Chinese Chemical Letters Vol. 16, No. 2, pp 237-240, 2005
http://www.imm.ac.cn/journal/ccl.html

Simultaneous Determination of Dopamine and Uric Acid at 2-Amino-5-mercapto-[1, 3, 4]triazole Self-assembled Monolayers Gold Electrode

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Abstract: A newly synthesized reagent 2-amino-5-mercapto-[1, 3, 4]triazole (MATZ) has been used to fabricate self-assembled monolayers (SAMs) on gold electrode for the first time. The SAMs electrode was characterized by electrochemical methods and scanning electronic microscopy (SEM), the SAMs electrode can be used to determinate dopamine (DA) and uric acid (UA) simultaneously with a detection limit of 8×10^{-7} mol/L for DA and 1×10^{-6} mol/L for UA respectively. The SAMs can also be used to detect the contents of DA and UA in synthetic urine sample with satisfactory results.

Keywords: 2-Amino-5-mercapto-[1, 3, 4]triazole, dopamine, uric acid, self-assembled monolayer.

Dopamine is the most typical neurotransmitters which mainly exists in brain tissue and fluids, the change of DA concentration can cause some diseases as Pakinstin's, uric acid is a main final product of purine metabolic alterations or disease appearance or as control during the use of chemotherapeutic drugs, so the accurate determination of DA and UA is of great importance. There are some reports about determination DA or UA using electrochemical methods[1-3], however, there are few reports about determination of UA and DA simultaneously using SAMs modified electrode. In the present paper, a newly synthesized reagent MATZ was used to self-assemble on gold for the first time and the SAMs electrode was characterized by electrochemical methods and SEM, Osteryoung square wave voltammetry (OSWV) was used to detect UA and DA simultaneously.

Experimental

The gold electrode (Φ=2 mm) was treated as reference[3] and immersed in 0.05 mmol/L MATZ methanol solution for 24 h and MATZ self-assembled monolayers (MATZ/Au SAMs) was obtained. The cyclic voltammetry (CV) and OSWV were performed with

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CHI604 and BAS CV-50w electrochemical analyzer with conventional three-electrode cell, MATZ/Au SAMs as the working electrode, a saturated calomel as the reference and Pt wire as the counter electrode. MATZ was synthesized as the reference[4], the structure of MATZ was characterized by FTIR and NMR. The SAMs was characterized by HITACHI X-650 SEM and a. c. impedance in the frequency range of 0.05 to 10^5 Hz in the formal potential of $Fe(CN)_6^{3-/4-}$ (0.22 V *vs.* SCE).

Results and Discussion

$Fe(CN)_6^{3-}$ was used as the electrochemical redox probe to investigate the electrochemical properties of the MATZ/Au SAMs. The cyclic voltammograms (CVs) of MATZ/Au SAMs electrode showed that the redox peak current decreased and peak splitting increased than that of bare Au, which indicated that MATZ had assembled on the Au surface and blocked the mass transfer of $Fe(CN)_6^{3-}$. **Figure 1** shows the SEM images of bare Au and MATZ/Au SAMs. The surface of MATZ/Au SAMs turned to orderliness than that of bare Au and there was membrane above the Au substrate, which verified the results obtained from electrochemical methods. **Figure 2** showed the Nyquist plots of bare Au and MATZ/Au SAMs. There was a straight line in all frequency at bare Au and a semi-circle in high frequency and a 45^0 line in low frequency at the MATZ/Au SAMs electrode, which also indicated that MATZ had assembled on Au. **Figure 3** showed the CVs of the mixture of DA and UA at MATZ/Au SAMs and bare Au electrode in 0.04 mol/L Britton-Robinson buffer solution (BR) (pH=5). A rather broad oxidation peak was obtained and the potentials of DA and UA were indistinguishable at bare Au, but the SAMs resolved the merged voltammetric peak into two well-defined voltammetric peaks. The individual response of DA showed a quasi-reversible process, the redox potentials of DA appeared at 0.28 V and 0.19 V, while the redox potentials appeared at 0.43 V and 0.04 V at bare Au. With regard to UA, similar studies to those done for DA, a sharp irreversible oxidation peak appeared 0.524 V at MATZ/Au SAMs electrode, while the electrochemical oxidation of UA at bare Au appeared a plain peak that almost could not be measured. All the experimental results indicated that MATZ/Au SAMs promoted the electrochemical reactions of DA and UA. **Figure 4** showed the Osteryoung square wave voltammograms (OSWVs) of UA and DA in 0.04 mol/L BR at bare Au and MATZ/Au SAMs electrode. As can be seen from the OSWVs that the oxidation peaks of DA and UA can not be separated at bare Au, while the oxidation peaks of DA and UA can be separated about 0.24 V with the potential of 0.26 V for DA and 0.5 V for UA at the MATZ/Au SAMs electrode. **Figure 5** shows the OSWVs simultaneous increasing the concentration of DA and UA, the inset was the calibration plot between the peak currents *vs.* the concentration of DA and UA. The linear regression equation for DA was I_p (10^{-7} A)=2.495+0.971C (C: 10^{-5} mol/L) with a coefficient of 0.9966 in the range of 2.5×10^{-6} to 5×10^{-4} mol/L, the detection limit (3σ) was 8×10^{-7} mol/L. With regard to UA, from 5×10^{-6} to 1×10^{-4} mol/L, I_p (10^{-7} A) =-15.76+2.84C (C: 10^{-5} mol/L) (r=0.9998), the detection limit (3σ) of UA was 1×10^{-6} mol/L.

The results of interfering experiments showed that 20 folds of ascorbic acid and 100 folds of urea, adenine, glucose did not interfere the simultaneous determination of DA and

UA when the relative standard derivation was 5%. Under the optimum conditions, the oxidation peak potential of ascorbic acid appeared at 0.15 V, while the oxidation peak potential of DA appeared at 0.26 V, so ascorbic acid did not interfere the determination of DA and UA. The MATZ/Au SAMs electrode was used to detect uric acid in urine sample diluted with 10 times BR (pH=5), the measured value of UA was 1.22 mmol/L in healthy person urine which coincided with other reports[5]. The determination results of synthetic urine sample were shown in **Table 1**.

Figure 1 The SEM images of bare Au (a) and MTAZ/Au SAMs (b)

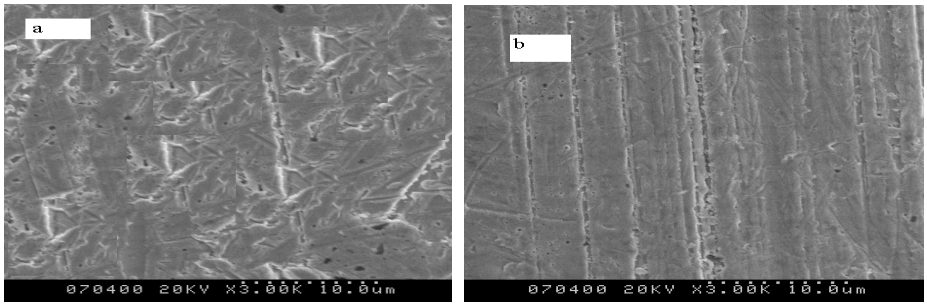

Figure 2 The Nyquist plots of bare Au (a) and MATZ/Au SAMs (b)

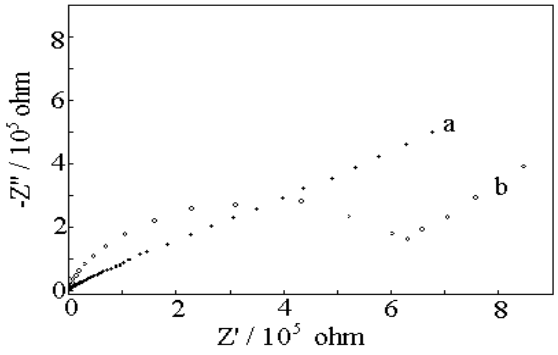

Figure 3 The CVs of mixture (DA+UA) at bare Au (a) and MATZ/Au SAMs (b)

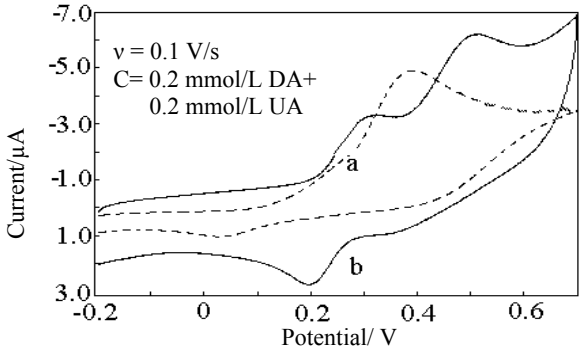

Figure 4 The OSWVs of mixture of DA and UA in BR (pH=5) at bare Au (a) and MTAZ/Au SAMs (b)

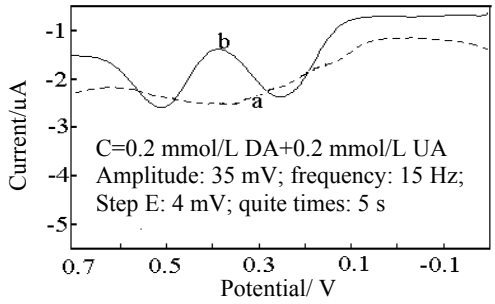

Figure 5 The OSWVs of mixture with DA and UA increasing simultaneously. Inset: calibration plot of DA and UA

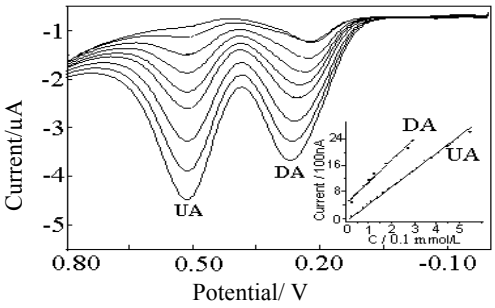

Table 1 The determination of DA and UA in synthetic urine sample

NO.	UA found (10^{-4} mol/L)	DA found (10^{-4} mol/L)	RSD / % n=6	Recovery for DA / %	Recovery for UA / %
1#	1.71	0.195	3.4	97.5	98.0
2#	2.24	0.692	2.6	98.9	102.0

1#: Diluted urine sample added 0.50 mmol/L UA and 0.20 mmol/L DA
2#: Diluted urine sample added 1.0 mmol/L UA and 0.70 mmol/L DA.

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Received 5 January, 2004