RESEARCH PAPER

Novel Green and Facile Synthesis of Co_3O_4 Nanoparticles: Characterization and Its Electrochemical Applications in Simultaneous Determination of Dopamine and Mefenamic Acid

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ABSTRACT

In this work, we report the novel green synthesis of Co_3O_4 nanoparticles (Co_3O_4NPs) using extract of Elaeagnus angustifolia leaves plant as a mild and non-toxic stabilizing agent. The synthesized Co_3O_4NPs was characterized by field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and FTIR spectroscopy. In order to obtain its applicability, the carbon paste electrode (CPE) modified with the Co_3O_4NPs and graphene oxide (GO) (Co_3O_4NPs/GO/CPE) was fabricated as anew sensor for trace determinations of dopamine (DA) and mefenamic acid (MFA). The electrochemical investigations on DA and MFA were carried out by application of differential pulse voltammetry (DPV), cyclic voltammetry (CV) and chronoamprometry (CA) methods. The results showed that Co_3O_4NPs as the modifier in the proposed sensor can accelerates the electron transfer reactions of DA and MFA. Under the optimum conditions, the electrode provides a linear response versus DA and MFA concentrations in the range of 0.5-250 μM and 1-500 μM, with a detection limit of 0.15 μM and 0.3 μM, respectively. The modified electrode exhibited some advantages such as convenient preparation, good stability, high sensitivity and selectivity toward DA and MFA determination.

INTRODUCTION

Neurotransmitters are biochemical molecules that transmit signals from a neuron across the synapse to the target cell and are therefore essential for the functioning of the central and peripheral nervous systems[1]. Dopamine (DA) is a neurotransmitter playing essential roles in the cardiovascular and central nervous Functions. Therefore, high dopamine level indicate cardiotoxicity leading to rapid heart rates, hypertension, and heart failure On the other hand, low level of dopamine in the central nervous system are implicated as a major source of a number neurological diseases such as Parkinson's disease, Schizophrenia, Alzheimer's disease, stress and depression[2, 3]. DA is derived from an amino acid, phenylalanine, which must be obtained through the diet [4]. Several various methods have been used for determination of DA, mostly using HPLC, capillary electrophoresis , chemical processes and SERS[5]. However, many of these methods are expensive and are not

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available in every laboratory. The electrochemical methods have attracted attention because of their practicality, sensitivity, accuracy, low cost and portability [6-8].

Mefenamic acid (MFA) is a non-steroidal anti-inflammatory drug (NSAID) that is pharmaceutically used to reduce mild and moderate pain such as headaches, tooth pain, pain after surgery, dysmenorrhea, osteoarthritis, and rheumatoid arthritis. In higher doses, this compound decreases inflammation [9]. MFA works as a pain reliever by acting on the cyclooxygenase (COX) pathways and influencing prostaglandin synthesis, which is involved in inflammation and pain response. Intake of MFA results in gastrointestinal side effects (such as vomiting, diarrhea), hepatic necrosis, liver injury, morbidity, and even mortality in humans. To reduce the side effects, it is taken through oral routes and with food [10]. The general methods for the determination of MFA include spectrophotometry, chemiluminescence, capillary electrophoresis, colorimetric, mass spectrometry and HPLC [11]. Some of these techniques are expensive and time-consuming for the analysis. Electrochemical techniques using modified electrodes are convenientsince they are easy to handle, less expensive, and have better sensitivity [12].

Several techniques include chemical methods are used to prepare nanoparticles. The disadvantages of chemical reduction techniques are the toxicity of chemical reducing agent and high cost. For this reason, There are intention of scientist to use of green synthesis methods to prepare nanoparticles Simplicity, economical friendliness, low cost, no need to use high pressure, energy, temperature and toxic chemicals are some of many advantages of these green synthesis methods[13, 14]. The extracts of leaves of E. angustifolia L. contain phenolic and flavonoid compounds, which have antioxidant properties. Phytochemical studies of the plant extract indicate the presence of flavonoid compounds, polysaccharides, phenol carboxylic acids, amino acids [15, 16]. Thus, plant can be used as an important source for bioreduction of metallic ions and production of nanoparticles considering the potent antioxidants contained in it [17]. The extracts of leaves of E. angustifolia L. as a stabilizing, reducing and masking agent, has recently been used for the synthesis of Co_3O_4NPs.

Nowadays, synthesis and application of nanomaterials in different field of investigations are growing rapidly [18-20]. Carbon nanostructures have been greatly studied due to their excellent chemical and physical possessions and numerous application. Graphene oxide (GO) a nonconductive hydrophilic carbon material, sheets of graphene is composed by epoxides, alcohols, ketone carbonyls, and carboxylic groups. GO usually was synthesized by exfoliation of graphite with strong oxidizing agents.

In this work, we report the application of Co_3O_4NPs synthesized by the green method, using extract of Elaeagnus angustifolia leaves plant, to prepare a modified carbon paste electrode(CPE) as Co_3O_4NPS/GO/CPE to obtain a suitable sensor for simultaneous determination of MFA and DA in aqueous solutions.

MATERIALS AND METHODS
Chemicals and reagents
DA and MFA were purchased from the Aldrich chemical company as analytical grade. materials were of commercial reagent grade. Cobalt chloride hexahydrate ($CoCl_2.6H_2O$) was obtained from Merck chemical company. The most of the chemicals were analytically grade and they were used as received. Phosphate buffer solutions (PBS) were prepared by appropriate amount of stock solutions of 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4. The most of electrochemical experiments on UA and HIS were achieved in 0.1 M phosphate buffer solution at pH of 7 otherwise stated. Fresh Elaeagnus angustifolia L.leaves were obtained from Arak suburb (Shazand, Iran). All solutions were prepared using double distilled deionized water.

Preparation Elaeagnus angustifolia L.leaves extract
The fresh Elaeagnus angustifolia L.leaves were washed thoroughly with tap water and subsequently using deionized water. After drying at ambient temperature in shade, leaves were grounded to yield a fine powder. Briefly, 10 gr of leaf was grinded initially, then stirred with 175 mL deionized water at 100° C for 60 min and was filtered for three times using Whatman filter paper to obtain the extract.

Synthesis of Co_3O_4 Nanoparticles
The synthesis of Co_3O_4NPs was carried out using cobalt chloride hexahydrate ($CoCl_2.6H_2O$) material

in the process of green synthesis method. Initially, fresh Elaeagnus angustifolia L.leaves extract (E) was added to 0.1 M solution of CoCl$_2$.6H$_2$O (S) in the volume ratio of 1:1 (E/S), then the solution was stirred rapidly. Immediately the solution was warmed at 80 °C for a 15 min time. After cooling down to room temperature, the obtained colloids were collected and washed by distilled water. Then the solution was centrifuged at 1800 rpm for 2h. The precipitate was rinsed two times by ethanol and deionized water then filtered. Finally deposit was initially vacuum-dried at 80 °C for 2h and then calcined in oven at 700 °C for five hours to obtain Co$_3$O$_4$NPs.

Synthesis of graphene oxide (GO)

Graphene oxide (GO) was synthesized by using modified Hummer's method [32]. Briefly, a 360:40 mL (9:1) combination of concentrated H$_2$SO$_4$ and H$_3$PO$_4$ was added to 3.0 g graphite and stirred stilly. Subsequently 18.0 g KMnO$_4$ was added gently then the solution was heated up to 50 °C while stirred for 12 h. Afterward the solution was cooled to room temperature, then 3 ml cold H$_2$O$_2$ with 400 ml frozen deionized water was added to it and stirred vigorously to obtain yellow color solution. Then the deposit

was centrifuged, and the remained solid material was washed in succession with distilled water, HCl (2M), and ethanol three times, respectively. Finally, the precipitate followed by filtration and then vacuum-dried for 12 h at 70 °C to obtain a brown powder of graphene oxide.

Instrumentation

Electrochemical measurements were carried out using Co$_3$O$_4$NPs/GO/CPE as the working electrode, Ag/AgCl 3 M KCl as the reference electrode and platinum wire as an auxiliary electrode. Differential pulse voltammetry (DPV), cyclic voltammetry (CV) experiments were carried out using a Sama instrument/potentiostat (Electro Analyzer System, Iran) and chronoamperometry (CA) experiments were carried out using a Autolab PGSTAT 30 Potentiostat/Galvanostat (EcoChemie, Netherlands). The pH measurements were performed with a Metrohm 744 pH meter. The analyses were carried out using Sigma VP Zeiss-scanning electron microscope electron microscope (SEM). Fourier transform infrared (FT-IR) spectra were recorded as pressed KBr discs using a Unicom Galaxy Series FT-IR 5000 spectrophotometer. The XRD patterns were registered by X-ray diffraction instrument (PHILIPS, model PW3040/60).
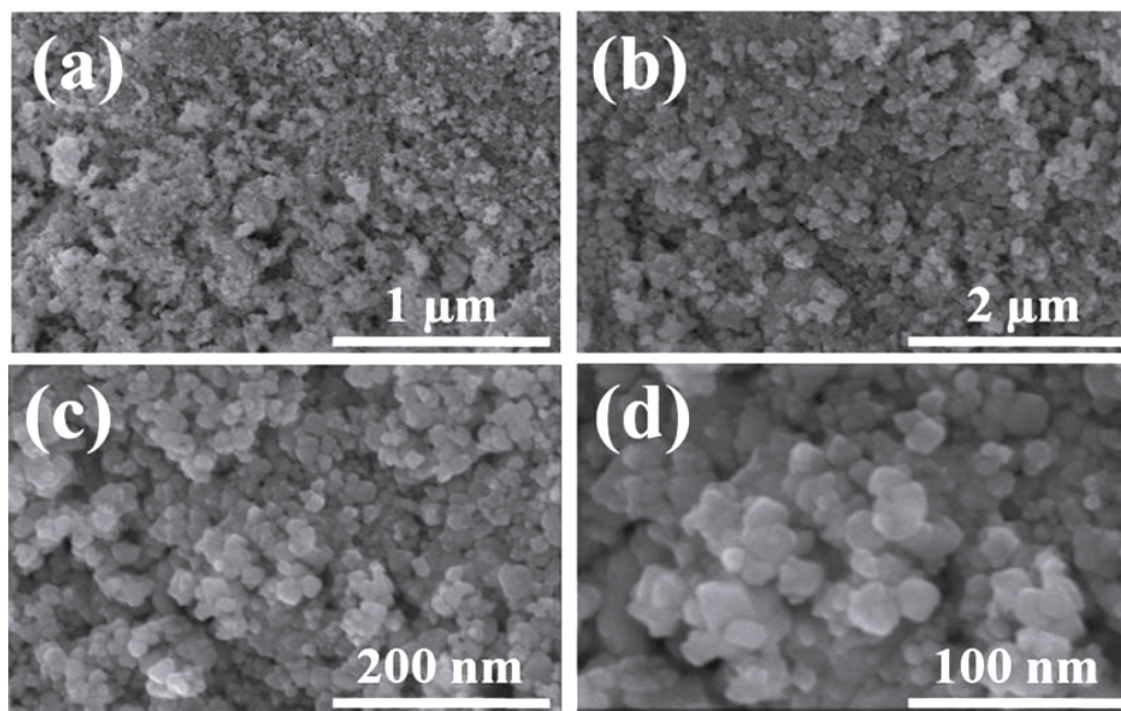

Fig. 1. SEM image of green synthesized Co$_3$O$_4$ nanoparticles in different magnification.

Fabrication of Co₃O₄ NPs/GO/CPE

The modified carbon paste electrode was prepared by grinding appropriate amounts of GO and Co₃O₄NPs and graphite powder with two drops of nujol oil, until a homogenous paste was obtained. The paste was then packed into a narrow syringe with internal radius 3 mm. Then a copper wire in middle of the packed syringe was inserted to act as electrical conductor. Prior to use, the Co₃O₄NPs/GO/CPE was polished on a piece of weighing paper and rinsed with distilled water to obtain a Uniforms surface. Before running any electrochemical experiment, the solution was stirred for 120 seconds.

RESULTS AND DISCUSSION

Characterization of Co₃O₄NPs

FESEM was used to obtain the structural characteristics of Co₃O₄NPs (Fig. 1). FESEM images with various magnification of Co₃O₄NPs show that the particles are perfectly uniform with a narrow size distribution in the range of 25-35 nm. The surface of the synthesized nanoparticles is very smooth. The low dimensions of the particles

provide high surface area for the synthesized Co₃O₄NPs. There are several report on application of NPs with high surface area for modification of CPE [21-22]. Therefore, combination of Co₃O₄NPs and porous GO suggest high response for the modified CPE.

The XRD Pattern of Co₃O₄NPs is demonstrated in Fig. 2. The X-ray diffraction pattern was obtained with Cr Kα radiation as the X-ray source, that was recorded in the range of 2θ as 28-107°. The results showed that a few the corresponding peaks at 56.015, 64.993 and 98.900 are in accordance with JCPDS No. 01-072-1474 which belong to CoO nanoparticle. In addition, the relevant peaks at 28.395, 47.225, 55.441, 58.669, 68.920, 87.839, 94.648 and 106.390 are in consistent with JCPDS No. 00-042-1467 which belong to Co₃O₄. Therefore, it seems that during the synthesis the mixture of two oxidation states of cobalt oxide would be obtained which is in accordance with previous reports [23, 24] .

FTIR spectrum of Elaeagnus angustifolia Leaves extract (Fig. S1) demonstrates the functional groups of its polyphenolics that are responsible for the reduction of metal ions [25]. A broad peak
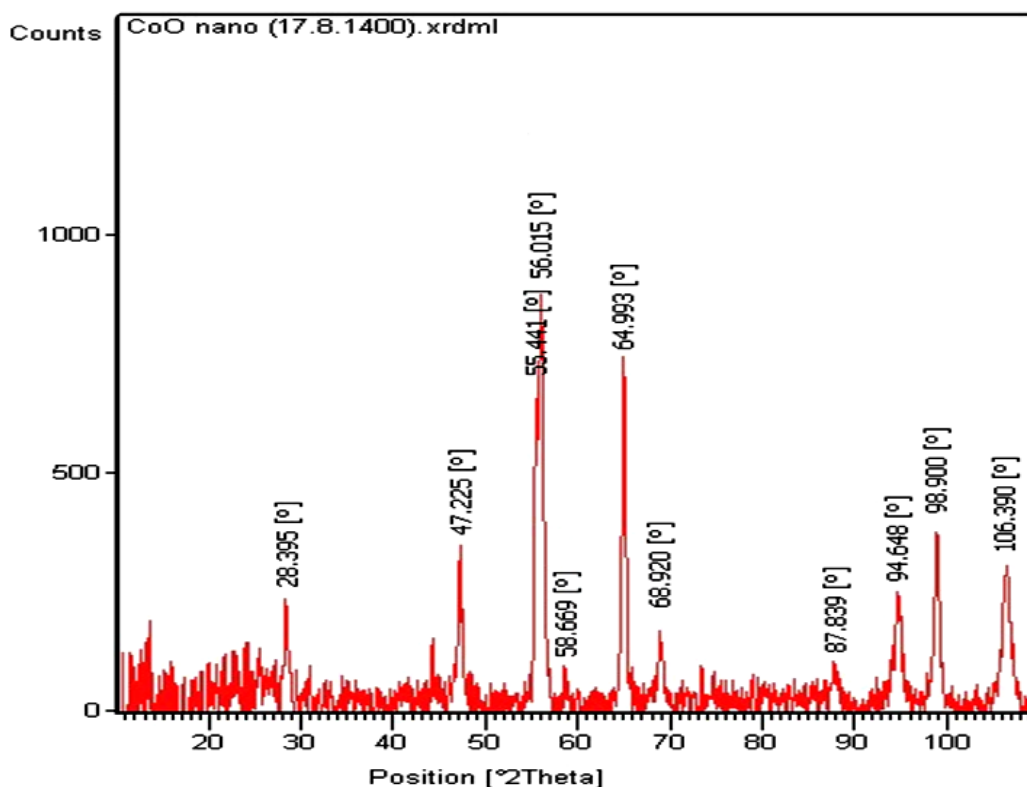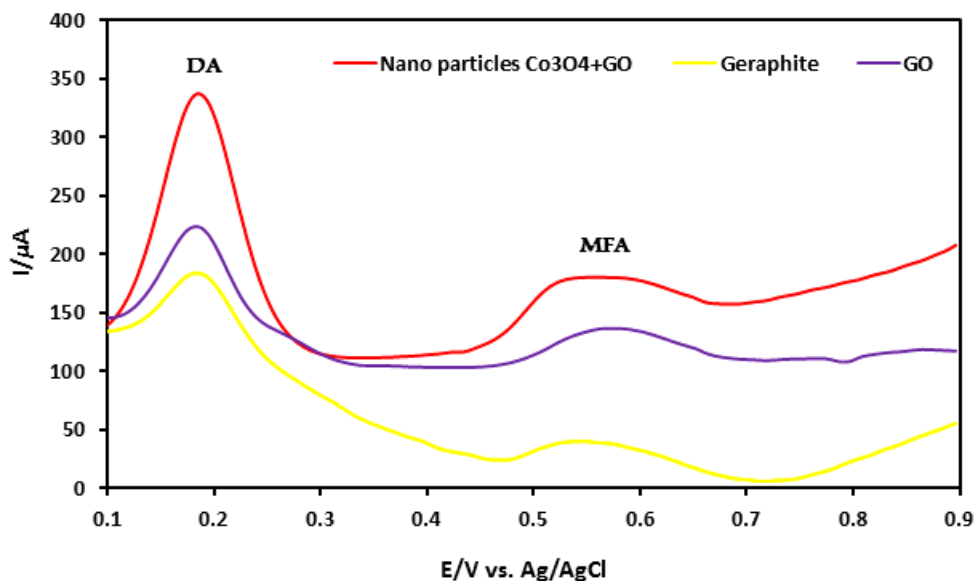

Fig. 2. The XRD Pattern Co₃O₄NPs.

Fig. 3. Differential pulse voltammograms of DA and MFA at (a) Geraphite (bare), (b) GO/CPE and (c) Co$_3$O$_4$NPs/GO/CPE

at 3447 cm^{-1} exhibited the (O—H) functional groups in polyphenols. The FTIR spectrum of Co$_3$O$_4$NPs indicated in Fig. S2. The peaks at 2923 and 2853 cm^{-1} can be assigned to vibration modes of the (–CH) group. The characteristic peak of the (C=C) functional group was centered at approximately 1624 cm^{-1}. The strong bands present at approximately 1437 cm^{-1} were assigned to the symmetric stretching modes of (O-C=O)

group[26] . The relatively strong peak at 857 cm^{-1} can be assigned to the out-of-plane bending vibrational modes of the (–CH) group. The peaks at 875, 644 and 569 cm^{-1} can be assigned to the vibration mode of the (Co-O) group. Fig. S3 shows the FTIR spectrum of GO with the wide absorption band at 3420 cm^{-1} corresponds to (O—H) functional groups. The presence of the peak in 1729 cm^{-1} relating to (C=O) stretching
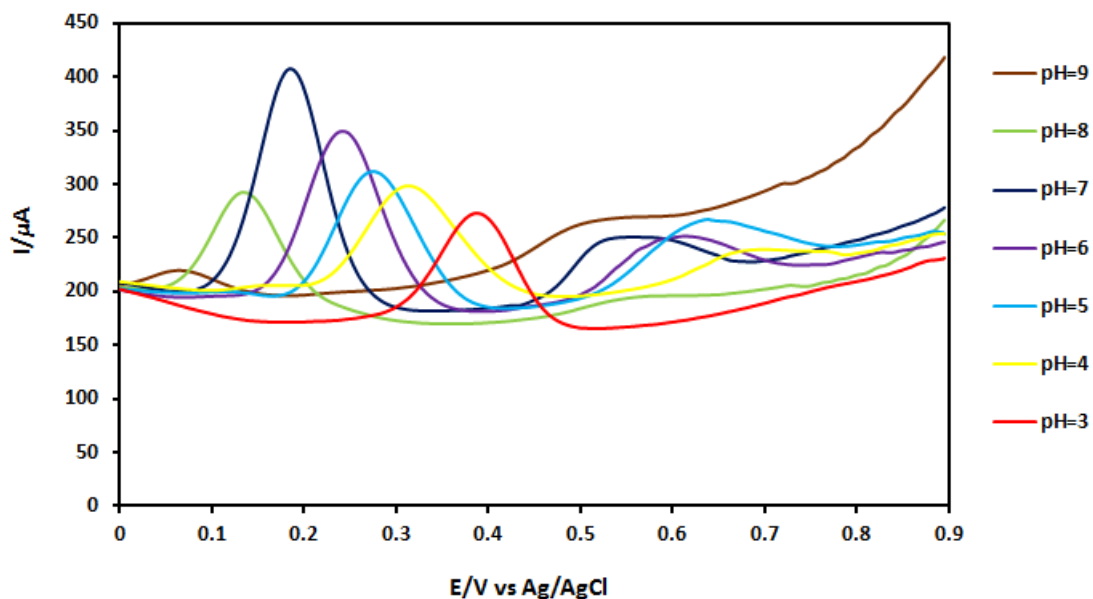

Fig. 4. Differential pulse voltammograms (DPV) of 200 μM DA and 200 μM MFA compounds at Co$_3$O$_4$NPs /GO/CPE in solution of 0.1 M phosphate buffer solution at different pH of 3, 4, 5, 6, 7, 8 and 9.

vibration, peak in the range of 1624 cm⁻¹ relates to tensile vibrations (C = C) of the double bond of a hexagonal ring. These three bands approve the main and hexagonal structure of graphene oxide. Although the peak in the range of 1115 and 1437 cm⁻¹ are corresponding to (C—O) epoxy group and (C—O) bond in alkoxy group in GO relatively [27].

Electrochemical studies of DA and MFA on GO/ Co₃O₄NPs/ CPE

The DPV experiments revealed that the oxidation peak currents of DA and MFA are dependent on the percentage of Co₃O₄NPs and GO in the modified electrode. In order to optimize the percentage of the components several DPV experiments were carried out. The best results were obtained at percentage of 6% for GO and 8% for Co₃O₄NPs in the modified electrode (not shown).

Fig. 3 shows the results of DPV results at bare and modified CPE in phosphate buffer solution (pH = 7). The results were obtained in solution of 200 µM DA and 200 µM MFA at (a) bare CPE, (b) GO /CPE and (c) Co₃O₄NPs/GO/CPE. According to the results the highest oxidation peak currents were obtained at Co₃O₄NPs/GO/CPE which leads to excellent sensitivity of the modified electrode in simultaneous determination of DA and MFA.

Optimization of Operational Parameters
Effects of Electrolytes and pH

To investigate effect of type of electrolytes on electrochemical oxidations of DA and MFA, several buffers such as phosphate, citrate, acetate, ammonia and Briton-Robinson solution with a concentration of 0.1 M at pH of 7 were prepared. The results of DPV experiments revealed that DA and MFA produce higher oxidation peak currents

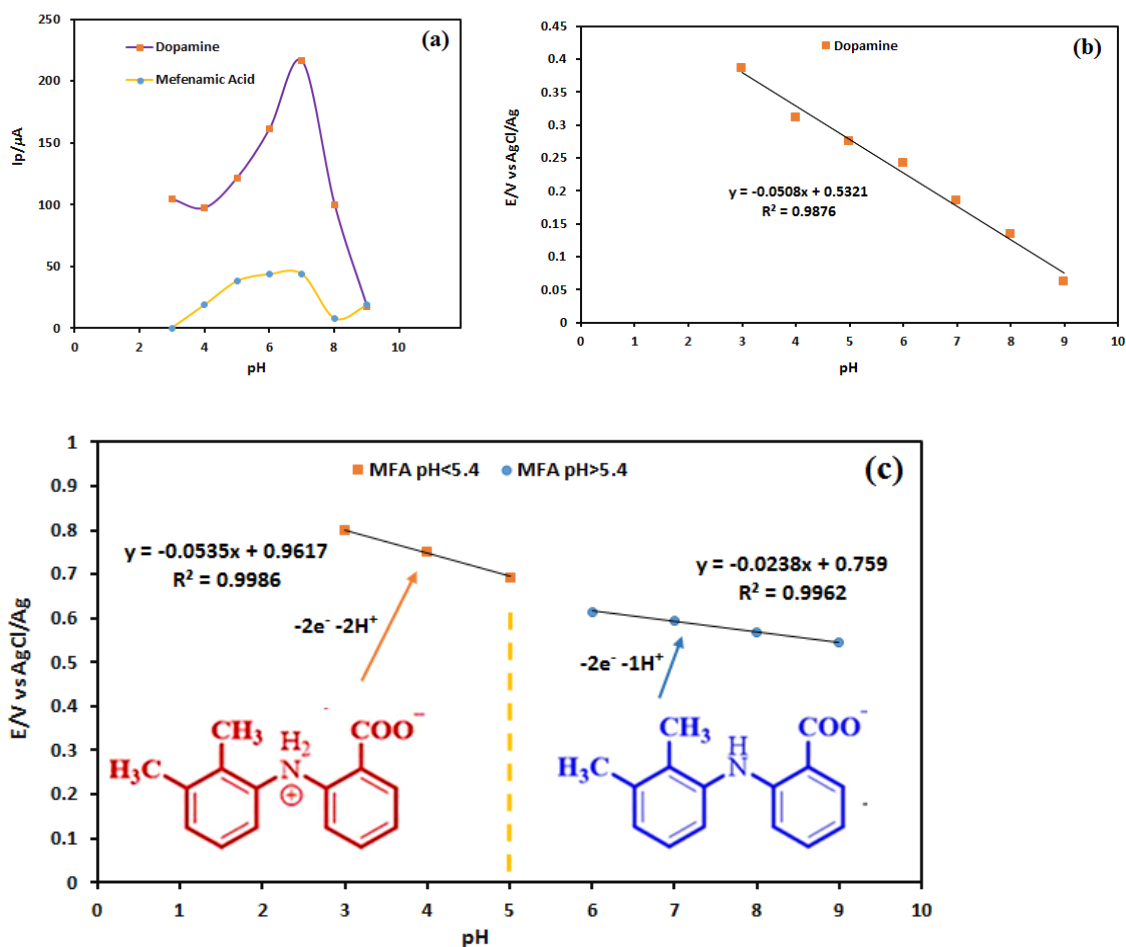Fig. 5. Effect of variation of pH : (a) Plot of anodic peak currents (Ipa) of DA and MFA as a function of pH values. (b) Plot of potential values as a function of pH values for DA and (c) Plot of potential values as a function of pH values for MFA.

in phosphate buffer (not shown). Therefore, phosphate buffer solution was chosen as the best electrolyte.

The effect of pH on response of the proposed sensor was studied by measuring the oxidation peak currents of 200 μM DA and 200 μM MFA in 0.1 M phosphate buffer solution in the pH range of 3 to 9 (Fig. 4).

The results of the experiments Fig. 5a showed that the oxidation peak current of DA and MFA improves with increasing pH in the range of 3 to 7 and reaches to its maximum value at pH of 7 and then at higher pH values the corresponding oxidation peak currents are decreased. As a result, phosphate buffer solution with pH of 7 was chosen as the optimum pH for next experiments. Figs. 5b and 5c show relationship between oxidation peak potentials of DA and MFA with pH. The results showed that by the variation of pH, the corresponding oxidation peak potentials for DA and MFA vary linearly with pH as follows:

Epa (V) = 0.5321 - 0.0508pH   (R^2= 0.9876)   DA

Epa (V) = 0.9617 - 0.0535pH   (R^2 = 0.9986) pH<5.4

Epa(V)=0.759 - 0.0238pH.   (R^2= 0.9962) pH>5.4   MFA

According to these relations, the slopes are near to 0.059 V, which is the Nernstian slope, suggesting that an equal number of electrons and protons were involved in the electrochemical oxidation of DA and MFA. However at pH higher than 5.4 for MFA the slope changed to 0.0238V which suggest mechanism of oxidation with two electron and one proton involved in such pH range. Similar behavior are reported previously [28, 29]. The mechanism for oxidations of DA and MFA are shown in Fig. S4.

Effects of Accumulation Time

One of the factors that effects on response of the modified electrode toward oxidation of DA and MFA is accumulation time due to its effect on adsorption of the analysts. In order to obtain the best accumulation time, DPV experiments were carried out in the solution of 200 μM DA and 200 μM MFA with 0.1 M phosphate buffer solution (pH = 7) at the modified electrode in accumulation time range of 0 to 130 s(Fig. 6). The results showed that oxidation peak current of DA and MFA grow with increasing accumulation time up to120 seconds. At longer time, saturation of the electrode surface occurs by the adsorbed
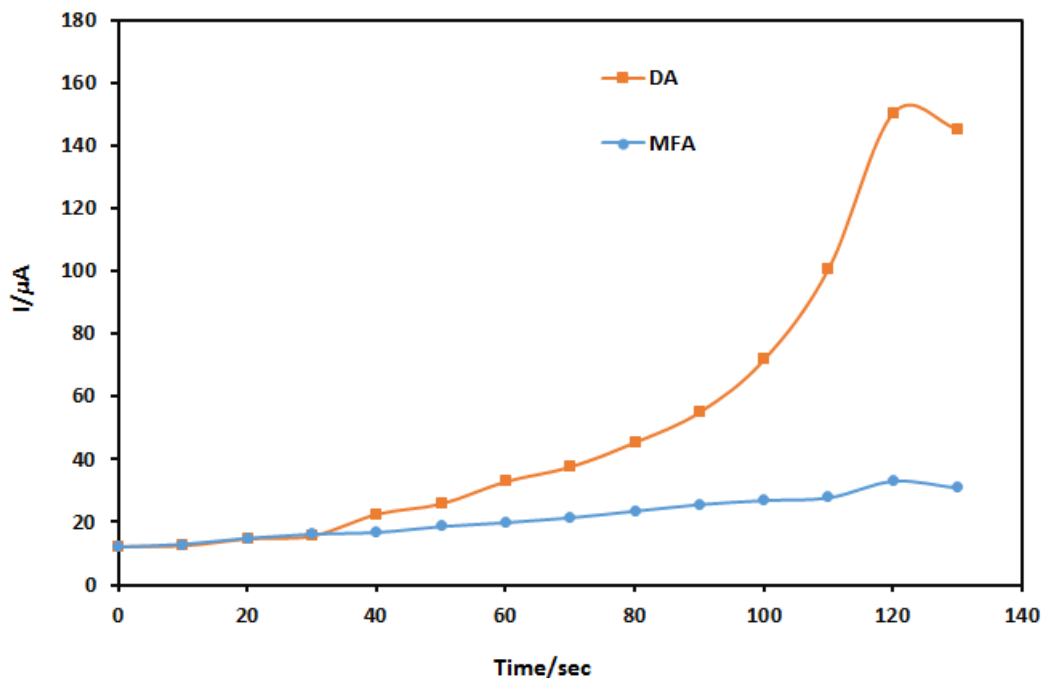

Fig. 6. Effect of accumulation time on the differential pulse voltammogram peak currents of 200 μM DA and 200 μM MFA in 0.1 M phosphate buffer solution (pH = 7) at Co$_3$O$_4$NPs/GO/CPE.

compounds and the corresponding anodic peak currents remains almost constant. Therefore, the accumulation time of 120 seconds was chosen as the most appropriate accumulation time for experiments.

Linear dynamic range and detection limit of the method

To evaluate the linear relationship between, oxidation peak currents of DA and MFA concentrations, DPV techniques were used at Co₃O₄NPs/GO/CPE under optimum conditions and the corresponding calibration diagrams were obtained (Fig. 7). For DA, the linear dynamic range was in the range of 0.5 µM to 250 µM with a calibration equation of Ip (µA) = 1.0096 C (µM) + 10.578 (R² = 0.989) that a detection

limit of 0.15 µM was obtained. For MFA, the linear dynamic range was between 1 to 500 µM with a calibration equation of Ip (µA) = 0.1246C (µM) +3.2951(R²=0.9912) that a detection limit of 0.3 µM was obtained. The literature survey showed that this the first report on simultaneous determination of DA and MFA using a novel sensor based on green synthesized Co₃O₄NPs which provide wide linear dynamic range and low detection limit

Stability, Repeatability, and Reproducibility of the Co₃O₄ NPS/GO/CPE

In order to evaluate the stability of the modified electrode in solution, the decrease in peak currents was measured by determining during repetitive DPV measurements of DA and MFA
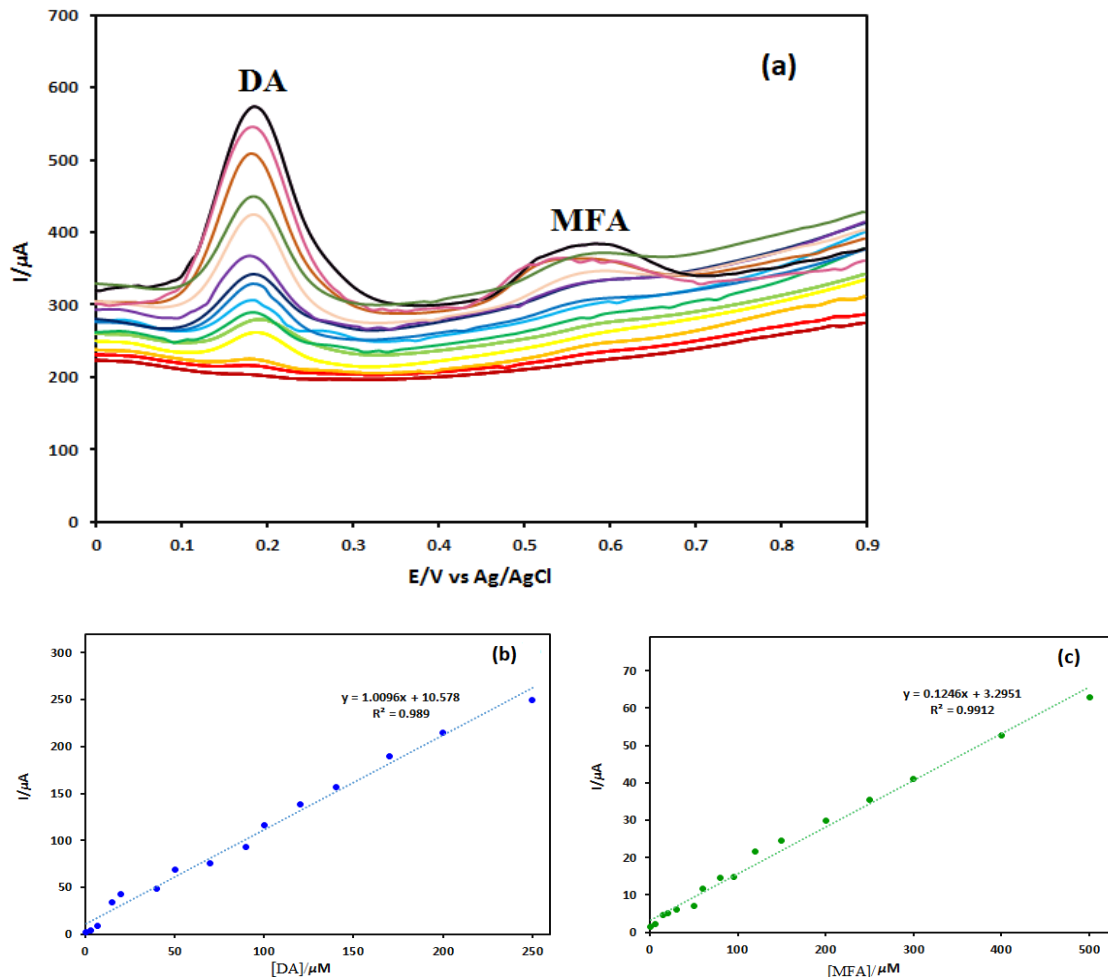

Fig. 7. (a) Differential pulse voltammograms for different concentrations of DA and MFA in various concentrations.(b)Plot of the oxidation peak currents as a function of DA concentration from 0.5 until 250 µM and (c) Plot of the oxidation peak currents as a function of MFA concentration from 1 until 500 µM

after the modified electrode was placed in a 0.1 M phosphate buffer solution with pH of 7 under wet and dry conditions. Under wet condition, the oxidation peaks current of DA and MFA after eight times measurements during 7 hours showed only 1.6 % and 5.4 % decrease of corresponding oxidation peak currents, respectively. In order to obtain stability of the modified electrode under dry condition, the modified CPE was stored in air for specific period of time. After 7 days, the anodic peak current of 200 µM UA and 200 µM HIS were measured using DPV method in 0.1 M PBD at pH of 7. The results showed that the oxidation peak currents of DA and MFA were decreased only about 2.5 % and 8.6 %, respectively. The results indicate good stability of the proposed modified as a sensor for simultaneous determination of DA and MFA

To evaluate the repeatability of the method, repetitive DPV measurements were performed in a solution of 200 µM DA and 200 µM MFA in a 0.1 M phosphate solution with pH of 7. The results of eight consecutive determinations indicated good reproducibility with a relative standard deviation (RSD) of 0.4 % for DA and 1.8 % for MFA, respectively. The results showed admissible

reproducibility for the electrochemical response of the sensors. According to the results, the Co$_3$O$_4$NPs/GO/CPE was not subjected to surface contaminate during the voltammetry analysis that makes the sensor excellent in terms of repeatability.

Chronoamperometric measurements

The diffusion coefficient (D) of DA and MFA at Co$_3$O$_4$ NPs/GO/CPE can also be determined by Chronoamperometry method (Fig. 8a and 8b). Chronoamperometric determinations were carried out at the modified electrode by applying separate potentials of 200 mV and 575 mV for DA and MFA, respectively. In accordance to Cottrell equation[30], for an electroactive material with a diffusion coefficient of D, currents due to electrochemical reactions, are described by the following equation:

$$I = n\ FA\ C\ D^{\frac{1}{2}}\ t^{-\frac{1}{2}}\ \pi^{-\frac{1}{2}}$$

In this equation D and C are diffusion coefficient (cm^2 s^{-1}) and the bulk concentration (mol cm^{-3}), respectively. In situations where there is a diffusion control (mass transport), a plot of I vs.
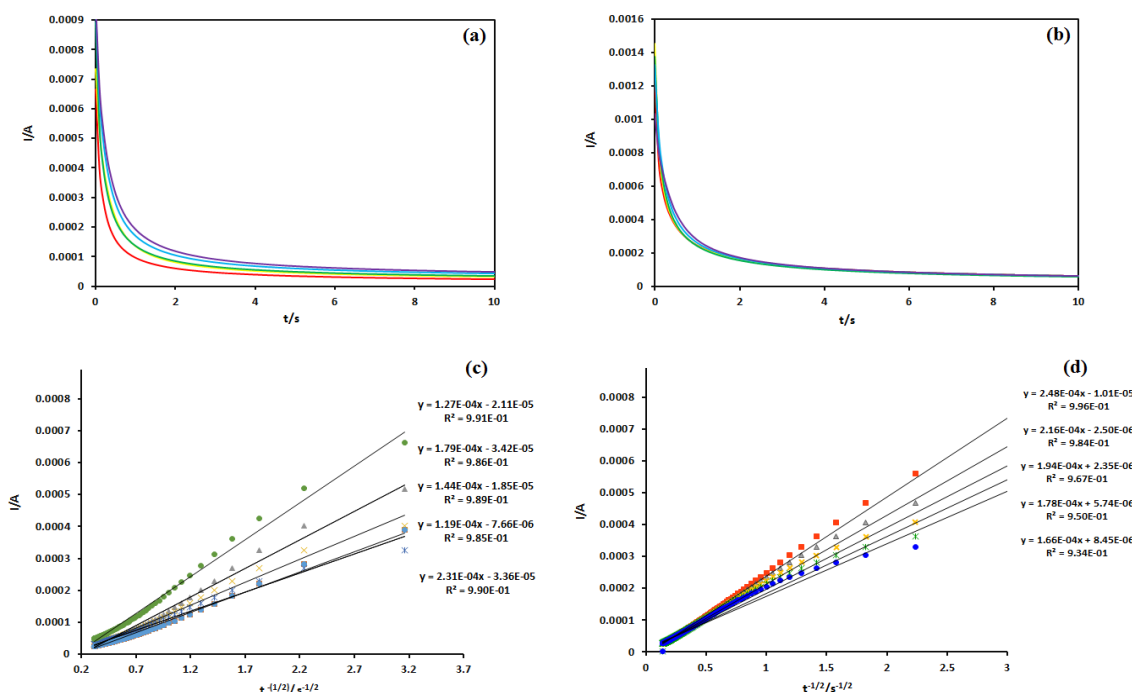

Fig. 8. (a) Chronoamperograms obtained in 0.1 M phosphate buffer solution (pH= 7.0) in the solutions of (a) 100, 200, 300, 400 and 500 µM of DA at Co$_3$O$_4$NPs/GO/CPE; (b) Chronoamperograms obtained in 0.1 M phosphate buffer solution (pH=7.0) in the presence of 100, 200, 300, 400 and 500 µM of MFA at Co$_3$O$_4$NPs/GO/CPE; (c) Plots of I vs. t$^{-1/2}$ obtained from chronoamperograms in (a) for DA and (d) Plots of I vs. t$^{-1/2}$ obtained from chronoamperograms in (b) for MFA

Table 1. Maximum tolerable concentration of interfering species.

Interfering species	DA $C_{int}/(\mu M)$	MFA $C_{int}/(\mu M)$
Glucose	650	700
Ascorbic acid	400	350
Aspartic acid	1600	1800
Uric acid	300	400
L-alanin	500	600
Na^+	700	800

C_{int} refers to interfering compound concentration

$t^{-1/2}$ is linear, and the value of D can be obtained from its slope. (Fig. 8c and 8d) show $I-t^{-1/2}$ diagrams of five different concentrations of DA and MFA, respectively. By using the Cottrell equation and the slopes related to these diagrams, the diffusion coefficients for DA and MFA were calculated as 4.98×10^{-5} cm^2 s^{-1} and 6.89×10^{-5} cm^2 s^{-1}, respectively

Effect of Interferences

In Table 1, the results of effects some possible interferences of different species on the oxidation of peak currents of 200 µM DA and 200 µM MFA on the GO/Co_3O_4NPs/CPE in a solution of 0.1 M PBS with pH of 7 is given under the optimum conditions. The concentrations presented in this Table represent the concentrations of the interferent (C_{Int}) that gives an error of ≤ 5% in determinations of DA and MFA.. The data showed that interferences are only noteworthy at relatively high concentrations which confirm that the suggested method is expected to be free from interferences from common components with high selectivity.

CONCLUSION

In this study the green synthesis of Co_3O_4NPs with Elaeagnus angustifolia leaves Platystegius plant extract is reported. In order to investigate the application of Co_3O_4NPs, it was used with GO to fabricate Co_3O_4NPs/GO/CPE as a sensor for simultaneous determination of DA and MFA. The interfering study of some species showed no significant interference with determination of DA and MFA. The simple fabrication procedure, high speed, repeatability, high stability, low detection limit and wide linear dynamic range, propose that sensor is an attractive candidate for practical applications.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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