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Simultaneous Voltammetric Determination of Ascorbic Acid, Dopamine and Uric Acid by the Poly(alizarin yellow R)/GCE

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A glassy carbon electrode (GCE) modified with the poly(alizarin yellow R) (PAYR) film was prepared by an electropolymerization method. Ascorbic acid (AA), dopamine (DA) and uric acid (UA) were determined by this electrode, and its electrocatalytic activity toward AA, DA and UA oxidation was clearly demonstrated. The separate oxidation peak potentials of 178, 115 and 293 mV were found for AA/DA, DA/UA and AA/UA, respectively. The oxidation peak currents were linear with the respective compound concentrations, the linear ranges were 80 μM to 2000 μM (AA), 2.3 μM to17.5 μM (DA) and 33 μM to 330 μM (UA), and the detection limits were 8.3 μM, 0.42 μM and 4.3 μM, respectively. Additionally, this electrode exhibited excellent performances characteristics including good selectivity, reproducibility and stability and was successfully used to detect DA in a real sample with satisfactory results.

Keywords: Alizarin yellow R, Ascorbic acid, Dopamine, Uric acid, Electropolymerization,

1. INTRODUCTION

Ascorbic acid (AA), dopamine (DA) and uric acid (UA) are important biomolecules in humans. Their real-time monitoring in biological samples and pharmaceutical preparations plays an important role in diseases diagnosis and has attracted intense interest. Recent studies have shown that these molecules are electrochemically active; therefore, electrochemical techniques have been considered potential approaches for their detection. However, because these molecules coexist in body fluids, their direct simultaneous assaying using ordinary electrodes is a nontrivial task [1]. Thus, the development of novel modified electrodes to simultaneously assay AA, DA and UA in mixtures has great potential in disease diagnosis. To date, various modified electrodes, including nanomaterials [2-6], self-assembled monolayers [7], layer-by-layer self-assemblies [8, 9] and polymer films [10], have been successfully

constructed for individual and simultaneous detection of these substances. Among these modified electrodes, the polymer-film-modified electrode has attracted researchers' attention due to its advantages and wide applications in the chemical fields [11-14].

In a previous study, we developed a method for simultaneous detection of AA, DA and UA based on a poly(2-(N-morpholine) ethane sulfonic acid)/RGO/GCE [15]. RGO/GCE was prepared by the drip method and showed poor stability. An electrode directly modified by the polymer film may also show good performance characteristics for detecting AA, DA and UA. In this paper, a PAYR-modified electrode was prepared and applied to detect AA, DA and UA. Based on the experimental results, a sensitive method for the determination of AA, DA and UA in routine analysis was developed.

2. EXPERIMENTAL

2.1. Chemicals and Apparatus

AA, DA, UA and alizarin yellow R (Sigma, USA), L-lysine, L-cysteine, L-tyrosine, glucose and other reagents were obtained from Nanjing Chemical Reagent, (Nanjing, China). PBS (0.1 M) was obtained by using Na_2HPO_4 and NaH_2PO_4, and the pH was adjusted by the addition of either H_3PO_4 or NaOH. The reagents used in this work were of analytical reagent grade. Doubly distilled water was used as the solvent for the preparation of the solutions.

CV was carried on a CHI660A electrochemical workstation manufactured by Shanghai Chenhua Instruments, China. During the experiment, a three-electrode system (a saturated calomel electrode, a platinum wire, and modified electrode) was used. Electrochemical measurements were carried out in an electrochemical cell in N_2 atmosphere over the solution.

2.2. Preparation of the PAYR/GCE

The PAYR/GCE was prepared [16] using the following process: the bare GCE was systematically polished by using 1.0, 0.3 and 0.05 μm Al_2O_3 and cleaned with anhydrous ethanol and doubly distilled water for 1 min and was then immersed in 0.1 M PBS (pH 7.0) solution containing 0.5 mM AYR. CV measurements were carried with a potential range of -1.0 and +2.2 V at 100 mV s^{-1} for 15 scans to form the PAYR/GCE.

3. RESULT AND DISCUSSION

3.1. Scan electron microscopy characterization of PAYR/GCE

SEM was used to verify the successful preparation of the modified electrode. Fig. 1 displays the typical morphologies of the different electrodes. A clear change in the morphology is observed for the PAYR/GCE that was similar to the morphology changes described in previous reports [16,17]. This indicated that PAYR was successfully electropolymerized onto the surface of electrode and the PAYR/GCE was fabricated.

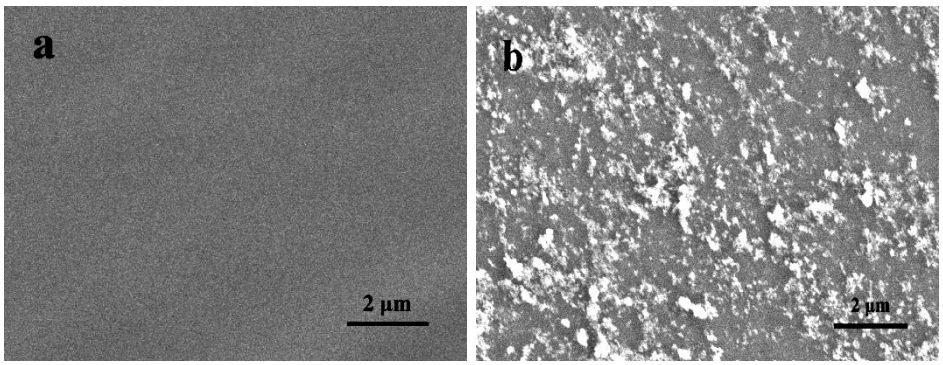

Figure 1. SEM images of the bare GCE (a) and the PAYR/GCE (b).

3.2. Single oxidation of AA, DA and UA

Electrocatalytic activities towards the oxidation of AA, DA and UA using the PAYR/GCE were studied by CV. Fig. 2 shows the CVs of AA (fig. 2A), DA (fig. 2B) and UA (fig. 2C) at different electrodes in 0.1 M PBS (pH 7.0). Curves (a) and (b) show the CVs of the GCE and the PAYR/GCE without AA, DA and UA, respectively. Curves (c) and (d) show the CVs of the GCE and the PAYR/GCE with AA, DA and UA, respectively. Compared with the GCE, the PAYR/GCE can considerably enhance the anodic peak currents of AA, DA and UA, and shows more negative oxidation peak potentials. This indicates that the PAYR/GCE has excellent electrocatalytic activities toward the oxidation of AA, DA and UA.

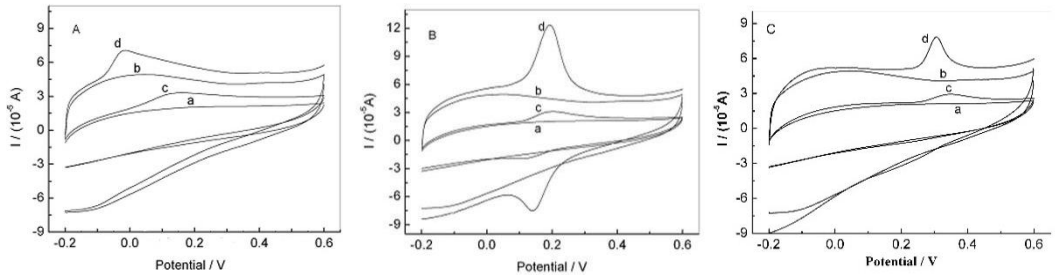

Figure 2. CVs of AA (fig. 3A), DA (fig. 3B) and UA (fig. 3C) at the bare GCE and PAYR/GCE in 0.1 M PBS (pH 7.0). Curves (a) and (b) correspond to the bare GCE and PAYR/GCE in the absence of AA, DA and UA, respectively. Curves (c) and (d) correspond to the bare GCE and PAYR/GCE in the presence of AA (0.6 mM), DA (0.6 μM) and UA (0.5 mM), respectively. Scan rate: 100 mVs^{-1}.

3.3. Effect of pH

The pH was varied in the range of 4.0–9.0 to study its effect on the CV response of AA, DA and UA. Fig. 3 shows the relationship between the oxidation peak currents and pH, respectively. As the pH increased, the oxidation peak current of AA decreased slightly until it reached 7.0. For pH = 8, the oxidation peak current of AA increased. Upon a further increase in the pH, the oxidation peak current decreased. For DA, the oxidation peak current increased with increasing pH until the pH reached 7.0, and the oxidation peak current decreased for pH values exceeding 7.0. For UA, the oxidation peak

current decreased with increasing pH. In addition, as the pH increased, all of the oxidation peaks of AA, DA and UA shifted in the negative direction, indicating that protons participated in the processes that these molecules undergo on the electrodes. These results are similar to those reported in previous studies [18-21]. PBS (pH 7.0), which is much closer to physical conditions, was chosen for use in the subsequent experiments.

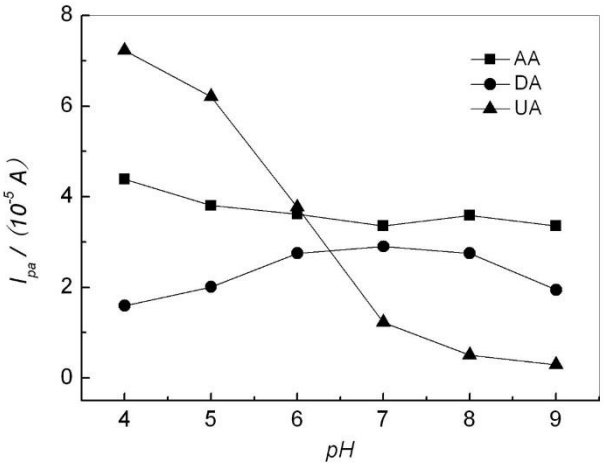

Figure 3. pH vs. the oxidation peak currents of AA, DA and UA.

3.4. Separation of the CV responses of AA, DA and UA

Fig. 4 shows the CVs of the AA, DA and UA solutions at different electrodes in 0.1 M PBS (pH 7.0). No oxidation peak was observed in the CV of the GCE (a) and the PAYR/GCE (b). Figs. 4c and d show the CVs of the AA, DA and UA solution at the bare GCE and PAYR/GCE, respectively. A broad peak is observed in fig. 4c, suggesting that the bare GCE could not distinguishably detect AA, DA and UA. However, for PAYR/GCE (fig. 4d), three well-separated peaks corresponding to the oxidation of AA, DA and UA were obtained, and the oxidation peak potentials were 15, 193 and 308 mV, respectively, which were sufficient to simultaneously detect these molecule in a solution mixture [22-25].

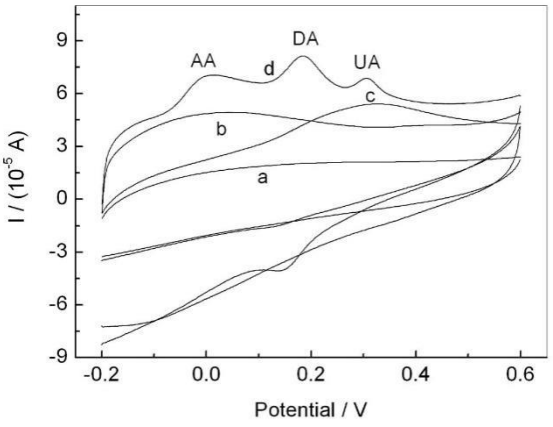

Figure 4. CVs of 0.1 M PBS (pH 7.0) without (a, b) and with (c, d) the mixture containing AA (0.6 mM), DA (20 μM) and UA (0.3 mM) at the bare GCE (a, c) and the PAYR/GCE (b, d). Scan rate:100 mVs^{-1}.

3.5. Simultaneous detection of AA, DA and UA

Figure 5a shows that for a constant concentration of DA and UA, the peak current of AA increased with increasing concentration.

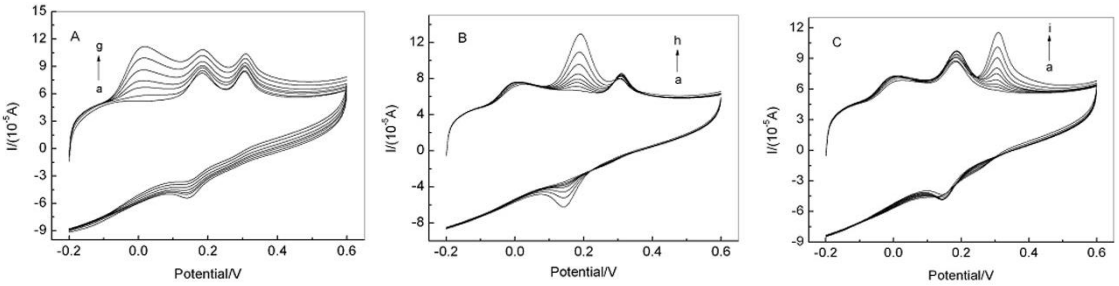

Figure 5. CVs for the mixture containing AA, DA and UA with different concentrations in 0.1 M PBS (pH 7.0) at the PAYR/GCE. (A), DA (23 μM), UA (0.8 mM) and AA (a–g: 0, 0.117, 0.331, 0.544, 0.864, 1.29 and 1.72 mM); (B) AA (0.533 mM), UA (0.8 mM) and DA (a–h: 2.0, 7.0, 11.6, 16.3, 23.3, 42, 72.3 and 133 μM); (C) AA (0.533 mM), DA (28 μM) and UA (a–i: 0, 0.033, 0.0667, 0.133, 0.3, 0.533, 1.033, 1.7 and 3.03 mM).

Additionally, the change in the AA concentration did not significantly affect the peak current and peak potential of the other two compounds. Similarly, as shown in Figs. 5b and c, while maintaining a constant concentration of the other two compounds, the oxidation peak current of DA or UA increased with increasing concentration of DA or UA. These results confirmed that AA, DA and UA in the mixture sample could be simultaneously determined based on PAYR/GCE.

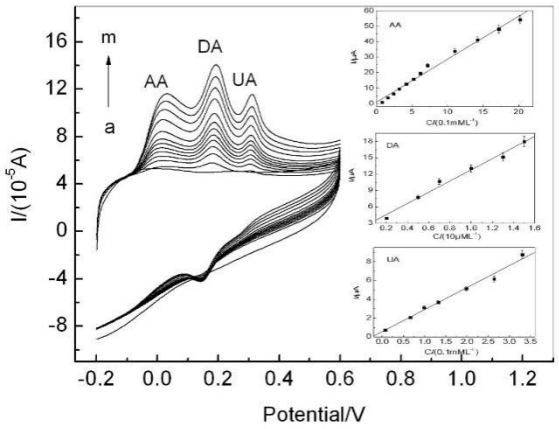

Figure 6. CVs of the mixture containing AA, DA and UA at the PAYR/GCE in 0.1 M PBS (pH 7.0) with a scan rate of 100 mVs^{-1}. Concentrations (from a to m): 0, 0.08, 0.16, 0.24, 0.32, 0.42, 0.52, 0.62, 0.72, 1.1, 1.42, 1.72 and 2.0 mM for AA; 0, 2.3, 4.6×10^{-6}, 6.9, 9.2, 13, 17.5, 26.68, 31.28, 45.08, 58.88, 77.28 and 100 μM for DA; 0, 0.033, 0.066, 0.099, 0.132, 0.198, 0.264, 0.33, 0.429, 0.594, 0.858, 1.188 and 1.848 mM for UA. Inset: Oxidation peak currents vs. the concentrations of three compounds.

As the concentrations of these three compounds increased simultaneously, their oxidation peak currents at the PAYR/GCE increase accordingly and show linear dependence on the respective compound concentrations (fig. 6). The linear ranges for AA, DA and UA were 80 μM – 2000 μM, 2.3

μM –17.5 μM and 33 μM – 330 μM, respectively, and the linear equations were i_{AA} = 0.82 + 2.79 c_{AA} (c_{AA}: 0.1 mM) (r = 0.9944) with a detection limit of 8.3 μM (*S/N* = 3), i_{DA} = 2.50 + 10.29 c_{DA} (c_{DA}: 0.01 mM) (r = 0.9926) with a detection limit of 0.42 μM (*S/N* = 3) and i_{UA} = 0.57+ 2.34 c_{UA} (c_{UA}: 0.1 mM) (r = 0.9928) with a detection limit of 4.3 μM (*S/N* = 3), respectively. Compared with the performances of the previously reported modified electrodes [2,3,26,27], this electrode show excellent analytical performance for detecting AA, DA and UA (**table 1**).

Table 1. Comparison of linear ranges and detection limits with the values reported in previous studies

Ref.	Methods	Linear range (μM)			Detection limit (μM)			Δ Ep (mV)		
		AA	DA	UA	AA	DA	UA	AA/DA	DA/UA	AA/UA
[2]	CV	69-1348	22-440	62-2499	-	-	-	120	170	290
[3]	CV	15-240	6-960	50-800	1.4	0.7	4.5	164	127	291
[26]	DPV	10-1600	6-100	22-350	8.3±0.1	1.7±0.1	3.7±0.2	168	87	255
[27]	CV	19.7-98.8	19.7-98.8	19.7-98.8	-	-	-	163	127	290
This work	CV	80-2000	2.3-17.5	33-330	8.3	0.42	4.3	178	115	293

3.6. Interference experiments and analytical application

The effects of various foreign species on the detection of 0.4 mM AA, 50 μM DA and 0.3 mM UA were investigated. As described above, the mutual interference of AA, DA and UA is negligible. Other effects from common coexisting substances were also studied. The experimental results indicated no obvious interference for detecting AA, DA and UA coexisting with the following compounds: L-lysine (L-Lys) (20), L-cysteine (L-Cys) (20), L-tyrosine (L-Tyr) (20), and glucose (20), with the concentration ratio given in the parentheses. PAYR/GCE was applied for the analysis of AA, dopamine hydrochloride injection and UA in a mixed sample by CV to indicate the reliability of the method for assaying a real sample. The experiment results are shown in **table 2**. The recovery rate is reasonable, indicating that the proposed method can be effectively used for sample determination.

Table 2. Detection of AA, dopamine hydrochloride injection and UA in the mixture

S. No	DA injection (μM)	AA added (μM)	AA added (μM)	DA		AA		UA	
				Found (μM)	Recovery	Found (μM)	Recovery	Found (μM)	Recovery
1	2.5	105	400	2.57	102.8%	111.47	106.2%	393.38	98.35%
2	3.0	130	550	2.92	97.33%	120.29	92.53%	536.32	97.51%
3	9.0	155	830	9.29	103.23%	170.04	109.7%	835.04	100.61%

4. CONCLUSION

Herein, a PAYR/GCE system was prepared and used to assay AA, DA and UA and their mixture; a clear electrocatalytic activity for the oxidation of AA, DA and UA was demonstrated, and large peak separations between AA, DA and UA were found. This means that PAYR/GCE can individually or simultaneously detect these three compounds with good reproducibility, stability, sensitivity and selectivity. In addition, the modified electrode could determine DA in a real sample with good performance characteristics. The excellent performances of the developed electrode indicates its strong potential for application in the assaying of AA, DA and UA in clinical tests.

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