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Zirconia/Poly(oxalic acid) Modified Carbon Paste Electrode for Electrochemical Investigation of Uric Acid in Presence of Dopamine and Ascorbic Acid

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The electrochemistry of uric acid in the presence of dopamine and ascorbic acid was studied by cyclic voltammetry at a carbon paste electrode modified with zirconia and oxalic acid to get zirconia/poly(oxalic acid) modified carbon paste electrode (ZrO₂/POA/CPE). The modified electrode could resolve well the anodic peaks of uric acid, dopamine and ascorbic acid and also showed far better sensitivity for uric acid (two folds) compared to bare carbon paste electrode. Scan rate studies indicated that the electrode process was both diffusion and adsorption controlled. The limit of detection (LOD) and limit of quantification (LOQ) of the modified electrode for uric acid were found to be 5.07×10^{-7} M and 1.69×10^{-6} M respectively. The recovery percentage of uric acid in human urine and human blood serum were found to be 92 and 97 respectively with ZrO₂/POA/CPE in the real sample analysis. The modified electrode was found to be very selective, sensitive, inexpensive, stable and provide a good possibility for applying the technique in the routine analysis of biomolecules in medicine and analytical chemistry.

Keywords: Dopamine, Uric acid, Ascorbic acid, Zirconia, Oxalic acid, Cyclic voltammetry.

INTRODUCTION

Dopamine, uric acid and ascorbic acid are biologically important and electrochemically active biomolecules which coexist in the extracellular fluids of mammalian brain. The detection of these compounds [1] is important not only for diagnostic studies but also for pathological research. Our concern in this work is for the detection of uric acid in the mixture. Uric acid (2,6,8-trihydroxy purine) and other oxypurines are main final products of purine metabolism [2,3] in human body. Abnormal concentrations of uric acid in human blood serum and urine is the indicator for diseases such as gout, hyperuricemia and leschnyhan syndrome [1,4]. For such reasons the detection of uric acid is quite important. However, one of the major problems frequently encountered in the electrochemical detection of these compounds is the serious interference caused by coexisting compounds. For the resolution and independent detection of these compounds several methods are being used. Some of them are fluorescence studies [5], spectrophotometry [6,7], HPLC [8], flow injection methods [9] and electrochemical methods [10,11]. In the present work, electrochemical method was used for the fabrication of zirconia/poly(oxalic acid) modified carbonpaste electrode (ZrO₂/POA/CPE) which inturn was used for the

detection of uric acid. For the preparation of ZrO₂/POA/CPE, first the carbon paste was bulk modified with zirconia particles and then surface modified by electropolymerization of oxalic acid. This is an inexpensive and easy to fabricate modified electrode in contrast to some of the modified electrodes fabricated in the past. Some of these electrodes used expensive substrates such as gold as modifier [12], some used glassy carbon electrodes [13] which involved complicated and time consuming methods of preparation.

Zirconia used in the bulk modification of the bare carbon paste electrode (BCPE) has certain typical characteristics which made it to be used as a modifier. It is an inorganic metal oxide with some highly desirable properties such as chemical inertness, thermal stability, hardness, good resistance [14,15] and less toxic even at extreme conditions. It is used as electrode material due to its wide band gap energy (5.78 eV) [16,17] and the absence of photocatalytic activity under solar light.

Further, in the surface modification, the polymer film formed on the surface of BCPE has good stability, more active sites, strong adherence to the electrode surface and gave good reproducibility [18,19]. Surface modified electrodes were also found to show low residual currents over a wide range and have feeble chances of electrode fouling which improve the sensitivity and selectivity of the electrode [20,21].

EXPERIMENTAL

Uric acid, dopamine and ascorbic acid were obtained from Himedia chemicals. Stock solutions of uric acid were prepared by dissolving it in 0.1 M sodium hydroxide, dopamine in 0.1 M perchloric acid and ascorbic acid in double distilled water. Oxalic acid and all other chemicals were of analytical grade and were used without further purification. The stock solution of 0.1 M oxalic acid was prepared by dissolving it in distilled water. 0.1 M phosphate buffer solutions (PBS) of pH 7 and other pHs were prepared by mixing standard stock solutions of 0.2 M Na_2HPO_4 and 0.2 M NaH_2PO_4 in appropriate quantities. All the experiments were conducted at room temperature.

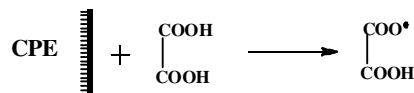
Cyclic voltammetry and DPV measurements were made with CHI610D electrochemical analyzer controlled by a personal computer. A conventional three electrode was used for the investigation. A standard calomel electrode (SCE) was used as reference electrode, platinum wire was used as counter electrode, a bare and zirconia/poly(oxalic acid) modified carbon paste electrodes were used as working electrodes. Systronics made digital pH meter MKVI was used for pH measurement of different solutions. The surface morphology of BCPE and $\text{ZrO}_2/\text{POA}/\text{CPE}$ were studied using scanning electron microscope.

Preparation of bare carbon paste electrode: To prepare bare carbon paste electrode, graphite powder and silicon oil were hand mixed in the ratio of 70:30 (w/w) using an agate mortar to get a homogenous paste. The paste so obtained was used to fill tightly a PVC tube of 3 mm internal diameter and the electrical contact to the paste was provided with a copper wire and the surface of the electrode was smoothened by polishing on a weighing paper.

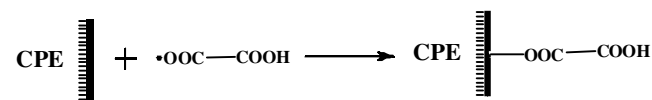
Preparation of zirconia/poly(oxalic acid) modified carbon paste electrode: 70 % (0.24 g) graphite powder, 30 % (0.04 mL) silicon oil and 25 mg of zirconia were hand mixed thoroughly for 40 min using an agate mortar to get a bulk modified carbon paste electrode. The studies done by Lavanya *et al.* [17] proved that 25 mg of zirconia gave optimum current

for the detection of uric acid. Later, this bulk modified electrode was immersed in 1 mM oxalic acid solution in 0.1 M PBS of pH 7 for electropolymerization in the potential window of -0.75 to 1.25 V at the scan rate of 50 mV/S for 15 cycles using cyclic voltammetry. The resulting polymerization cyclic voltammetry is shown in Fig. 1(a). The process of polymerization is shown in **Scheme-I**. As shown in the scheme, the process of polymerization takes place by free radical mechanism. First in the presence of the modified electrode oxalic acid free radical is generated which then gets attached to the electrode as the carbon atoms of graphite electrode contain unpaired electrons. Then the remaining oxalic acid molecules get attached to the already attached molecule one by one to form the polymer on the surface of the graphite electrode. After polymerization the electrode was thoroughly rinsed with distilled water to remove any traces of unreacted oxalic acid and used for further studies.

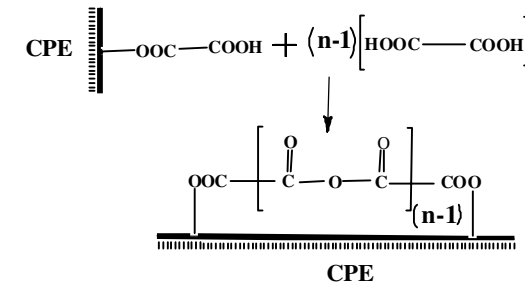
1. Oxalic acid free radical formation



2. Bonding to CPE



3. Polymerisation at CPE



Scheme-I: Polymerization mechanism of oxalic acid

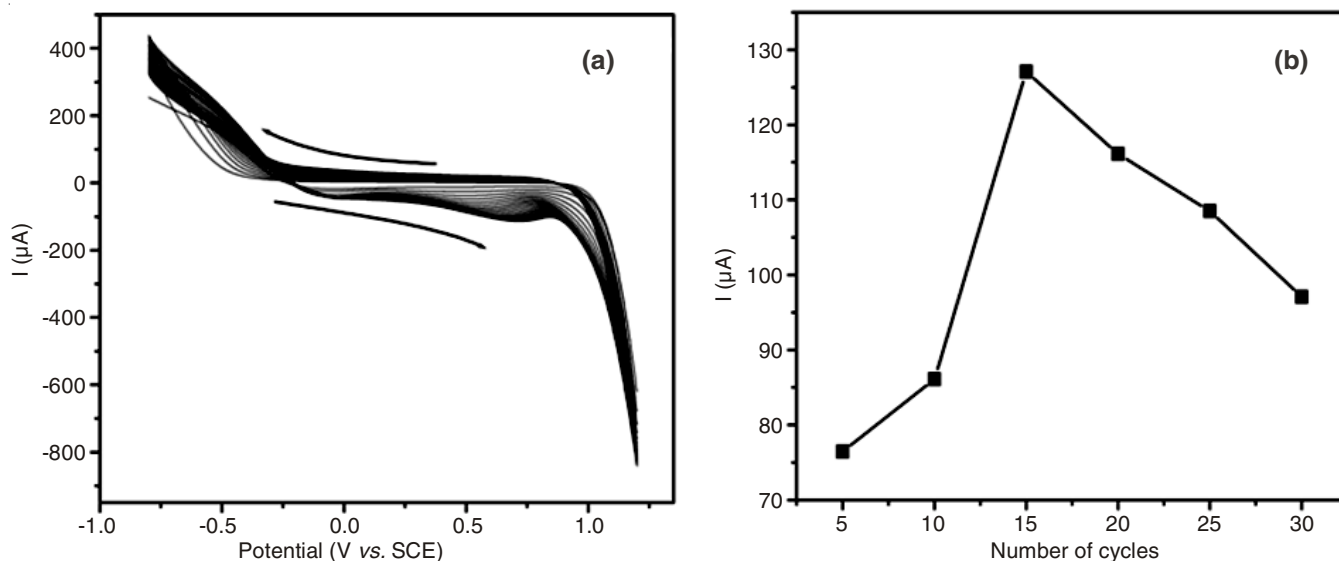


Fig. 1. (a) Cyclic voltammogram for the electropolymerization of oxalic acid on bare carbon paste electrode for 15 cycles at the scan rate of 50 mV/S, (b) Dependence of anodic peak current on the number of cycles of polymerization for uric acid detection

RESULTS AND DISCUSSION

Electrochemical investigation of uric acid at $\text{ZrO}_2/\text{POA}/\text{CPE}$: The effect of number of cycles of polymerization on the sensitivity of the modified carbon paste electrode was investigated. The optimum sensitivity for determination of uric acid was obtained at 15 cycles shown in Fig. 1(b). It is clear from the figure that up to 15 cycles the anodic peak current (I_{pa}) was increased, at 15 cycles the current response was maximum and after that the current response was decreased. The increase of current up to 15 cycles may be due to gradual covering of the surface of carbon paste electrode with poly-(oxalic acid) film and thus gradual increase in the number of active sites. At 15 cycles the entire surface is covered with the polymer film. This corresponds to maximum number of active sites and so there is maximum current response. However, after 15 cycles the current decreased as there is no further increase in the number of active sites [22] and also the thickening of the polymer layer might have decreased the permeability.

Fig. 2(a) and 2(b) are the SEMs of surfaces of BCPE and $\text{ZrO}_2/\text{POA}/\text{CPE}$. From the Fig. 2(a) it is visible that the surface

of BCPE is uneven and rugged, whereas the surface of $\text{ZrO}_2/\text{POA}/\text{CPE}$ as in Fig. 2(b) is quite even. This confirms that after electropolymerization polymer layer was formed on the surface of carbon paste electrode.

Electrocatalytic oxidation of uric acid at $\text{ZrO}_2/\text{POA}/\text{CPE}$: Cyclic voltammeteries of uric acid at BCPE (dotted line curve), poly(oxalic acid) modified carbon paste electrode (POA/CPE) (dashed line curve) and $\text{ZrO}_2/\text{POA}/\text{CPE}$ (solid line curve) are shown in Fig. 3(a) recorded in the potential range of -0.2 V to 0.7 V at 50 mV/S scan rate. It is evident from the figure that I_{pa} at $\text{ZrO}_2/\text{POA}/\text{CPE}$ is 2 folds and at POA/CPE 1.4 folds to that at BCPE. This result indicates that $\text{ZrO}_2/\text{POA}/\text{CPE}$ has the best sensitivity. This may be attributed to more number of active sites at $\text{ZrO}_2/\text{POA}/\text{CPE}$ compared to POA/CPE and BCPE. $\text{ZrO}_2/\text{POA}/\text{CPE}$ has active sites due to both zirconia particles and polymer film whereas POA/CPE has active sites only due to polymer film of oxalic acid. One of the main contributors for the increased sensitivity for the detection of uric acid at $\text{ZrO}_2/\text{POA}/\text{CPE}$ is the interaction of oxalic acid polymer layer on the surface of the carbon paste electrode with the uric acid molecules as shown in **Scheme-II**. The hydrogen

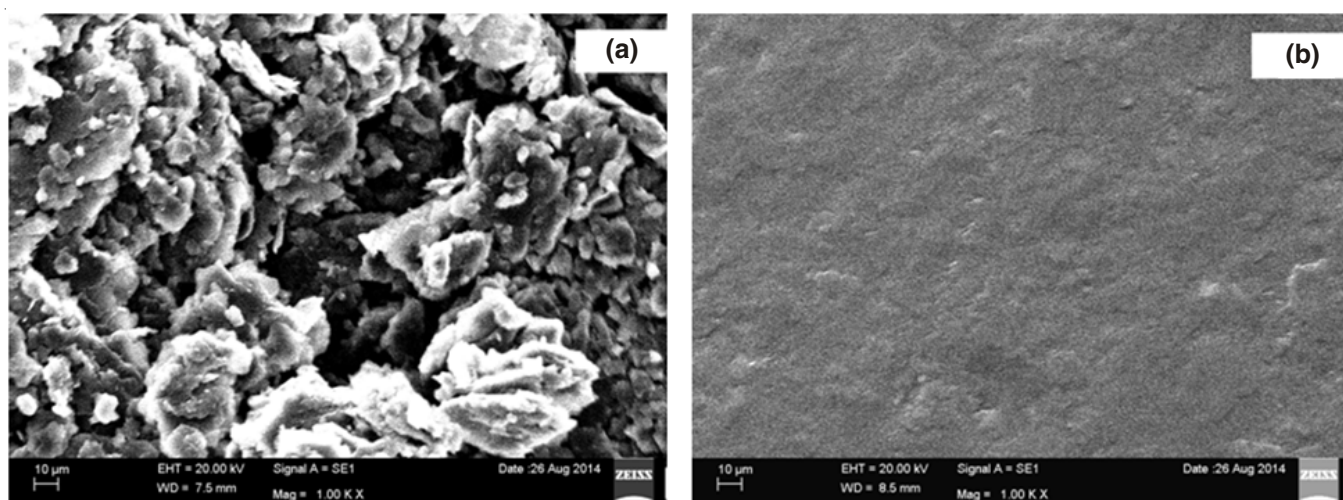


Fig. 2. Scanning electron microscopic images of (a) bare carbon paste electrode, (b) poly (oxalic acid) modified carbon paste electrode

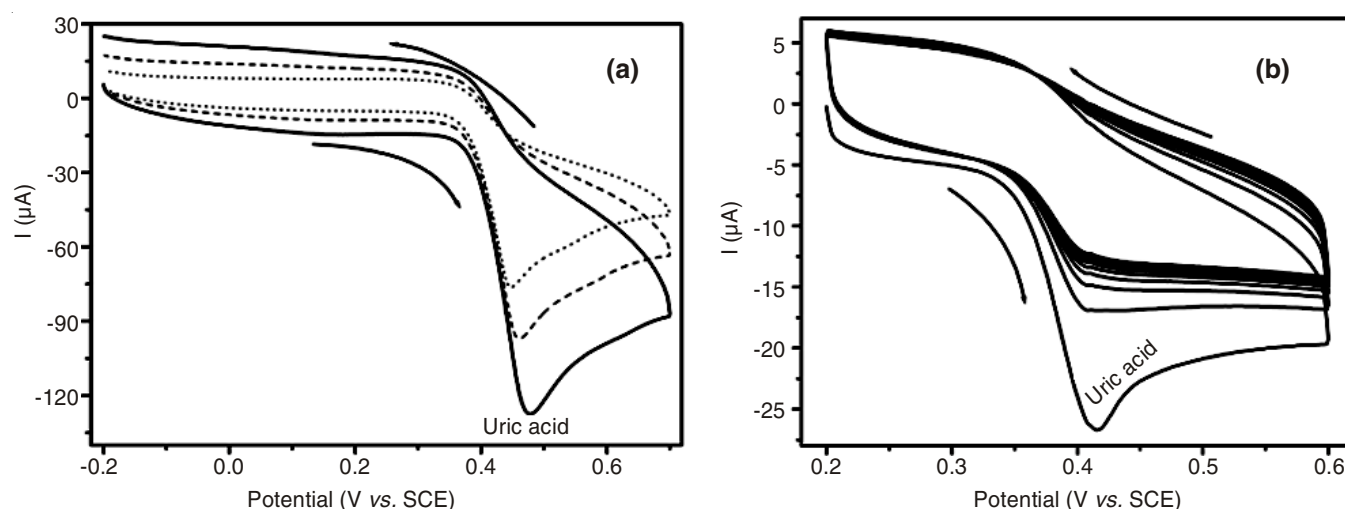
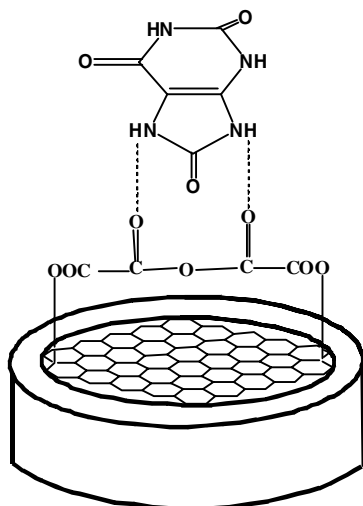
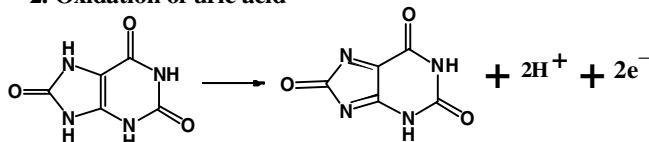


Fig. 3. (a) Cyclic voltammogram of 1 mM uric acid in 0.1 M PBS of pH 7 at BCPE (dotted line curve), POA/CPE (dashed line curve) and $\text{ZrO}_2/\text{POA}/\text{CPE}$ (solid line curve) at 50 mV/s scan rate, (b) Cyclic voltammograms of 1 mM uric acid for 15 multiple cycles on $\text{ZrO}_2/\text{POA}/\text{CPE}$ at 50 mV/s scan rate to test the stability of the electrode

1. Interaction of uric acid with zirconia/POA/CPE



2. Oxidation of uric acid



Scheme-II

atoms on the two nitrogen atoms of the five membered ring of the uric acid molecule form hydrogen bonds with the carbonyl oxygen atoms of the oxalic acid polymer. This makes the two N-H bonds weak thus making the oxidation process of uric acid easier.

Electrochemical investigation of stability and reproducibility of $\text{ZrO}_2/\text{POA}/\text{CPE}$: Because the procedure for electrode preparation is easy and rapid, it is not so important for the electrode to be stable for prolonged period. However, the stability and reproducibility of the modified electrode was investigated for uric acid. It was investigated by running 15

cycles on 1 mM uric acid solution. The cyclic voltammetric curves for the above are shown in Fig. 3(b). Cyclic voltammetric curves for almost all the cycles are overlapping (I_{pa} between 12.5 to 13.0 μA at 0.44 V E_{pa}) indicating that the electrode is fairly stable and giving reproducible results.

Effect of scan rate: The scan rate effect was studied to understand the electrode process. Hence, the cyclic voltammetry of uric acid was recorded by varying the scan rate from 50 to 300 mV/S at $\text{ZrO}_2/\text{POA}/\text{CPE}$ as shown in Fig. 4(a). I_{pa} was increased with increase in scan rate (v) as per the Fig. 4(a). The plots of I_{pa} versus v ($I_{pa} = 2.046 \times 10^{-4} \times v + 6.54987 \times 10^{-5}$) and I_{pa} versus \sqrt{v} ($I_{pa} = 1.569811 \times 10^{-4} \times \sqrt{v} + 3.86044 \times 10^{-5}$) are shown in Fig. 4(b) (inset of Fig. 4(a)) and Fig. 4(c), respectively. Both the plots are linear with correlation coefficients (R) 0.99759 and 0.99329, respectively. This result indicates that the electrochemical oxidation of uric acid at $\text{ZrO}_2/\text{POA}/\text{CPE}$ is both adsorption controlled and diffusion controlled.

Effect of the solution pH: To optimize the electrochemical response of the modified electrode for the oxidation of uric acid, the effect of pH was studied. As the pH increased from 5.5 to 8.0, the anodic peak potential (E_{pa}) of uric acid shifted gradually to negative value representing the participation of protons in the electrochemical oxidation process. The anodic peak current (I_{pa}) was increased gradually until attaining a maximum value at pH 7 and then decreased [Fig. 5(a)] and corresponding DPV is shown in Fig. 5(b) at various pH values. The slope of E_{pa} versus pH plot is found to be 52 mV/pH. This indicates that equal number of electrons and protons are involved in the oxidation process [23].

Simultaneous determination of uric acid, dopamine and ascorbic acid at $\text{ZrO}_2/\text{POA}/\text{CPE}$: In order to examine the sensitivity and selectivity of $\text{ZrO}_2/\text{POA}/\text{CPE}$, the electrochemical behaviour of a mixture of 0.2 mM uric acid, 0.1 mM dopamine and 2 mM ascorbic acid was investigated using cyclic voltammetry in 0.1 M PBS of pH 7 in the potential window of -0.2 V to 0.7 V at 50 mV/S scan rate. The resulting cyclic voltammetry is shown in Fig. 6(a). At BCPE (dotted

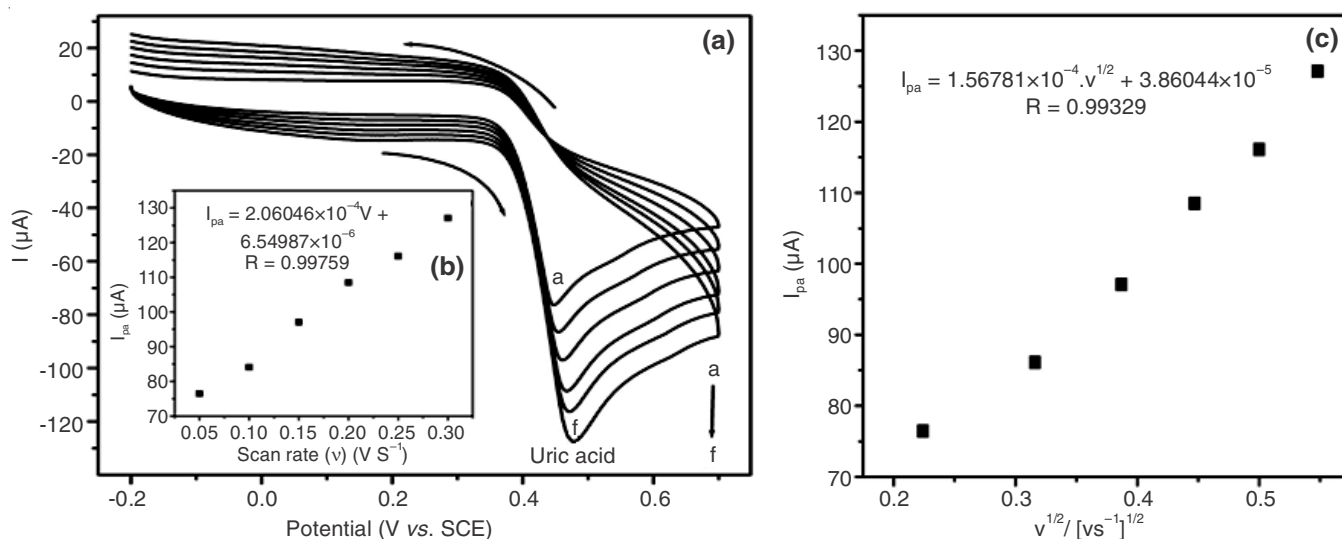


Fig. 4. (a) Cyclic voltammograms of 1 mM uric acid on $\text{ZrO}_2/\text{POA}/\text{CPE}$ at different scan rates (a-f: 50, 100, 150, 200, 250 and 300 mV/s) in 0.1 M PBS of pH 7, (b) The plot of anodic peak current versus the scan rate (v) [inset of Fig. 4(a)], (c) The plot of anodic peak current versus the square root of scan rate (\sqrt{v})

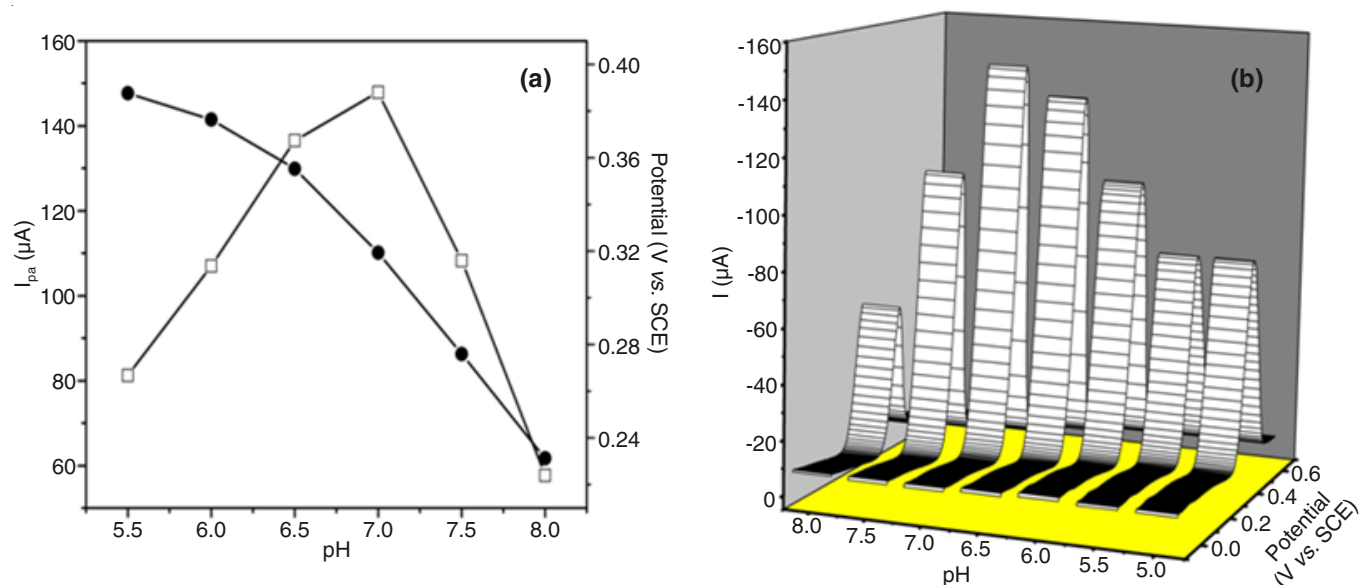


Fig. 5. (a) The plot of anodic peak current, peak potential *versus* pH for 1 mM uric acid on $ZrO_2/POA/CPE$ at different pH (5.5, 6.0, 6.5, 7.0, 7.5 and 8) at the scan rate of 50 mV/S, (b) DPVs of uric acid at different pH

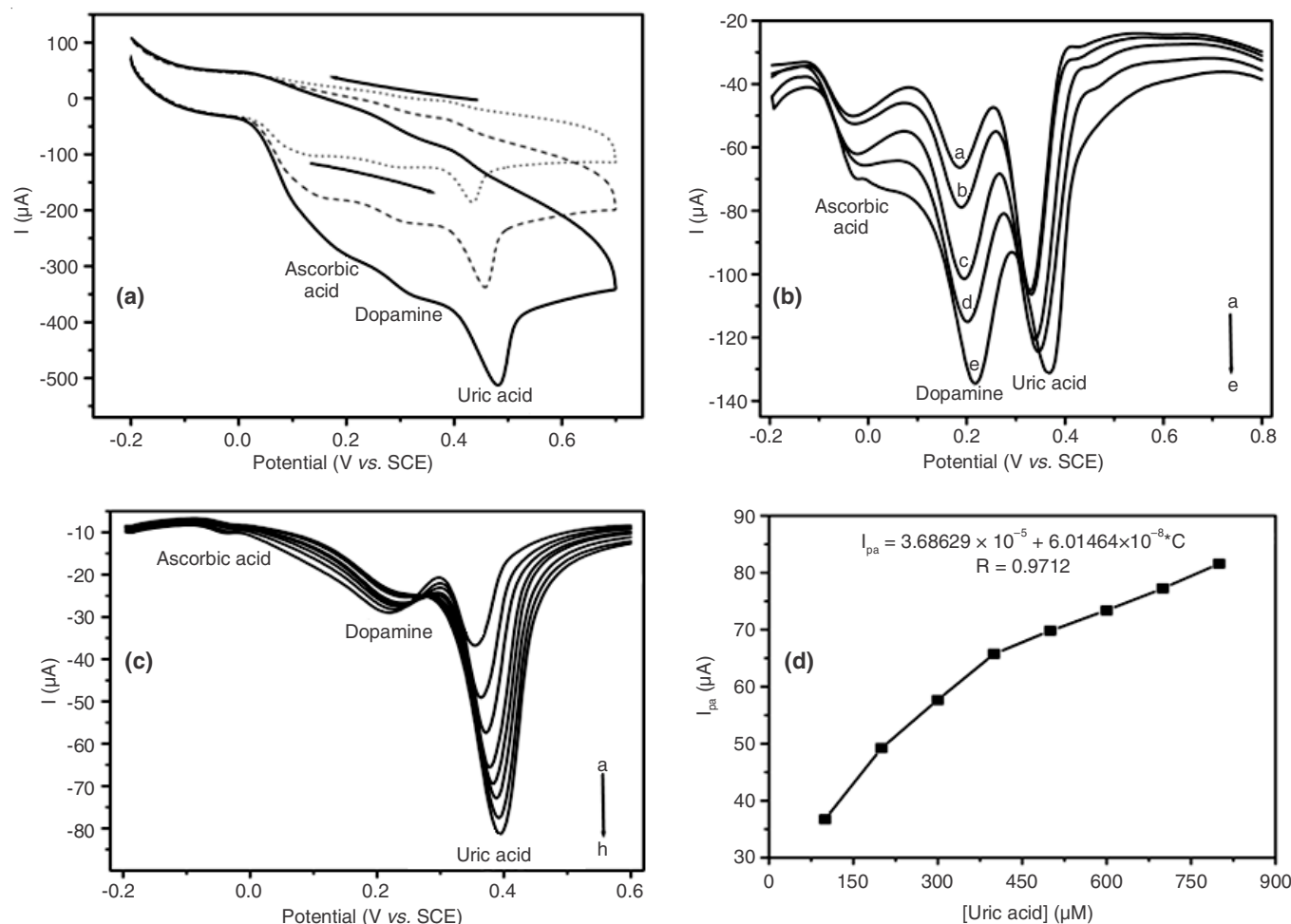


Fig. 6. (a) Cyclic voltammogram for simultaneous determination of 0.2 mM uric acid, 0.1 mM dopamine and 2 mM ascorbic acid mixture at BCPE (dotted line curve), POA/CPE (dashed line curve) and $ZrO_2/POA/CPE$ (solid line curve) in 0.1 M PBS of pH 7 at the scan rate of 50 mV/s, (b) DPVs of uric acid, dopamine and ascorbic acid mixture by varying the concentrations of all the components [a-e: uric acid (0.1 to 0.5 mM), dopamine (0.05 to 0.25 mM) and ascorbic acid (1 to 5 mM)], (c) DPVs of uric acid, dopamine and ascorbic acid mixture by varying the concentration of uric acid (a-h: 0.1 mM to 0.8 mM) keeping dopamine and ascorbic acid concentrations fixed at 0.02 mM and 1 mM respectively, (d) anodic peak current *versus* uric acid concentration in the simultaneous determination of uric acid, dopamine and ascorbic acid

line curve), ascorbic acid and dopamine could not be detected separately. Only one broad band at 0.115 V was observed indicating the co-oxidation of dopamine and uric acid [23]. The fouling of the BCPE surface by the oxidation products results in a single voltammetric peak for dopamine and ascorbic acid [24,25]. At POA/CPE (dashed line curve) and $\text{ZrO}_2/\text{POA}/\text{CPE}$ (solid line curve) all the three peaks were clearly separated indicating that modification lead to selectivity. There is conspicuous increase in anodic peak currents at modified electrodes indicating the better sensitivity. On the whole $\text{ZrO}_2/\text{POA}/\text{CPE}$ electrode has the best selectivity and sensitivity.

Simultaneous determination of uric acid, dopamine and ascorbic acid was also carried out by DPV as shown in Fig. 6(b) in the potential window of -0.2 V to 0.8 V at $\text{ZrO}_2/\text{POA}/\text{CPE}$ keeping scan rate at 50 mV/S. The oxidation peaks were well separated and I_{pa} of each of them increased linearly with increase in concentration of the each component.

Interestingly I_{pa} for uric acid increased linearly with increase in its concentration from 0.1 mM to 0.8 mM at 0.390 V in the mixture of uric acid, dopamine and ascorbic acid keeping the dopamine and ascorbic acid concentrations fixed at 0.1 and 1 mM respectively. Corresponding DPV is shown in Fig. 6(c) and I_{pa} versus concentration of uric acid plot is shown in the Fig. 6(d).

Effect of uric acid concentration on modified electrode:

The limit of detection (LOD) and limit of quantification (LOQ) of the $\text{ZrO}_2/\text{POA}/\text{CPE}$ were estimated for uric acid using DPV as this technique has higher current sensitivity and better resolution than cyclic voltammetry. The electrochemical response obtained is shown in Fig. 7(a). It is clear from the figure that the I_{pa} was increased linearly with increase in concentration of the analyte uric acid in the concentration interval of 10 to 700 μM . Fig. 7(b) is the plot of I_{pa} versus concentration of uric acid. It is linear ($I_{\text{pa}} = 0.363326 \times C + 1.49904 \times 10^{-6}$) with correlation coefficient (R) of 0.9968. From this plot the LOD and LOQ of $\text{ZrO}_2/\text{POA}/\text{CPE}$ were found for uric acid using the formulae (1 and 2) [26,27].

$$\text{LOD} = 3S/M \quad (1)$$

$$\text{LOQ} = 10S/M \quad (2)$$

where S is the standard deviation and M is the slope. The LOD and LOQ were found to be $5.07 \times 10^{-7} \text{ M}$ (0.507 μM) and $1.69 \times 10^{-6} \text{ M}$ (1.69 μM) respectively which is good enough for its application in the field of analytical chemistry and medicine. Comparison of LOD of $\text{ZrO}_2/\text{POA}/\text{CPE}$ with other electrodes for the detection of uric acid is shown in the Table-1.

Modified electrode	Linear range (mol L ⁻¹)	LOD (mol L ⁻¹)	Ref.
MWCNT/GCE	1.0×10^{-5} – 2.0×10^{-3}	1.0×10^{-6}	28
PDBF/GCE	1.0×10^{-6} – 2.5×10^{-4}	2.0×10^{-7}	29
PNGB/CPE	1.3×10^{-5} – 7.5×10^{-4}	5.0×10^{-7}	30
Nano-Au/p-TA/GCE	1.6×10^{-5} – 2.8×10^{-4}	8.9×10^{-7}	31
MWCNT/CCE	5.5×10^{-7} – 9.0×10^{-5}	4.2×10^{-7}	32
ECP/CPE	3.0×10^{-8} – 2.4×10^{-4}	1.2×10^{-8}	33
N-DHPB/MWCNT/PE	5.0×10^{-6} – 4.2×10^{-4}	2.0×10^{-6}	34
$\text{ZrO}_2/\text{POA}/\text{CPE}$	1.0×10^{-5} – 7.0×10^{-4}	5.1×10^{-7}	Present work

Real sample analysis: Practical applicability of $\text{ZrO}_2/\text{POA}/\text{CPE}$ was demonstrated by quantitative determination of uric acid in human urine and blood serum samples. Blood serum sample was obtained from the Health Centre, Sri Venkateswara University, Tirupati, India. Human urine sample without any pretreatment was diluted 50 times using 0.1 M PBS of pH 7. Then solutions of three different concentrations of uric acid were prepared by spiking different amounts of uric acid in to the matrix of urine solution. DPV measurements were made for each of the concentrations four times. By using mean peak current of four repeated DPVs and the calibration curve shown in Fig. 7(b), uric acid concentration was estimated in urine. This was compared with the spiked uric acid concentration to get the recovery percentage. Similarly, blood serum was also diluted 50 times and found the recovery percentage of uric acid as discussed in the case of urine. The recovery

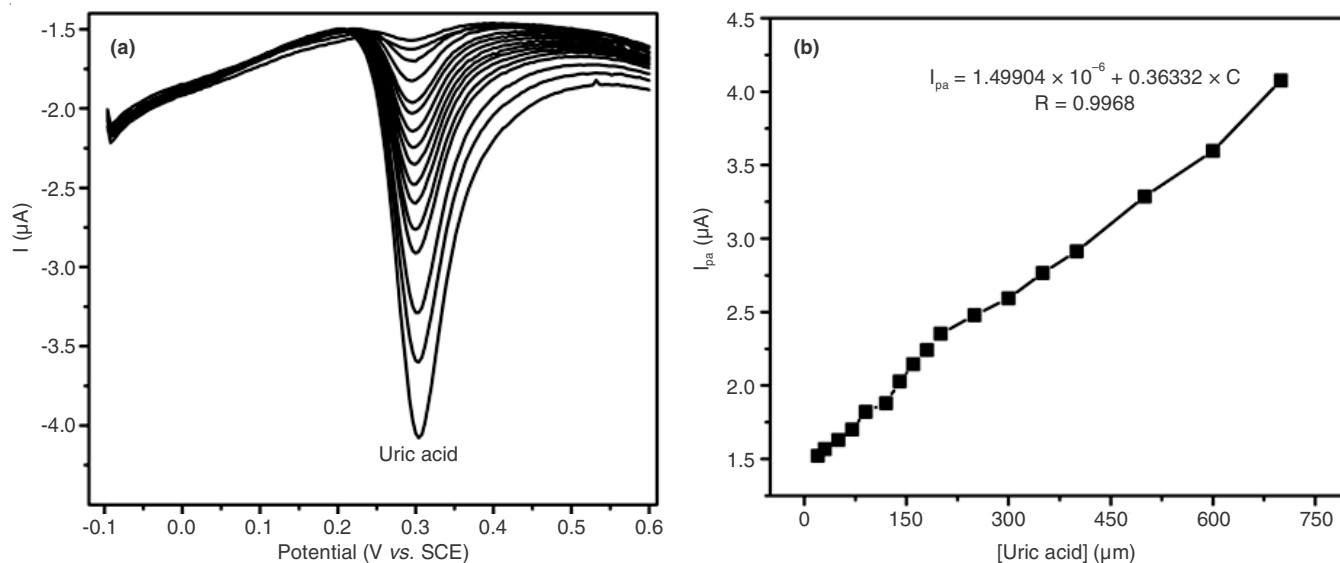


Fig. 7. (a) DPVs for various concentrations of uric acid (10 to 700 μM) at $\text{ZrO}_2/\text{POA}/\text{CPE}$ in 0.1 M PBS of pH 7 at the scan rate of 50 mV/S, (b) The plot of anodic peak current versus concentration of uric acid

percentage of uric acid in human urine and blood serum sample were found to be 92 and 97, respectively. All these results are shown in Table-2.

TABLE-2
DETERMINATION AND RECOVERY RESULTS OF
URIC ACID IN HUMAN URINE AND BLOOD SERUM

Sample	Spiked (M)	Found (M)	Recovery (%)	RSD (%)
Human urine	0.1	0.090	90	5.2
	0.2	0.180	90	3.4
	0.3	0.290	96	2.1
Average: 92				
Human blood serum	0.1	0.095	95	2.5
	0.2	0.180	90	2.9
	0.3	0.320	106	5.4
Average: 97				

Conclusion

The studies on $\text{ZrO}_2/\text{POA}/\text{CPE}$ indicated that it exhibits an excellent electrocatalytic activity for the oxidation of uric acid, dopamine and ascorbic acid. The problem of overlapping of voltammetric responses for dopamine and ascorbic acid at BCPE due to their co-oxidation was effectively overcome by the modified electrode. The polymer film formed on the surface of carbon paste electrode was found to be stable and uniform. The electrode preparation is easy, inexpensive. Sensitivity, selectivity and detection limit of the $\text{ZrO}_2/\text{POA}/\text{CPE}$ are excellent. All these virtues make it a good contender for the preparation of the analytical tools for the detection of biomolecules such as uric acid, dopamine and ascorbic acid in analytical chemistry and medicine.

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