolved in 1.0 mL of water. Urine samples was diluted with 0.1M PBS (pH=7) and appropriate amount of these diluted samples were transferred to the electrochemical cell for the determination of each species by DPV method. The standard addition method was used for testing recovery. The analytical results summarized in table 2, which clearly indicate the potential application of ERGO/PPy/CCE for determination of DA and UA in real sample.

Table 2. Experimental results for the determination of DA and UA in samples.

Sample	Added (µM)	Found[a] (µM)	Recovery (%)
Human blood serum 1[b]	-	-	-
	10	10.2 ± 0.3	102
Human blood serum 2[b]	-	-	-
	20	20.6 ± 0.4	103
Urine 1[b]	-	36.3 ± 0.9	-
	20	55.8 ± 0.5	97.5
Urine 2[b]	-	63.2 ± 0.7	-
	40	102.4 ±0.4	98

[a] Mean value ± standard deviation (n = 3).
[b] The dilution factor is 10 for human blood serum and 50 for urine sample.

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4. Conclusion

In this work we have fabricated a homemade CCE based on MTMOS modified with ERGO-PPy nanocomposite simply by electro-polymerization. The XRD analysis and FT-IR spectroscopy further confirmed oxidation of graphite and synthesizing of GO. The electrochemical reduction of GO composite was investigated in 0.1 M KCl at 0 to –1.2 V by 3 scan at scan rate of 100mV/s. This modified electrode was applied successfully as DA and UA sensing platform and the electrochemical experiments showed that this modified electrode can determine DA and UA simultaneously in presence of AA with high concentration level. Based on this method, a new biosensor was successfully developed for determination of DA and UA in human blood serum and urine samples.

Acknowledgement

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