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Nano TiO_2-PEDOT Film for the Simultaneous Detection of Ascorbic Acid and Diclofenac

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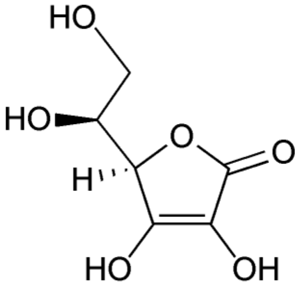
Glassy carbon electrode (GCE) and indium tin oxide coated glass electrodes (ITO) have been successfully modified with the manual coatings of nano TiO_2 particles following with the electrochemical deposition of electroactive polymer poly (3, 4-ethylenedioxythiophene (PEDOT). Nano TiO_2-PEDOT polymer film modified electrodes were found as more stable and electrochemically active in pH 7.0 PBS solutions. The nano TiO_2-PEDOT polymer film successfully electrocatalyzes the ascorbic and diclofenac in pH 7.0 PBS solution. It also simultaneously detects the AA and diclofenac in the successive linear ranges. Utilizing the differential pulse voltammetry (DPV) the sensitivity and detection limits of the nano TiO_2-PEDOT polymer film for the detection of AA and diclofenac were found as 8.14 and 4.6 $\mu A\ \mu M^{-1}\ cm^{-2}$, 0.02 and 0.03 µM. Furthermore, the proposed film modified GCE was found as more stable and holds the good life time for the repeatable detection of these compounds, respectively.

Keywords: Nano TiO_2, PEDOT, cyclic voltammetry, differential pulse voltammetry, simultaneous detection, diclofenac, ascorbic acid, electrochemistry, chemical sensors.

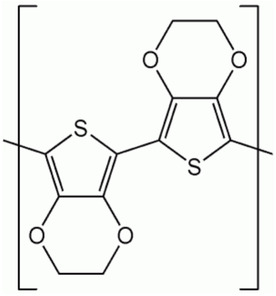
1. INTRODUCTION

Ascorbic acid (AA) known as vitamin C most popular nutrient found in fruits and vegetables. AA plays as important antioxidant in the human metabolism. AA deficiency results in the scurvy, immunity deficiency, and wound healing, anticancer and anti tumor activity. [1-4]. In electroanalytical chemistry, detection and determination of AA is the major important analysis. AA directly interferes with other neurotransmitters like dopamine (DA), uric acid (UA) and the bare electrode fails to show individual electrooxidation peaks for the detection of these compounds.



Scheme-1. Chemical Structure of Ascorbic acid

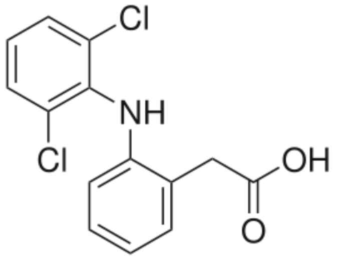
In electroanalysis, electrode surface modifications using nanomaterials and various methods and their direct employment in the electrocatalytic applications were found as suitable for detection and determination of various types of important chemical compounds [5-11]. In this, particularly, nanomaterials modified electrodes showed well defined individual responses for these compounds in the mixture solutions. In particular, metal oxides based nanomaterials keen a special interest for the detection and determination of these compounds. For example, gold nanoparticles modified titania nanotube arrays for the amperometric determination of AA [12], TiO_2 nanoparticle carbon paste electrode for the determination of AA in the presence of UA and folic acid [13] and methylene blue immobilized cellulose acetate with TiO_2 for the detection of AA were reported [14].



Scheme-2. Poly (3, 4-ethylenedioxythiophene)

On the other hand, poly (3, 4-ethylenedioxythiophene) known as PEDOT is a highly stable conducting polymer holds the low redox potential, utilized for the electrode surface modifications and successfully employed for the various types of electrocatalytic applications. For example, nickel hexacyanoferrate and PEDOT hybrid film was employed for the selective electroanalysis of AA [15], multi-walled carbon nanotubes-PEDOT film for the simultaneous determination of AA, DA and UA and H_2O_2 [16] and metal hexacyanoferrate with PEDOT polymer composite film for the selective detection of AA, DA and UA were reported [17].

Next, diclofenac known as non-steroidal anti-inflammatory drug mainly utilized as an analgesic agent to reduce inflammation and pain in the certain conditions. In most of the countries it has been utilized as a drug to cure minor aches, pains and fever associated with common infections. Therefore, detection and determination of diclofenac is an important criterion in the pharmaceutical analysis.



Scheme-3. Chemical Structure of Diclofenac

Various types of analytical techniques have been found as suitable for the detection and determination of diclofenac. In this, employment of electrochemical methods by utilizing film modified electrodes was found as easier, convenient and reliable for the detection and determination of diclofenac. Previously, various types of potentiometric, membrane and voltammetric sensors were reported for the detection of diclofenac. They are; determination of diclofenac in pharmaceutical preparations using a potentiometric sensor immobilized in a graphite matrix [18], determination of diclofenac in pharmaceuticals and urine samples using a membrane sensor based on the ion associate of diclofenac with rhodamine B [19], potentiometric determination of diclofenac in pharmaceutical formulation by membrane electrode based on ion associate with base dye [20, 21] and manganese (III) porphyrin-based potentiometric sensors for diclofenac assay in pharmaceutical preparations [22] were reported.

In voltammetric sensors, various types of electrodes [23], molecularly imprinted film modified carbon electrodes [24], nano-structured electrochemical sensing film constructed by multi-wall carbon nanotubes–surfactant composite [25], an edge-plane pyrolytic graphite electrode with single-wall carbon nanotubes [26], edge plane pyrolytic graphite electrode and its determination in human urine [27], Cu-doped zeolite-expanded graphite-epoxy [28], nickel hydroxide-modified nickel electrode [29] and Ni–curcumin-complex-modified electrode [30] for the detection of diclofenac were reported. Therefore, detection and determination of AA [31-33] and diclofenac combination is a vital and new one. In particular, developing a new type of sensor for the simultaneous detection and determination of AA and diclofenac will be more useful for the detection of these compounds in the real life. Hence, in this report we have particularly focused to develop an electrochemical sensor for the simultaneous detection of AA and diclofenac by utilizing commercially available nano TiO_2 particles and electroactive polymer PEDOT. Previously, PEDOT combined molecularly imprinted TiO_2-modified electrode was successfully reported for the detection of nicotine [34]. Here we have modified the GCE by manually coating nano TiO_2 particles following with the electrochemical deposition of PEDOT polymer film. Electrochemical characterization and surface analysis of nano TiO_2-PEDOT film have been carried out using CV, EIS and SEM techniques. Further this type of sensor successfully employed for the detection and determination of AA and diclofenac in lab and real samples, respectively.

2. MATERIALS AND METHODS

2.1. Reagents

Titanium (IV) oxide (anatase, particle size < 25 nm, 99.7 % trace metal basis) and EDOT and Diclofenac sodium salt were purchased from Sigma Aldrich (USA). 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 phosphate buffer solution (PBS) of pH 7.0 was prepared from Na_2HPO_4 (0.05 M) and NaH_2PO_4 (0.05 M). Purified nitrogen gas was passed through all the experimental solutions.

2.2. Apparatus

Electrochemical measurements like cyclic voltammetry (CV), differential pulse voltammetry (DPV) were performed by using CHI 1205A and CHI 410A analyzers. A conventional three-electrode cell were used at the 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. All the potentials mentioned in all experimental results were referred to standard Ag/AgCl (saturated KCl) reference electrode. Surface morphology of the fabricated films was studied by SEM (Hitachi S-3000H, Japan). Here for the convenience indium tin oxide (ITO) thin film coated glass electrodes have been used for SEM analysis. Electrochemical impedance studies (EIS) were performed by using ZAHNER impedance analyzer (ZAHNER Elektrik Gmbh & Co KG, Germany).

2.3. Fabrication of Nano TiO_2-PEDOT film modified GCE

Bare glassy carbon electrode was initially polished with 0.05μm alumina powder on BAS polishing pad and ultrasonically cleaned using double distilled deionized water. Further the electrode was modified by drop casting 10 μl of nano TiO_2 particles (2 mg dissolved in 10 ml ethanol) and kept in air for the drying process. Further the modified GCE has been immersed in the pH 1.5 H_2SO_4 solution containing 0.01 M EDOT monomer for the electrochemical deposition [35] of PEDOT, in the potential scan range between 0.2 and 1V, at the scan rate of 0.1 V s^{-1} for twenty cycles. Next the nano TiO_2-PEDOT polymer film modified GCE was further rinsed with double distilled water and used for the further electrochemical studies.

3. RESULTS AND DISCUSSION

3.1. CV, EIS and SEM analysis of nano TiO_2-PEDOT Film

Fig. 1(A) shows the electrochemical fabrication of PEDOT polymer film on the nano TiO_2 particles coated GCE surface. Here the electrochemical fabrication of the PEDOT polymer film conditions has been followed from the previous literature report [16,13]. Similar type of consecutive CVs has been obtained for the nano TiO_2 film coated GCE and shows that the EDOT monomers were successfully electropolymerized onto the nano TiO_2 particles modified GCE surface. Next the Fig. 1(B) shows the different scan rate studies of the nano TiO_2-PEDOT film modified GCE in pH 7.0 PBS.

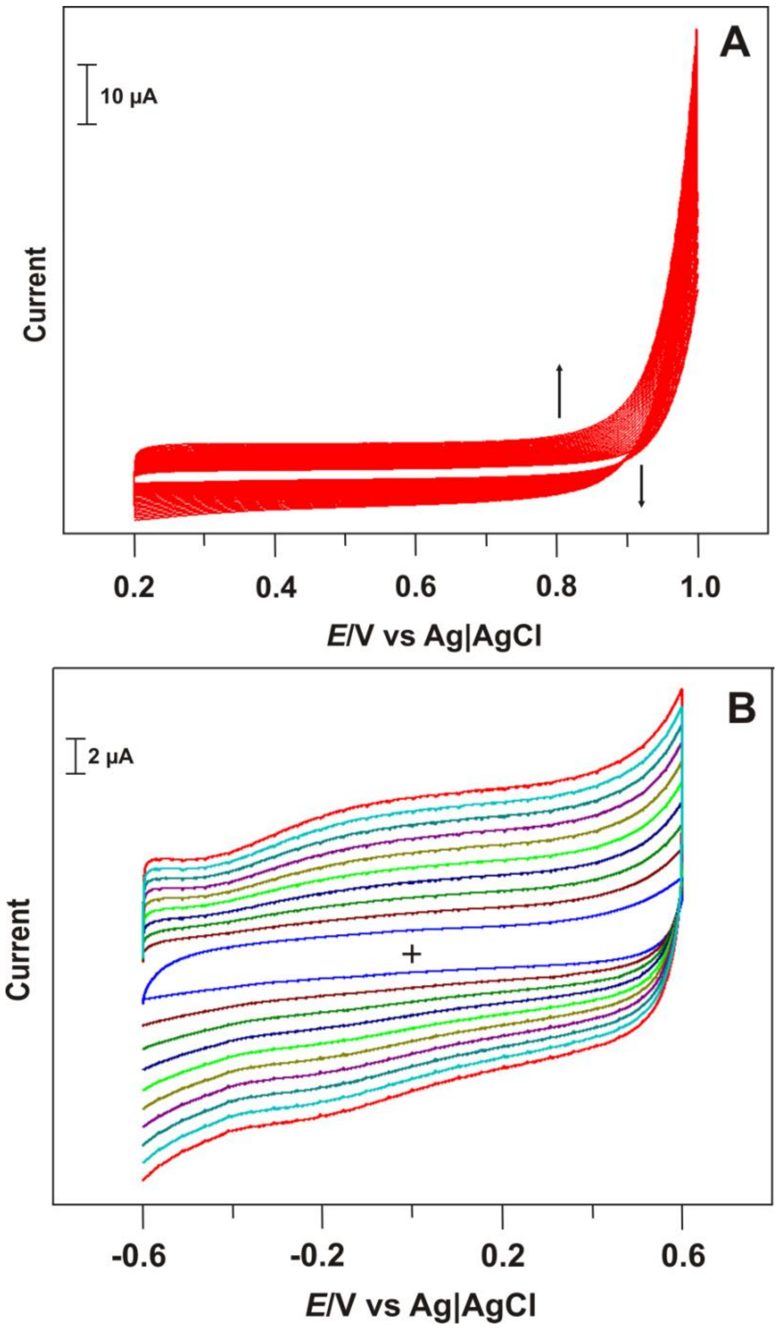


Figure 1. (A) Continuous CVs of PEDOT film growth on the nano TiO_2 particles modified GCE in pH 1.5 H_2SO_4 solution containing 0.01 M EDOT in the potential scan between 0.2 to 1 for twenty cycles at the scan rate of 0.1 V/s. **(B)** Different scan studies of the nano TiO_2-PEDOT film modified GCE in pH 7 PBS solution at the scan rate of 0.01 to 0.1 V/s.

Here for the increasing scan rates (0.01-0.1 V/s) the background current response of the film were clearly increasing which shows that the film is electrochemically active and stable. In the next step electrochemical impedance spectroscopy (EIS) has been employed for the further detailed electrochemical analysis of the proposed film.

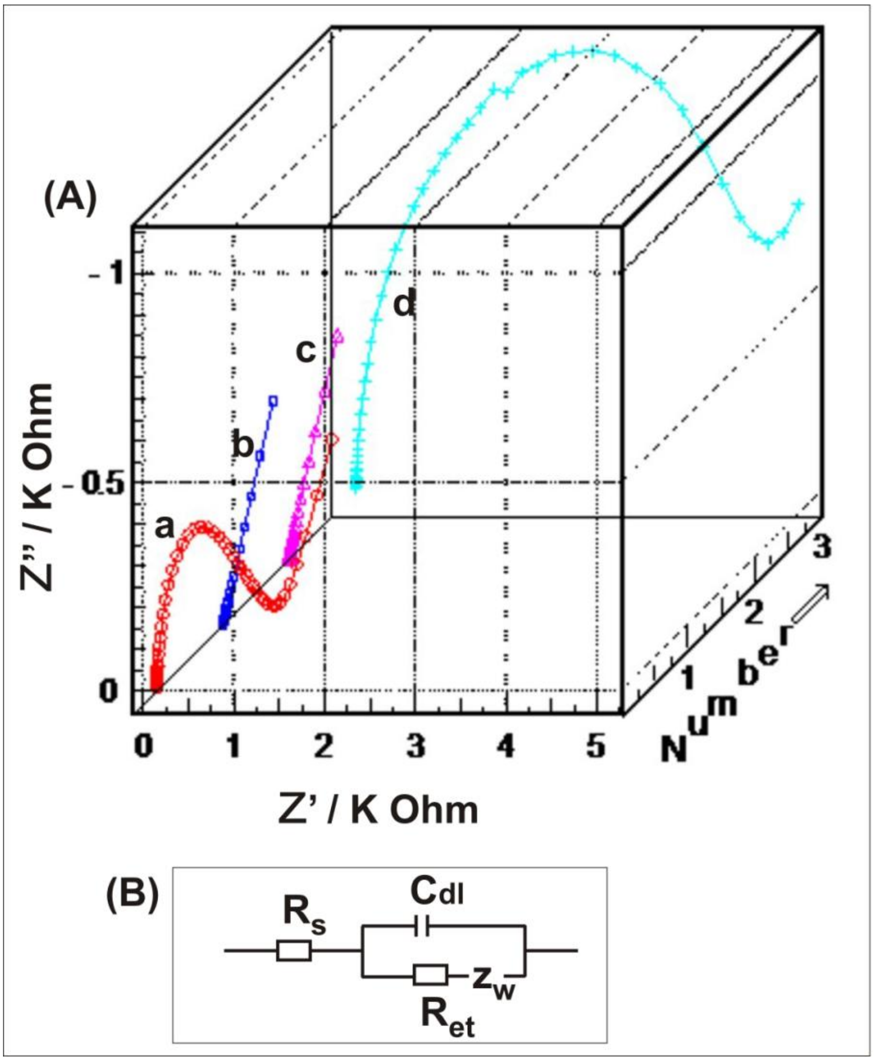


Figure 2. (A) EIS three dimensional view of (a) bare, (b) nano TiO_2-PEDOT film, (c) PEDOT film and (d) nano TiO_2 modified GCE in pH 7.0 PBS containing 5 mM $[Fe(CN)_6]^{3-/4-}$. **(B)** Randles equivalent circuit model for the proposed films.

EIS is an exact method to elucidate the electrochemical properties of the proposed film. Here the EIS analysis has been studied by analyzing the Nyquist plots of the corresponding films. Fig. 2 (A) shows the three dimensional view of the Nyquist plots for (a) bare, (b) nano TiO_2-PEDOT film, (c) PEDOT film and (d) nano TiO_2 modified GCE in pH 7.0 PBS containing 5 mM $[Fe(CN)_6]^{3-/4-}$ and the Fig. 2(B) shows the Randles equivalent circuit model for the proposed film. Here the respective semicircle parameters correspond to the electron transfer resistance (R_{et}), solution resistance (R_s) and double layer capacity (C_{dl}) of the films. Here in Fig. 2 curve (d) exhibits EIS spectra of nano TiO_2 particles with the larger semi circle and higher electron transfer resistance (R_{et} = 2.188 K Ohm). Next the bare GCE exhibits small semi circle with the R_{et} value of 980.1 ohm. At the same time, both PEDOT and nano TiO_2-PEDOT film modified GCEs exhibit as like straight lines with a very low R_{et} values (5.051 and 7.92 ohm).

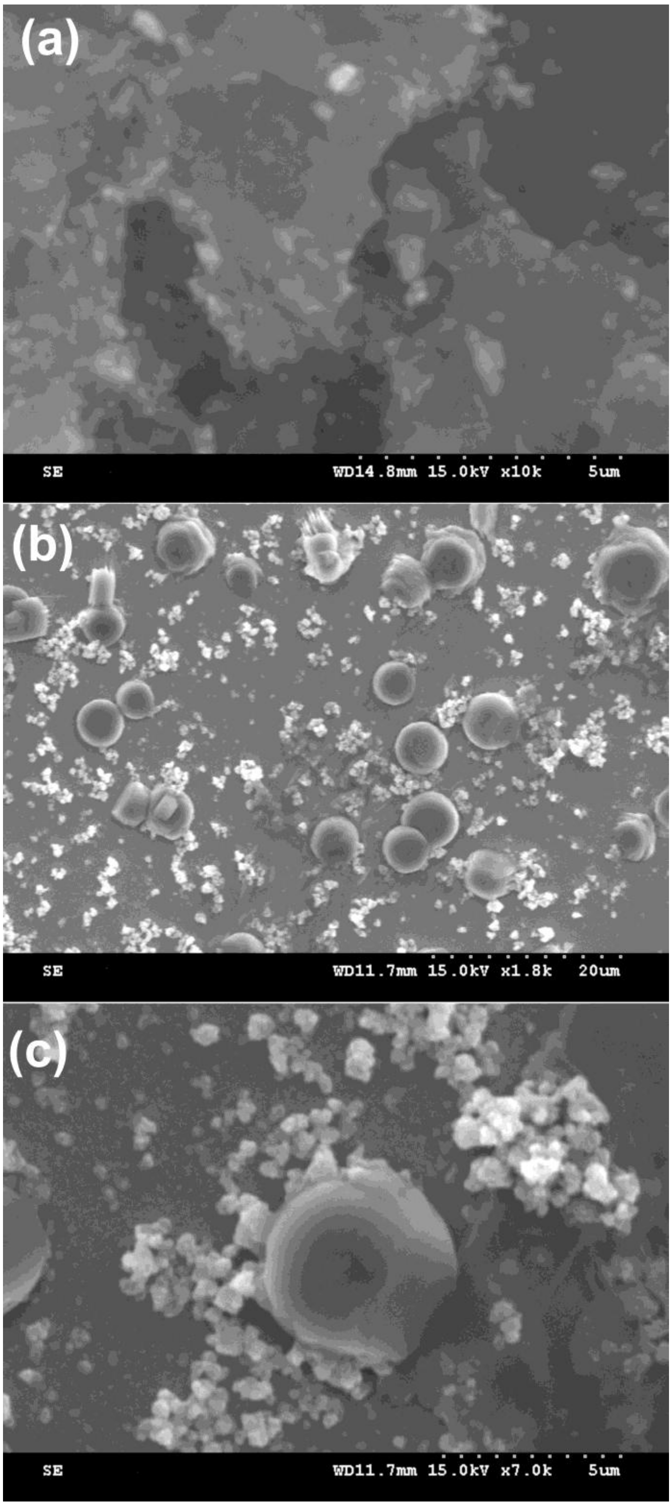


Figure 3. SEM images of **(a)** PEDOT, **(b)** nano TiO_2-PEDOT (lower magnification) and **(c)** nano TiO_2-PEDOT (higher magnification) modified ITO.

This results clearly show that the only TiO_2 modified GCE have poor conducting behavior comparing with the bare GCE. This may be due to the high roughness nature of the nano TiO_2 particles. Further this result clearly denote that only PEDOT film possess the very low electron transfer resistance comparing with all the other modifications. At the same time, in PEDOT-nano TiO_2

particles combination, the electron transfer resistance value was found as very low. This may be due to the PEDOT, which act as an electroactive polymer easily transfers the electrons to the GCE surface, respectively. Furthermore, nano TiO_2-PEDOT film's R_{et} value is slightly higher than only PEDOT because; the roughness nature of the nano TiO_2 particles which has been coated as a first layer onto the electrode surface. However, comparing with the only TiO_2 particles modified surface, the nano TiO_2-PEDOT film modified surface possess higher electrochemical activities, respectively. All these values have been obtained by fitting Randles equivalent circuit model (fig. 2(B)) for the corresponding impedance spectroscopic results and the maximum error percentage for the proposed films were found as less than 1 %.

Next Fig. 3 shows the SEM pictorial representations of various types of films modified ITO. Here fig. 3(a) image represents the only PEDOT, (b) and (C) images exhibits the lower and higher magnifications of nano TiO_2-PEDOT films modified ITO surface. From the Fig. 3(a), we can notice that the PEDOT film has been deposited as distorted shaped thin sheet like structure. At the same time, after the coating of nano TiO_2 particles, the PEDOT deposition takes place with the same sheet type distorted thin film with few bead shaped structures. Here the nano TiO_2 particles were unevenly distributed on the electrode surface and in some areas have been coagulated together and displays like a bunch of nanoparticles. Also, from the fig. 3 (b) and (c) we can notice that some TiO_2 particles onto the PEDOT surface which denotes that both TiO_2 and PEDOT were in the well mixed condition and claims the partial bilayer structure. Finally, all these surface morphologies were taken on ITO and it may differ while comparing with the GCE surface modifications, respectively.

3.2. Simultaneous detection of AA and diclofenac

Nano TiO_2-PEDOT modified GCE could be directly employed for the simultaneous detection of AA and diclofenac. Fig. 4 represents the comparison study for the simultaneous detection of these compounds. In Fig. 4, CV curve a represents the Nano TiO_2-PEDOT film response and curve b represents the only PEDOT film, curve c and d represents the only TiO_2 modified and bare GCE response for the simultaneous detection of AA and diclofenac. Here comparing with bare electrode, the only PEDOT and only TiO_2 modified GCEs shows response for the individual electrocatalytic oxidation peaks for the AA and diclofenac. Comparing the nano TiO_2-PEDOT film with only PEDOT film and nano TiO_2 particles, nano TiO_2-PEDOT film shows well defined obvious electrocatalytic peaks [36] for detection of AA and diclofenac. At the same time, only nano TiO_2 modifications give two separate peaks which were not obvious like response found using nano TiO_2-PEDOT film. In this, AA oxidation takes place at around 0.21 V and diclofenac oxidation occurs at 0.37 V and reduction occurs at 0.34 V.

At the same time, only PEDOT film shows slight response for the detection of diclofenac and the AA electroxidation peak is not that much obvious one. Here the AA oxidation takes place as a diminished response with the peak potential at about 0.23 V and diclofenac oxidation takes place at 0.38 V and reduction occurs at 0.342 V.

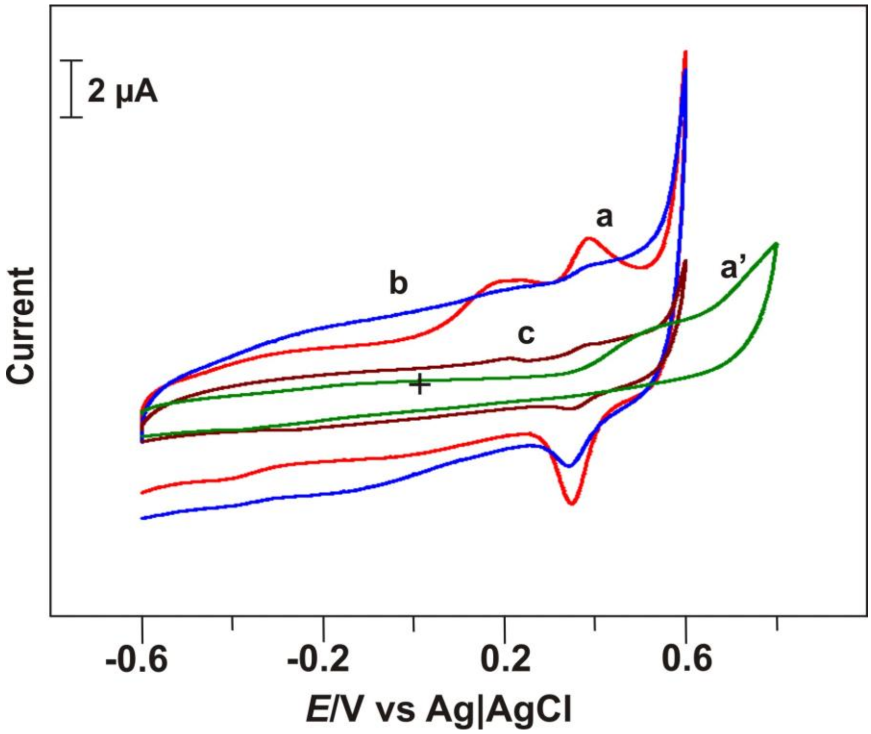


Figure 4. CV response in pH 7 PBS at (a) nano TiO_2 -PEDOT film, (b) PEDOT film, (c) nano TiO_2 particles modified and, (a') Bare GCE for the simultaneous detection of AA and diclofenac (AA and diclofenac concentration was 4.2×10^{-5} M).

Comparing these results, we can conclude that nano TiO_2-PEDOT film modification is more suitable for the simultaneous detection of AA and diclofenac with the other type of electrodes (PEDOT film, nano TiO_2 particles and bare GCE). This may be due to the presence of nano TiO_2 particles which acts as electroactive centers for the detection and determination of these compounds. In addition, the combination of electroactive polymer PEDOT as another layer on the nano TiO_2 particles surface clearly supports the simultaneous detection of AA and diclofenac. Therefore, based on this context, we conclude that the combination of nano TiO_2-PEDOT bilayer film is more suitable for this type of analysis. Here the AA oxidation occurs at 0.24 V and diclofenac oxidation and reduction takes place at around 0.38 and 0.34 V, respectively.

Finally, this CV results clearly depict the capability of the proposed film for the simultaneous detection of AA and diclofenac. In the next step, differential pulse voltammetry (DPV) has been employed for the simultaneous detection of these compounds. Fig. 5 (A) represents the DPV response of nano TiO_2-PEDOT film modified GCE for the simultaneous detection of AA and diclofenac. Here for the increasing concentrations (6-46 μM) of AA and diclofenac the corresponding electrooxidation peaks were increasing in the linear manner. Further the sensitivities of the nano TiO_2-PEDOT film for the detection of AA and diclofenac were 8.14 and 4.6 $\mu A\ \mu M^{-1}\ cm^{-2}$ with the correlation coefficients of R^2 0.908 and 0.983. The detection limit of TiO_2-PEDOT film for AA and diclofenac were found as 0.02 and 0.03 μM. Here the inset in the fig. 5 (A) shows the current vs. concentration calibration plot for diclofenac detection.

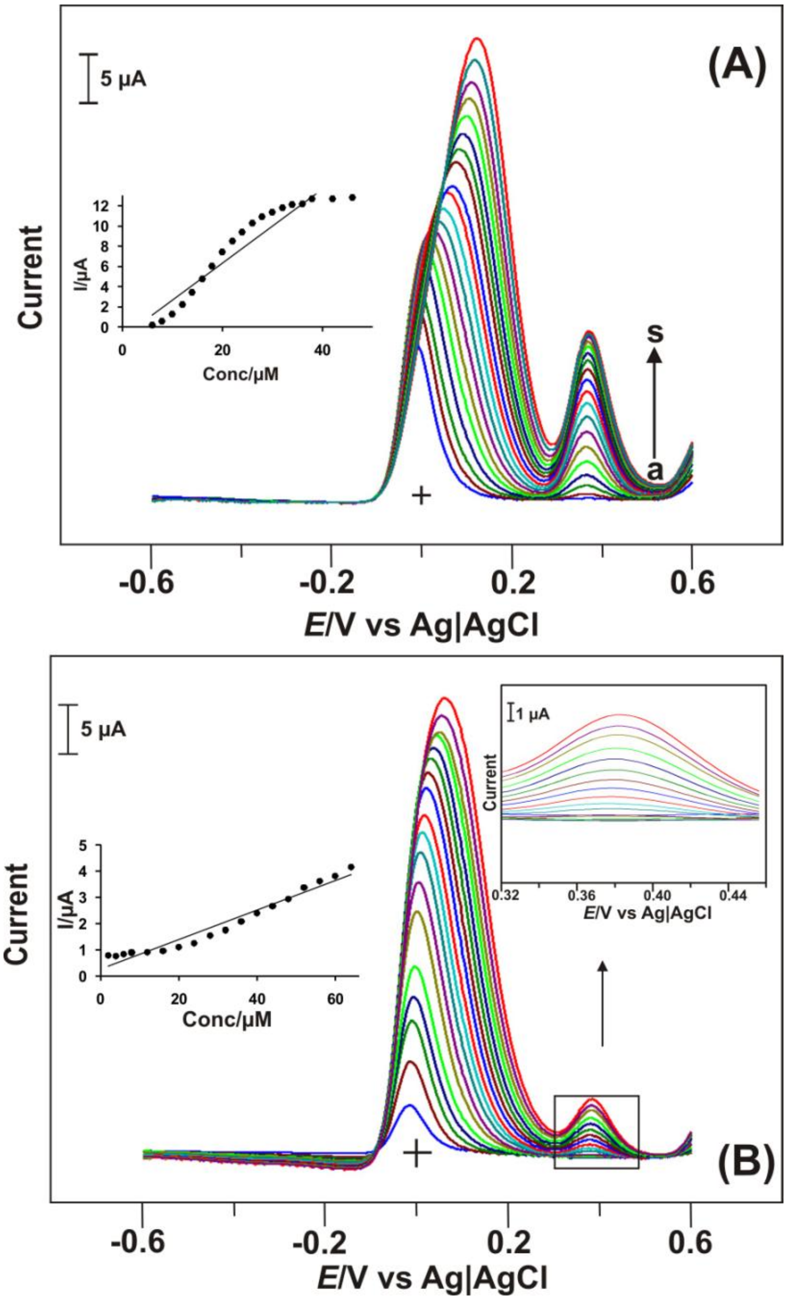


Figure 5. (A) DPVs of nano TiO_2-PEDOT film modified GCE response for the different concentrations of AA and diclofenac sodium salt (lab sample) in pH 7 PBS (AA and diclofenac concentrations were in the range of; 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 42 and 46 μM) Inset shows a current vs. concentration plot of diclofenac sodium salt determination. **(B)** DPVs of nano TiO_2 –PEDOT film modified GCE response for the different concentrations of AA and diclofenac (real sample) in pH 7 PBS (AA and diclofenac concentrations were in the range of ; 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 42 and 46 μM) Inset shows a current vs. concentration plot of diclofenac determination in real sample.

In the next step, for the real sample analysis, diclofenac tablet obtained from the local drug store was employed for the electrocatalytic studies. Fig. 5(B) shows the DPV response of nano TiO_2-PEDOT film for the simultaneous detection of AA and diclofenac (real sample). Here the diclofenac electrooxidation current response is not much as obvious comparing with the lab sample (Fig. 5(A)). This may be due to the presence of other additives in the tablet. Further the inset of Fig. 5(B)) shows the magnified view of the DPV response of diclofenac sample at the nano TiO_2-PEDOT film modified GCE. The sensitivity and the detection limit of the proposed film for the diclofenac detection (real sample) in pH 7.0 PBS were found as 0.715 µA μM^{-1} cm^{-2} and 1.62 µM. Next the inset in the fig. 5(B) shows the current vs. concentration calibration plot for the detection of diclofenac (real sample). In final, both the lab and real sample analysis results clearly validate that the proposed film is suitable for the simultaneous detection and determination of AA and diclofenac. Furthermore, this result clearly supports that the proposed film could be utilized to develop a real prototype type electrochemical sensor for the detection of these compounds, respectively.

3.3. Selective detection of diclofenac in the presence of AA

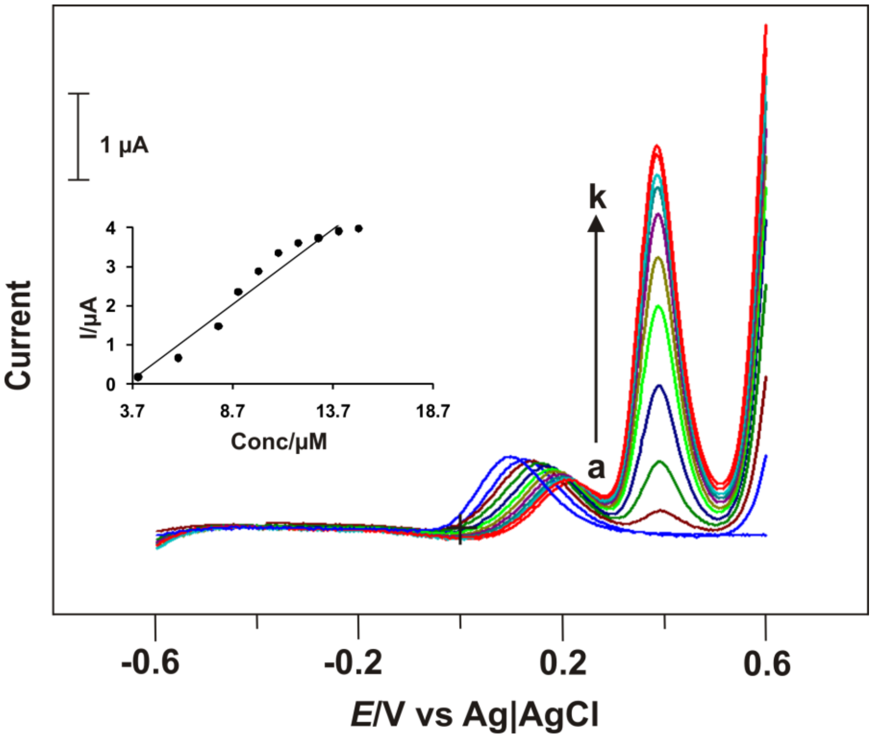


Figure 6. DPV response of nano TiO_2-PEDOT film modified GCE for the selective detection of AA and diclofenac. In the DPV curve a denotes the electrooxidation signal of AA (40 µM) and curve b-k shows the DPV responses for the detection of diclofenac in the range of 4, 6, 8, 9, 10, 11, 12, 13, 14 and 15 µM in the presence of AA (40 µM).

Not only limited to simultaneous detection, the nano TiO_2-PEDOT film has also been employed for the selective detection of diclofenac in the presence of higher concentrations of AA. The nano TiO_2-PEDOT film shows linear response for the detection of diclofenac in the presence of ascorbic acid. For the fixed concentration of AA (40 µM), and for the increasing concentrations of diclofenac in the range of 4 to 15 µM, film shows linear electrooxidation peak currents for the detection of diclofenac. Here the AA electrooxidation peak shifts to more positive potentials which may be due to the increasing concentrations of diclofenac which slightly interfere with the AA signals, respectively. Further the inset of Fig. 6 shows the current vs. calibration plot for the detection of diclofenac.

3.4. Repeatability, reproducibility and stability studies

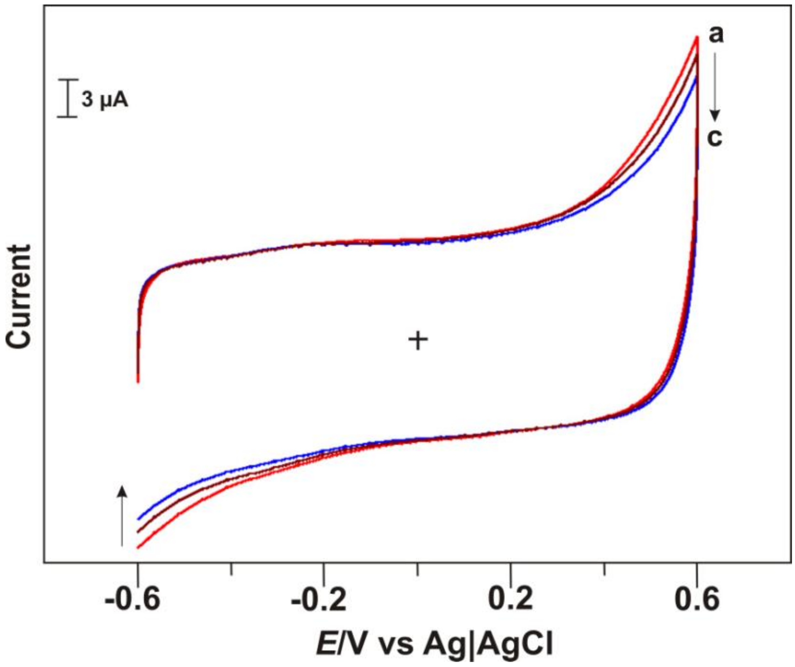


Figure 7. CV response of nano TiO_2–PEDOT film modified GCE in the pH 7 PBS: (a) at the initial stage, (b) after 6 hours, and (c) second day.

The repeatability of the nano TiO_2-PEDOT film for the detection of diclofenac (4.2×10^{-5} M, n=10) the RSD value was found as 3.12 %. Further the reproducibility for the detection of diclofenac was carried out using five glassy carbon electrodes and the RSD value was found as 4.9 %. The repeatability and the reproducibility values confirm that the proposed film was suitable for the detection and determination of diclofenac. Next the stability of the film has been examined by storing it at the room temperature in the open air condition. Fig. 7. Shows the CV response of the nano TiO_2-PEDOT film modified GCE in pH 7.0 PBS. Here curve a represents the background response at the initial stage (after the fabrication process), curve b is the response after six hours and curve c is the second day response. From the curve a-c, we can notice that the film was more active and stable in open air condition and there is slight decrease in its background current response (6.83 %). This confirms that the proposed film was electrochemically active and stable in the open air condition.

4. CONCLUSION

In conclusion, we have successfully fabricated a bilayer film modified GCE utilizing nano TiO_2 particles and the electroactive PEDOT film. This type of film has been found as electrochemically active and stable in pH 7.0 PBS. Moreover, it possesses the low electron transfer resistance and actively represents as electroactive film comparing with only nano TiO_2 particles modified GCE. Further the film has been successfully employed for the simultaneous detection of AA and diclofenac in pH 7.0 PBS. It showed acceptable linear response for the detection of both compounds. Also, it is capable to show the electrooxidation signals for the detection of diclofenac in the commercially available tablets. The special nature of this type of film is its stable electrochemical activities in the open air condition, respectively. Furthermore, these results will lead to use this type of film as potential substrate for the fabrication of real prototype electrochemical sensors for the detection of AA and diclofenac.

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