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In situ electrochemical synthesis of highly loaded zirconium nanoparticles decorated reduced graphene oxide for the selective determination of dopamine and paracetamol in presence of ascorbic acid

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ABSTRACT

Highly loaded zirconium oxide (ZrO_2) nanoparticles were supported on graphene oxide (ERGO/ZrO_2) via an in situ, simple and clean strategy on the basis of the electrochemical redox reaction between zirconyl chloride and graphene oxide ($ZrOCl_2$ and GO). The electrochemical measurements and surface morphology of the as prepared nanocomposite were studied using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and field emission scanning electron microscopy (FESEM). This ZrO_2 decorated reduced graphene oxide nanocomposite modified GCE (ERGO/ZrO_2) exhibits a prominent electrocatalytic activity toward the selective detection and determination of dopamine (DA) and paracetamol (PA) in presence of ascorbic acid (AA). The peaks of linear sweep voltammetry (LSV) for DA and PA oxidation at ERGO/ZrO_2 modified electrode surface were clearly separated from each other when they co-existed in the physiological pH (pH 7.0) with a potential value of 140 mV (between AA and DA) and 330 mV (between AA and PA). It was, therefore, possible to simultaneously determine DA and PA in the samples at ERGO/ZrO_2 nanocomposite modified GCE. Linear calibration curves were obtained for 9–237 μM of PA and DA. The ERGO/ZrO_2 nanocomposite electrode has been satisfactorily used for the determination of DA and PA in the presence of AA at pharmaceutical formulations in human urine samples with a linear range of 3–174 μM. The proposed biosensor shows a wide linear range, low detection limit, good reproducibility and acceptable stability, providing a biocompatible platform for bio sensing and bio catalysis.

1. Introduction

The synthesis and investigation of graphene based materials in different fields of science such as physics, chemistry, material science and nanotechnology has been increased, due to its excellent mechanical, electronic and thermal properties [1,2]. It also has an unique electrochemical properties such as fast electron transfer, excellent conductivity and even the wide electrochemical potential window have the ability to enhance the direct electron transfer at the bare electrodes have broadened their applications in the field of electrochemical biosensors [3]. Graphene sheets have tendency to form graphite due to the van der Waals force of attraction [4]. Moreover, due to its hydrophobic nature dispersion of graphene in aqueous media is difficult. Until now, versatile strategies have been employed by several researchers to attain large yield and high quality of graphene [5,6]. Besides, graphene sheets synthesized by much preferred chemical exfoliation method are not virtuous enough for nano electronics applications [7]. Conversely, the electrochemical reduction method is more efficient (without using any toxic solvents), for preparing high quality graphene sheets in large scale with short time to form exfoliated graphene oxide with high sensitive and low cost [8].

On the other hand, studies of nanoparticles and organized low-dimensional nanostructures have their unique capabilities to enhance mass transport, facilitate catalysis, increase surface area, and control an electrode's microenvironment [9]. Also, the nanoparticles provide a high surface-to-volume ratio and enhance the electron transfer kinetics [10]. ZrO_2 nanoparticles are an inorganic oxide, which have been demonstrated as an ideal material for the immobilization of biomolecules with oxygen groups because of its thermal stability, chemical inertness, lack of toxicity, and affinity for the groups containing oxygen [11]. The nanoparticles also

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provided a three-dimensional stage, and some of the restricted orientations also favored the direct electron transfer between the protein molecules and the conductor surface [12].

Dopamine (DA), uric acid (UA) and ascorbic acid (AA) are the important biomolecules which usually coexist together and considered as important molecules for physiological processes in human metabolism. UA and DA deficiencies result in several diseases and disorders [13–16]. The first species plays an important role in human brain and a loss of DA-containing neurons may result in some serious diseases such as Parkinson. The main difficulty with the electrochemical detection of DA in brain fluids is the coexistence of many interfering compounds. Acetaminophenol or paracetamol (PA) has been used comprehensively all over the world as a pharmaceutical pain reliever for patients for the relief of moderate pain for headache, backache and also used for reduction of fevers [17,18]. PA relives pain in the central nervous system and the concentration of it is high. In antagonistic, the physiological levels of DA are below 200 μmol L^{-1} [19], thus, researchers are keen on developing biosensor for the selective detection of dopamine (DA) and paracetamol (PA). But, determination of DA and PA on solid electrodes is challenging one due to the overlapping oxidation peak potentials. There are only few previously reported modified electrodes for the determination of these compounds, such as sodium dodecyl sulfate micelles as masking agent for electrochemical determination of DA in the presence of ascorbic acid [20], Pt–Au hybrid film modified electrode [21], Nafion/carbon coated iron nanoparticles chitosan composite film modified electrode [22] and for PA carbon coated nickel magnetic nanoparticles modified electrodes [23], electrochemically reduced graphene oxide/neodymium hexacyanoferrate modified electrodes[24], and simultaneous electrochemical determination of dopamine and acetaminophenol using multiwalled carbon nanotubes modified glassy carbon electrode [25]. These above reported electrochemical sensors satisfied many of the requirements such as specificity, speed of response, sensitivity and simplicity of preparation. However, the utility of solid-electrode-based sensors is often hampered by not having sufficient selectivity. In particular, complexity of real biological systems may result in overlapping voltammetric signals.

Herein, we report a simple co-electrodeposition method to prepare ERGO/ZrO_2 nanocomposite modified electrode. By taking advantage of the well-defined redox behavior of the ERGO/ZrO_2 nanocomposite, it was successfully employed for the selective electrocatalytic determination of PA and DA. This composite was prepared on GCE and ITO electrodes by simple two steps process by drop casting of GO followed by electrochemical reduction in the zirconyl chloride solution in PBS pH 5. As prepared nanocomposite electrode was characterized using surface analysis technique field emission scanning electron microscopy (FESEM) along with electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). ERGO/ZrO_2 modified electrode successfully separated PA and DA without AA interference and quantified in both lab and real samples, respectively.

2. Experimental

2.1. Apparatus

Electrochemical measurements like cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed by a CHI 1205A electrochemical analyzer. A conventional three-electrode cell was used at room temperature with glassy carbon electrode (GCE) (surface area = 0.07 cm^2) as the working electrode, Ag/AgCl (saturated KCl) electrode as reference electrode and a platinum wire as counter electrode. The potentials mentioned in all experimental results were referred to standard Ag/AgCl (saturated KCl) reference electrode. Surface morphology of the film was studied by FESEM (Hitachi, Japan). EIS were performed by using ZAHNER impedance analyzer (ZAHNER Elektrik Gmbh & Co. KG, Germany).

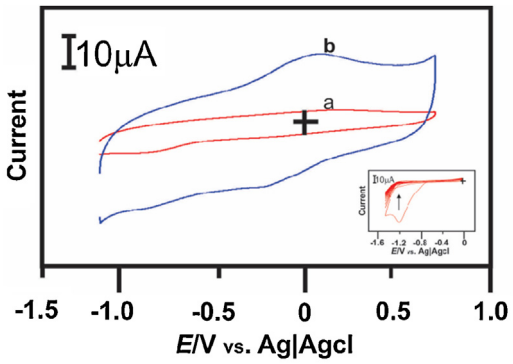


Fig. 1. Cyclic voltammograms obtained at (a) ZrO_2 (b) ERGO/ZrO_2 film modified GCEs in N_2 saturated 0.1 M PBS (pH 7) at Scan rate of 0.1 mV s^{-1}. Inset shows 30 consecutive cyclic voltammograms recorded at a GO-modified GCE in containing N_2 saturated 0.1 M PBS (pH 5) at scan rate of 50 mV s^{-1}.

2.2. Materials

Zirconyl chloride octahydrate ($ZrOCl_2$), graphite powder, ascorbic acid, dopamine and paracetamol were purchased from Sigma–Aldrich. AA, DA and PA solutions were prepared every day. The other chemicals (Merck) that are used in this investigation were of analytical grade (99%). All the solutions are prepared using double distilled water. Electrocatalytic studies were carried out in 0.05 M pH 7 PBS. Pure nitrogen gas was passed through all the experimental solutions for removing dissolved oxygen.

2.3. Electrochemical fabrication of ERGO/ZrO_2 nanocomposite modified electrode

Graphite oxide was synthesized from graphite by the modified Hummer's method [26–28]. The as-obtained graphite oxide was dispersed in water (0.5 mg/mL) and exfoliated by ultrasonication for 2 h to produce graphene oxide (GO). Prior to electrode modification, GCE was polished with 0.05 mm alumina slurry and Buehler polishing cloth. It was then washed with deionized water and ultrasonicated for 3 min each in water and ethanol to remove any adsorbed alumina particles or dirt from the electrode surface and finally dried. ERGO/ZrO_2 nanocomposite was fabricated on the GCE surface by a one-step process. 5 μl of GO dispersion was drop casted on the pre-cleaned GCE and dried in air oven at 30 °C. Then the GO modified GCE was shifted to an electrochemical cell with 4 ml of 0.05 M pH 7 PBS containing 5.0 mM $ZrOCl_2$. 10 consecutive cyclic voltammogram were recorded in the potential range between 0.7 and −1.1 V vs. Ag/AgCl reference electrode at the scan rate of 20 mV s^{-1} to obtain stable voltammogram [29]. The resulting ERGO/ZrO_2 film modified GCE was then rinsed with double distilled water and used for further electrochemical studies.

3. Results and discussion

3.1. Electrochemical characterization of ERGO/ZrO_2 nanocomposite film modified GCE

Fig. 1 represents the cyclic voltammograms of ZrO_2 nanoparticles and ERGO/ZrO_2 nanocomposite modified GCEs. The cyclic voltammogram of the reduction process of GO on GCE in 0.05 M pH

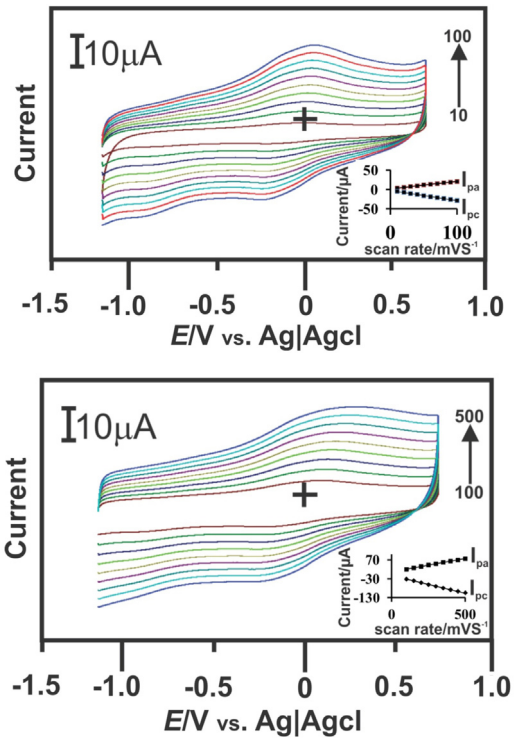


Fig. 2. (A) Cyclic voltammograms of ERGO/ZrO_2/GCE at different scan rates in 0.1 M PBS (pH 7) with various scan rate of 100–500 mV s^{-1}. (B) CVs of ERGO/ZrO_2/GCE at different scan rates in 0.1 M PBS (pH 7) with various scan rate of 10–100 mV s^{-1}. Inset in the figures shows a current vs. scan rate plot.

7 PBS containing 5.0 mM $ZrOCl_2$ is shown in the inset of Fig. 1. In the first cycle, a broad reduction peak around −1.2 V was observed, attributed to the reduction of oxygen functionalities of GO. In subsequent cycles, the reduction current at the negative potentials decreases considerably and disappears finally. This implies the formation of ERGO on the GCE surface, agreeing with the previous reports [30]. ERGO/ZrO_2 modified GCE shows enhanced reduction peaks at −0.8 V and −1.2 V, revealing that ZrO_2 nanoparticles are efficiently deposited onto the ERGO surface leading to the formation of ERGO/ZrO_2 nanocomposite modified electrode. As a control, ZrO_2 nanoparticles were deposited onto the surface of bare GCE (see curve (a) in Fig. 1). The background current of the ERGO/ZrO_2 nanocomposite modified GCE is 10 fold higher than that of ZrO_2 nanoparticles modified GCE, confirming that ERGO/ZrO_2 nanocomposite is successfully fabricated on the GCE. The formation of ZrO_2 on the electrode surface can be expressed by the following reaction mechanism.

$$ZrOCl_2 + e^- \rightarrow ZrOCl + Cl^- \quad (1)$$

$$2ZrOCl + 2H_2O \rightarrow 2ZrO_2 + 2HCl + H_2 \quad (2)$$

3.2. Different scan rate studies

Fig. 2A and B shows the cyclic voltammograms recorded at ERGO/ZrO_2 nanocomposite modified electrode in N_2 saturated 0.05 M pH 7 PBS at different scan rates. The ERGO/ZrO_2 nanocomposite film exhibits well-defined peaks currents at scan rate of 100 mV s^{-1}. These peak currents exhibit a linear dependence on the scan rates. The peak currents and peak potential separation increased with increasing scan rates between 100–500 mV s^{-1} (Fig. 2A) and 10–100 mV s^{-1} (Fig. 2B), respectively. This indicates that the electron transfer process occurring at ERGO/ZrO_2 nanocomposite film is a surface confined process. The peak currents (Ipa and Ipc) vs. scan rates plot is shown in Fig. 2(A and B) insets. Both Ipa and Ipc exhibited linear relationship with scan rates, R^2 = 0.999 and 0.999, respectively.

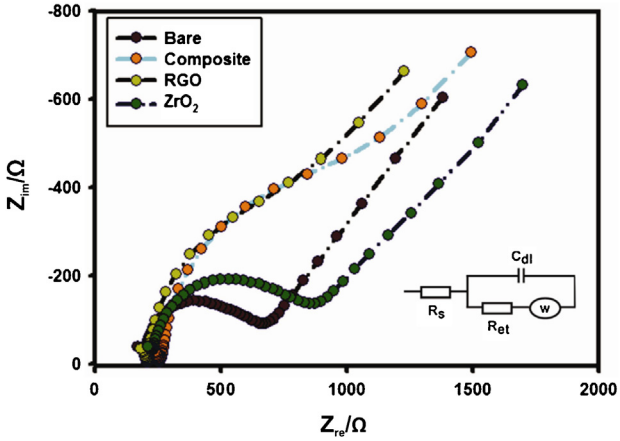


Fig. 3. EIS of bare, ERGO, ZrO_2, ERGO–ZrO_2 modified GCE in 5 mM $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ in 0.1 M PBS pH 7. Applied AC voltage: 5 mV, frequency: 0.1 Hz–100 kHz.

3.3. Investigation of electrochemical behavior of various film modified electrodes using EIS studies

EIS is an exact method to elucidate the electrochemical properties of the proposed film. The EIS analysis has been studied by analyzing the Nyquist plots of the corresponding films. Here the respective semicircle parameters correspond to the electron transfer resistance (Ret), solution resistance (Rs) and double layer capacitance (Cdl) of the films. The plot of the real component (Z_{re}) and the imaginary component Z_{im} (imaginary) resulted in the formation of a semi-circular Nyquist plot. From the shape of an impedance spectrum, the electron-transfer kinetics and diffusion characteristics can be extracted. The respective semicircle parameters correspond to the Ret and Cdl nature of the modified electrode. Fig. 3 represents the Nyquist plots for bare, ERGO, ZrO_2 and ERGO/ZrO_2 modified GCE in 0.05 M PBS pH 7 containing 5 mM $[Fe(CN)_6]^{3-/4-}$ and the inset shows the Randles equivalent circuit model for the proposed film. As can be seen in Fig. 3 the ERGO/ZrO_2 nanocomposite modified GCE exhibits a very small semicircle region, indicating a very low impedance of the film due to the high conductive nature of ERGO. The Ret value of ERGO/ZrO_2 nanocomposite modified GCE is 310 Ω, which is slightly higher than that of ERGO/GCE (300 Ω), but much lower than that of bare (Ret = 600 Ω) and ZrO_2 (Ret = 910 Ω) modified GCEs. Therefore, from these results we can believe that the nanocomposite film could be efficiently used for the various types of electrocatalytic reactions. A simplified Randles circuit model (Fig. 3 (inset)) has been used to fit the impedance spectra. The Randles circuit model well suites with the impedance spectroscopic results and the fit model error for the film was found as 5.9%. Finally the electrochemical impedance spectroscopic analysis clearly illustrates that the electrochemical behavior of the proposed ERGO/ZrO_2 nanocomposite film is excellent.

3.4. Morphological studies

The morphology and size of the ERGO, ZrO_2 and ERGO/ZrO_2 films on the ITO electrodes were examined by FESEM analysis. As can be seen from Fig. 4A, graphene sheets having wrinkled morphology with thickness 3–4 nm are formed. Fig. 4B shows the ZrO_2 nanoparticles coagulated each other over the ITO surface. Fig. 4C shows the image of the ERGO/ZrO_2 on the ITO substrate in which the ZrO_2

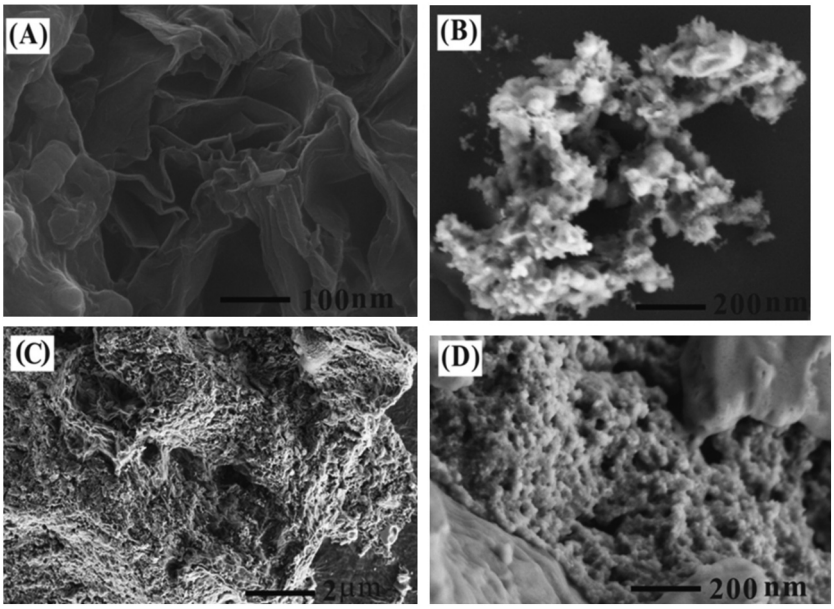


Fig. 4. FESEM images of (A) ERGO, (B) ZrO_2, (C) ERGO/ZrO_2 and (D) closer view of ERGO/ZrO_2 films at different magnifications.

nanoparticles are homogenously decorated throughout the wrinkle sheets of graphene and the distribution of the nanoparticles are almost uniform throughout the graphene layer and Fig. 4D shows the closer view of the ZrO_2 nanoparticles which are decorated on the graphene sheets. The immobilized ERGO/ZrO_2 nanocomposite film on the surface of ITO remains stable and there is no distortion in shape. Finally from these results, it is evident that the size and morphology for the formation of ZrO_2 nanoparticles were uniformly incorporated on the ERGO.

3.5. Selective detection of DA and PA in higher concentration of AA

ERGO/ZrO_2 nanocomposite modified GCE could be directly employed for the selective detection of DA and PA in presence of AA. Fig. 5 represents the comparison study for the selective detection of these compounds. In Fig. 5, the LSV curve a represents the bare GCE film response, curve b represents the only ZrO_2, curve c represents only ERGO and curve d represents the ERGO/ZrO_2 response for the selective determination of DA and UA. Comparing with the bare, ZrO_2, ERGO and ERGO/ZrO_2 modified GCE. The ERGO/ZrO_2 shows well-defined electrocatalytic peaks for the selective detection of DA and PA in presence of AA. At the same, only ERGO modification gives separate peaks, which were not as obvious as found using ERGO/ZrO_2 film.

Finally, this LSV results clearly depict the capability of the proposed ERGO/ZrO_2 film for the detection of DA and PA in presence of AA. This may be due to the presence of ZrO_2 nanoparticles which acts a electroactive centers for the detection and determination of these compounds, In addition, the combination of carbon material ERGO as another layer on the surface clearly supports the surface enhancement and as well as selective detection of DA and PA. Scheme 1 could explain the fabrication and electron mediating properties of ERGO/ZrO_2 nanocomposite composite film toward the selective oxidation of DA, PA in presence of AA.

In the next step, linear sweep voltammetry (LSV) has been employed for the selective detection of these compounds. Fig. 6 shows the LSV curves of DA and PA for various concentrations (in the presence of 1.5 mM AA) at the ERGO/ZrO_2 nanocomposite film modified GCE. Here the voltammetric response of DA and PA in the presence of AA shows two well-defined voltammetric potential peaks at 0.34 V and 0.53 V, respectively and enough separation occurred between the AA–DA (0.14 V) and AA–PA (0.33 V) oxidation peak potentials at the ERGO/ZrO_2 nanocomposite film modified GCE. Further the oxidation peak currents of DA and PA

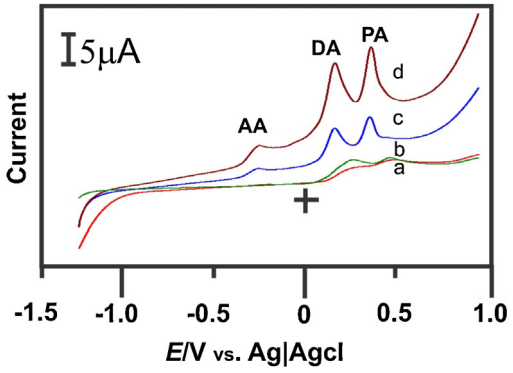


Fig. 5. Linear sweep voltammogram response of different electrodes for the selective determination of DA and PA (50 μM) in the presence of AA (50 μM) at (a) bare GCE, (b) only ZrO_2, (C) only ERGO and (d) ERGO/ZrO_2 GCE.

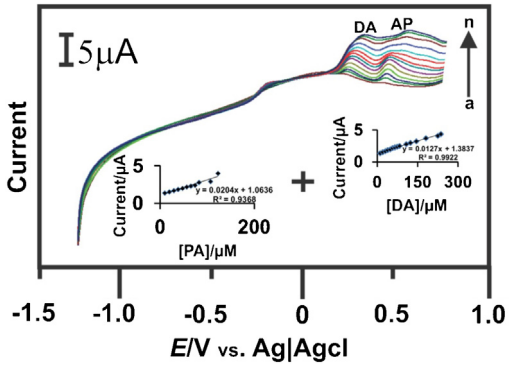
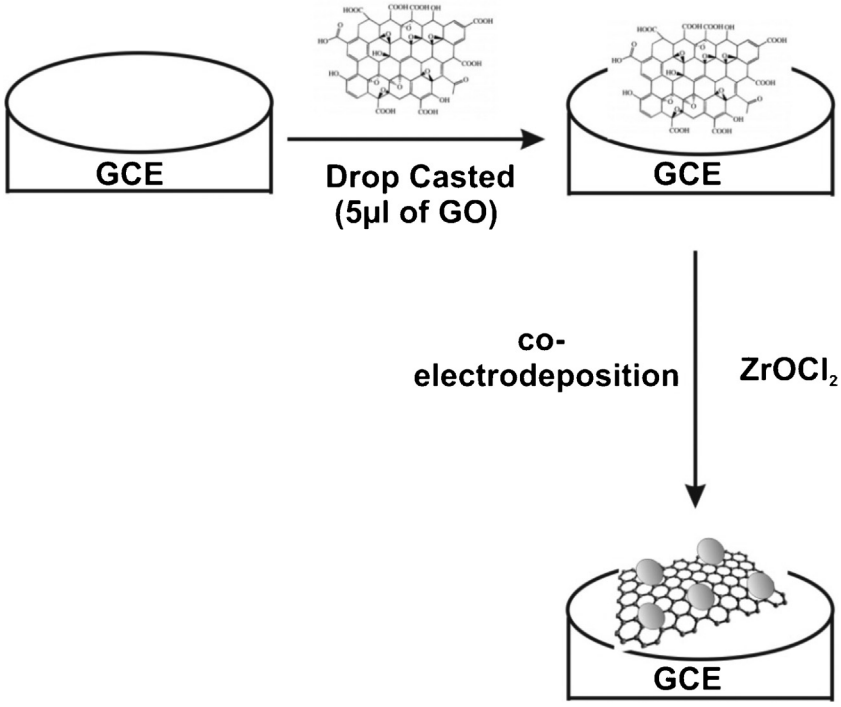


Fig. 6. LSV of ERGO/ZrO_2 nanocomposite film modified electrode for the selective determination of DA and PA in presence of AA (lab samples). DA and PA were in the linear range of (9–237 μM). Inset shows a current vs. concentration plot of DA and PA determination.



Scheme 1. Schematic representation of single step fabrication of ERGO/ZrO_2 nanocomposite modified electrode.

increases linearly in conjunction with increasing concentrations in the range of 9–237 μM. This results shows that the ERGO/ZrO_2 nanocomposite film modified GCE possess the specific electrocatalytic activity, which could be considered as the main reason for the successful anodic peak separation between the DA and PA in presence of AA. The inset of Fig. 6 shows the current vs. concentration plot for DA and PA in the presence of AA. Based on this calibration plot, the linear regression equation for DA has been expressed as $I\,(\mu A) = 0.0127\,C\,(\mu M) + 1.3837$, $R^2 = 0.9922$ and for PA has been expressed as $I\,(\mu A) = 0.0204\,C\,(\mu M) + 1.0636$, $R^2 = 0.9392$). The result shows that the proposed ERGO/ZrO_2 nanocomposite film modified GCE possess the capability for the selective detection and determination of DA and PA in presence of AA without any fouling effect.

3.6. Selective determination DA and PA in presence of AA in human urine samples

The practical analytical performance of the ERGO/ZrO_2 nanocomposite film modified GCE has been evaluated for the selective detection of DA and PA in presence AA in human urine samples. The dopamine injection solution (40 mg ml^{-1}), ascorbic acid (500 mg) and paracetamol (500 mg) tablets are utilized for the real sample analysis. Before the examination, freshly collected human urine sample (pH 6.7) were filtered several times using Whatman filter paper (grade 1). Filtered human urine samples were diluted in pH 7 PBS in the ratio of 1: 50. Fig. 7 shows the LSV response of ERGO/ZrO_2 nanocomposite film modified GCE for the detection of DA and PA in the presence of AA in human urine samples. Here also we can observe the well separated peaks for DA and PA in presence of AA (1.5 mM) with enough peak separation around 0.25 V for AA–DA and 0.44 V for AA–PA and the linear range was found to be 3–174 μM, respectively. The inset shows the current vs. concentration plot of DA and PA in human urine samples. The linear range dependence of LSV response on concentration of DA is expressed as $I\,(\mu A) = 0.0268\,C\,(\mu M) + 0.905$, $R^2 = 0.9968$ and for PA has been found as $I\,(\mu A) = 0.0278\,C\,(\mu M) + 0.9036$, $R^2 = 0.9978$). Based on these results, it clearly validates the capability of the proposed electrode for the detection of DA and PA (real samples) in human urine samples. A comparison of analytical parameters of ERGO/ZrO_2 nanocomposite modified GCE with other mediated dopamine and paracetamol sensors has been made and given in Table 1. Moreover, the maximum recovery was specified in Table 2. The recoveries obtained here validates the pertinent nature of the ERGO/ZrO_2 nanocomposite modified GCE for the sensor applications, respectively.

3.7. Selectivity of ERGO/ZrO_2 nanocomposite film for dopamine and paracetamol detection

The selectivity of the sensor is mandatory for practical applications. So we evaluated the selectivity of the sensor in presence of common interferences such as uric acid, glucose and hydrogen

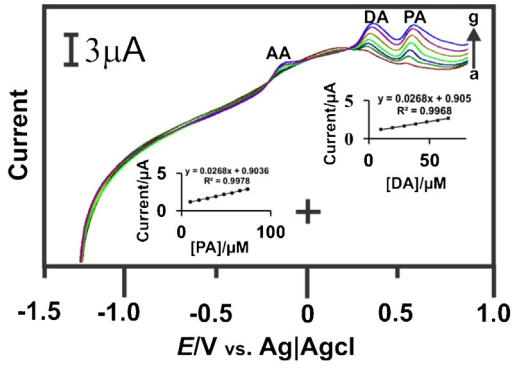


Fig. 7. LSV of ERGO/ZrO_2 nanocomposite film modified electrode for the selective determination of DA and PA in presence of AA (real samples) in human urine samples. DA and PA were in the linear range of (3–174 μM). Inset shows a current vs. concentration plot of DA and PA determination.

Table 1
Comparison table for DA and PA with various modified electrodes.

S. No.	Modified electrode	AA (mM)	DA (μM)	PA (μM)	Reference
1	Sulfhydryl-nano Au	0.15	20–145	–	[31]
2	Nano Au polyelectrolyte	1	5–100	–	[32]
3	Graphene/GCE	–	–	0.1–20	[33]
4	ERGO/ZrO_2	1.5	9–237	9–231	This work

Table 2
Determination result of DA and PA in human urine samples.

DA[a] injection sample	Added (μM)	Found (μM)	Recovery (%)	PA[b] tablet sample	Added (μM)	Found (μM)	Recovery (%)
1	5	4.9	98	1	30	28.8	96.2
2	10	9.92	99.2	2	40	38.9	97.4

[a] DA, dopamine injection.
[b] PA, paracetamol tablets.

peroxide in order to evaluate the selectivity ERGO/ZrO_2 nanocomposite film by using LSV studies is shown in Fig. 8. The concentration ratios were calculated by 1:2 (dopamine and paracetamol, interfering substance) ratio. From the experimental result it was observed that no obvious current response was observed for the addition of these interfering compounds and they obviously shows the anodic signals of dopamine and paracetamol apparently. This result validates that the proposed film overcomes the interference signals and successfully shows the dopamine and paracetamol detection signals in pH 7 PBS.

3.8. Repeatability, reproducibility and stability studies

The repeatability of the ERGO/ZrO_2 nanocomposite film modified film for the detection of DA and PA in the presence AA has been evaluated by the LSV studies. LSVs were recorded in pH 7 PBS at the scan rate of 100 mV s^{-1} in the presence of DA and PA at 237 μM, respectively. The fabricated sensor shows good repeatability with a relative standard deviation (RSD) of 4.5% for (n = 10) successive measurements. Moreover, it exhibits a good reproducibility with an RSD of 4.8% for 5 individual measurements. The repeatability and the reproducibility values confirm that the proposed film was suitable for the detection and determination DA and PA in the presence of AA. Next the stability of the nanocomposite film has been examined by storing it at the room temperature in the open air condition (figure not shown). After four weeks, it showed a stable behavior only with a gradual decrease (15%) from the initial current values.

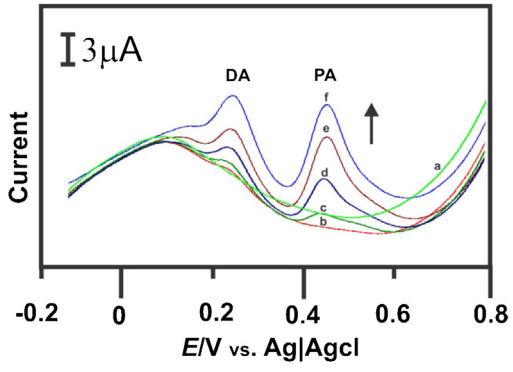


Fig. 8. LSV of ERGO/ZrO_2 nanocomposite film modified GCE for the DA and PA detection (a) blank, (b) DA and PA (10 μM), (c) DA and PA (20 μM) + ascorbic acid (40 μM), (d) DA and PA (40 μM) + H_2O_2 (80 μM), (e) DA and PA (60 μM) + glucose (100 μM) and (f) DA and PA (80 μM).

4. Conclusions

In conclusion, we have successfully fabricated ERGO/ZrO_2 nanocomposite film by a simple co-electrodeposition method. Fabricated nanocomposite film was examined by FESEM analysis. This study shows that, as prepared ZrO_2 nanoparticles were decorated on the ERGO sheets. The electrochemical activities of the ERGO/ZrO_2 nanocomposite film have been examined using CV and EIS analysis. The nanocomposite modified GCE well suited for the selective determination of DA and PA in the presence of higher concentration of AA (1.5 mM). The proposed ERGO/ZrO_2 nanocomposite modified GCEs remarkably suppressed the interference effect and showed two well-defined oxidation peaks for the selective determination of DA and PA. In addition, the high surface area of the nanocomposite film modified electrode is well suitable for the selective determination. Finally, the ERGO/ZrO_2 nanocomposite modified GCE also applied for the detection of DA and PA (real samples) in human urine samples.

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