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Simultaneous detection of dopamine and uric acid at cobalt (II) octanitro phthalocyanine modified carbon paste electrode

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ABSTRACT

Cobalt (II) octanitro phthalocyanine modified carbon paste electrode (Co (II) ONTPc/CPE) was fabricated and was applied to simultaneous determination of dopamine and uric acid. The modified electrode resolved the overlapped voltammetric responses of dopamine and uric acid in to two well defined cyclic voltammetric peaks. Our results showed that the electrocatalytic activity of Co (II) ONTPc/CPE is more when compared to bare CPE. This electrode can be used to allow the determination ‘of dopamine in the presence of uric acid. The modified electrode showed good selectivity, stability and antifouling properties.

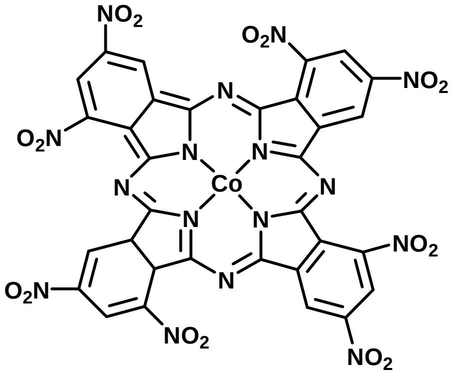
KEYWORDS

Cobalt
phthalocyanine;
Dopamine;
Uric acid;
Cyclic voltammetry.

INTRODUCTION

Dopamine (DA) is the most typical neurotransmitter which mainly exists in brain tissue and fluids, the change of DA concentration can cause some diseases as Parkinson’s. Uric acid (UA) is a primary product of purine metabolism. Its abnormal concentration level in the human body causes many diseases, such as gout, hyperuricaemia and Lesch-Nyan disease. Elevated UA concentration in serum causes kidney damage and cardiovascular disease. Therefore, the research of UA determination is of great importance in reality. Uric acid and ascorbic acid are both present in biological fluids such as blood and urine[1]. Uric acid is a main final product of purine metabolic alteration 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 of DA or UA using electrochemical methods[2-4], however, there are few reports about determination of UA and DA simultaneously using phthalocyanine modified carbon paste electrode[5]. Uric acid has been shown to rapidly adsorb onto carbon paste electrode surfaces[6-8] this phenomenon has led to the development of a controlled adsorption process for its selective determination in flowing stream Uric acid, the primary end product of purine metabolism, and ascorbic acid (AA) are both present in biological fluids such as blood and urine. It has been shown that extreme abnormalities of UA levels are symptomatic of several diseases[9]. As UA is electrochemically active at a carbon-based electrode, its electrochemical detection becomes one of the feasible methods[10]. Earlier electrochemical procedures based on the oxidation of UA at carbon-based electrodes in acidic solutions suffered from interference from AA which can be oxidized at a potential close to that of UA[11]. Various methods, such as an adsorption/medium exchange approach[12], enzyme-based techniques[13,14], chemically modified electrode[15-21] were developed to solve the UA detection problem. Until now, sensitive and selective methods still needed to be developed for the detection of UA due to its clinical significance.

Chemically modified electrodes are an active research area in many aspects of science and technology, having potential application in diverse fields. Some modified electrodes have been used to investigate the electrochemical behavior of uric acid, dopamine and ascorbic acid. Ling Mei Niu et al have studied electrochemical behavior of uric acid at Meso-2, 3-Dimercapto succinic acid self- assembled gold electrode[22]. Zonghua Wang group have modified graphite electrode for the simultaneous determination of dopamine and ascorbic acid[23]. α-Alanine covalently modified glassy carbon electrode was used to study ascorbic acid and dopamine[5]. Simultaneous electroanalysis of dopamine, ascorbic acid and uric acid by poly (vinyl alcohol) covalently modified glassy carbon electrode[24]. Simultaneous determination of dopamine and serotonin in presence of ascorbic acid and uric acid at poly (o-phenyl diamine) modified electrode have been studied[25,26].



Scheme 1: Structure of cobalt (II) octanitro phthalocyanine

In this paper, we report the fabrication of carbon paste electrode with octa nitro Cobalt (II) phthalocyanine. The modified electrode resolved the overlapped voltammetric responses of dopamine and uric acid in to two well defined cyclic voltammetric peaks. Structure of octa nitro Cobalt (II) phthalocyanine is shown in Scheme 1.

EXPERIMENTAL

Reagents and chemicals

Uric acid and dopamine were purchased from Aldrich. High-purity nitrogen was used for deaeration. All solutions were prepared with doubly distilled water. All chemicals were of analytical grade quality and were used with out further purification. The water used was a double distilled. All experiments were carried out at room temperature (≈ 295 K). The solutions were thoroughly deoxygenated by bubbling highly purified nitrogen and a nitrogen atmosphere was maintained over the solution. Phosphate buffer [prepared by mixing 0.2 M $Na_2 HPO_4 . 2H_2O$ and $NaH_2 PO_4 . H_2O$ of pH 4.5] solution was used as supporting electrolyte.

Apparatus and procedure

Electrochemical experiments were performed with EA-201 Electroanalyser [fabricated by Chemilink system, Mumbai, India] in a conventional three electrode electrochemical cell using carbon paste electrode as working electrode, platinum wire as a auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. The surface area of working electrode was 0.039 cm^2.

Preparation of the modified electrode

The graphite powder and silicone oil ratio was 70:30 % by weight and were mixed in an agate mortar for about 40 min. The carbon paste was packed in to the home made carbon paste electrode and then smoothened on a tissue paper till the surface become uniform. About 0.010 g of Cobalt (II) octa nitro phthalocyanine was mixed in carbon paste in an agate mortar and crushed for 20 min. and the prepared modified carbon paste was packed in to the home made carbon paste electrode.

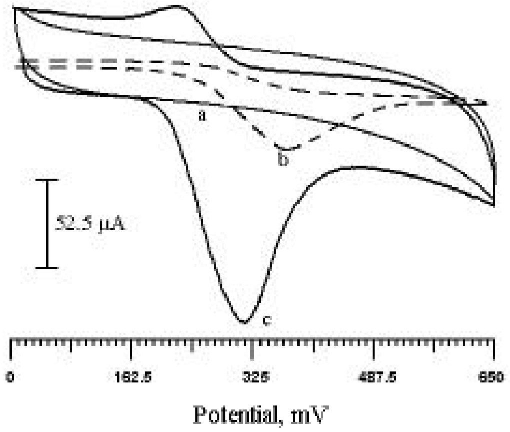


Figure 1: Cyclic voltammograms of (a) blank supporting electrolyte , (b) uric acid 1×10^{-3}mol L^{-1} at Bare CPE , (c) uric acid 1×10^{-3}mol L^{-1} at Co (II) ONTPc carbon paste electrode in phosphate buffer (pH 4.5); scan rate 100 mV s^{-1}

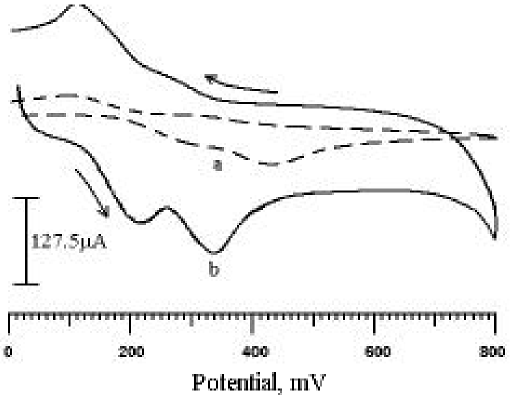


Figure 2: Cyclic voltammograms of simultaneous detection of dopamine 1×10^{-3} mol L^{-1} and uric acid 1×10^{-3} mol L^{-1} at (a) Bare CPE, (b) Co (II) ONTPc carbon paste electrode in phosphate buffer (pH 4.5); scan rate 100 mV s^{-1}

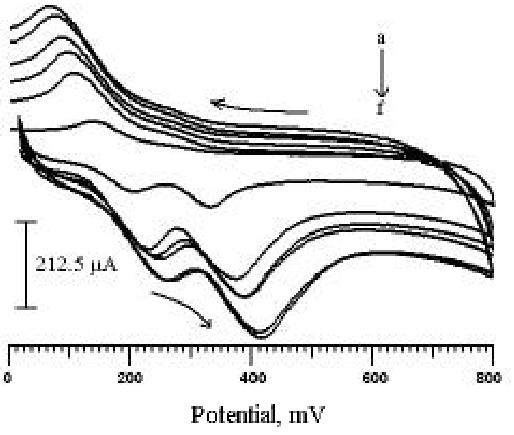


Figure 3: Cyclic voltammograms at different scan rate for simultaneous detection of dopamine 1×10^{-3} mol L^{-1} and uric acid 1×10^{-3}mol L^{-1} at Co (II) ONTPc carbon paste electrode in phosphate buffer (pH 4.5); [scan rate a-f; a: 25 mV s^{-1}, b: 50 mV s^{-1} c: 100 mV s^{-1}, d: 150 mV s^{-1}, e: 200 mV s^{-1}, f: 250 mV s^{-1}]

RESULTS AND DISCUSSION

Electrochemical modification of octanitro cobalt (II) phthalocyanine at carbon paste electrode

Carbon paste electrode was prepared by mixing graphite powder and silicone oil in the ratio 70:30 in an agate mortar for about 40 min. Then cobalt (II) phthalocyanine was added to the carbon paste in different ratio. Starting from 0.005 g to 0.030 g of phthalocyanine was added and then mixed together with carbon paste in an agate for about 20 min. The current signal was higher for 0.010 g of phthalocyanine and the same has been maintained to prepare phthalocyanine modified carbon paste electrode.

Electrochemical behavior of Uric acid at Co (II) ONTPc/CPE

From the cyclic voltammograms of Co (II) ONTPc/CPE in 0.02 mol L^{-1} phosphate buffer (pH 7.4), we observed no redox peak between 0.00 V and 1.0 V. Hence, this modified electrode provides a broad potential window to investigate the chemical behavior of uric acid. Figure 1 shows the cyclic voltammograms of UA at bare CPE, Co (II) ONTPc/CPE respectively. As can be seen in figure 1 shows the oxidation peak of UA is broad irreversible at about 315mV. In contrast, the oxidation current increased greatly and the peak potential shifted negatively to 315 mV at Co (II) ONTPc/CPE. The obviously increased peak current and decrease in the anodic over potential for the uric acid indicates the strong electrolytic function of Co (II) ONTPc/CPE with respect to UA. The shift in the over potential is due to a kinetic effect, hence a substantial increase in the rate of electron transfer from UA is observed[25]. This is attributed to the reversibility of the electron transfer processes[28].

Simultaneous detection of DA and UA at Co (II) ONTPc/CPE

The cyclic voltammograms of DA and UA at Co (II) ONTPc/CPE and bare CPE are shown in figure 2. As can be seen, UA and DA gives small CV peaks response when co-exist in the same sample. When Co (II) ONTPc/CPE was used as working electrode, the peak current increased resulting in the perfect separation of the voltammograms.This interesting aspect of

Co (II) ONTPc/CPE in the large background current attributable to the catalytically active surface.

The oxidation peak height of UA at Co (II) ONTPc/CPE is highest, which means the concentration of UA at Co (II) ONTPc/CPE was higher than that at bare CPE. Then, Co (II) ONTPc/CPE dissociated and diffused rapidly through the porous layer of the graphite surface. Thus phenomenon demonstrated that Co (II) ONTPc not only showed the advantage of Co (II) ONTPc. The anodic peak current i_{pa} exhibited a linear dependence of on the square root or 10 to 300 mVs^{-1}, which is typical for the signal of diffusion controlled electrode process as shown in figure 3.

CONCLUSION

The modification of the electrode surface by Co (II) ONTPc reduced the over potential of DA and UA by obtaining a large peak potential difference of 110 mV and the modification of Co (II) ONTPc/CPE significantly increased the sensitivity of DA and UA. The study has demonstrated that the Co (II) ONTPc/CPE not only exhibited a strong electro catalytic function towards the oxidation of DA and UA, but also resolved the overlapping anodic peaks of DA and UA in to two distinct peaks so that the UA and DA content can be detected selectively in a mixture. Importantly, this modified electrode showed good selectivity, stability and antifouling effects. The Co (II) ONTPc/CPE will hopefully be of good application for further sensor development.

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REFERENCES

[1] Zhongua Wang, Yiming Wang, Guoan Luo; The Analyst., **127**, 1353 **(2002)**.

[2] E.M.Strochkova, Ya.I.Tur'yan, I.Kuselman et al.; Talanta., **44**, 1923 **(1997)**.

[3] W.Zhang, Y.F.Xie, L.T.Jin et al.; J.Chromatography B., **791**, 217 **(2003)**.

[4] G.F.Yang, Z.M.Liu, A.Lu; Acta Chimica Sinica, **59(4)**, 594 **(2001)**.

[5] Mary Kim Halbert, Richard P.Baldwin; Anal.Chem., **57**, 591 **(1985)**.

[6] E.Gonzalez; Anal.Chem.Acta, **242**, 267 **(1991)**.

[7] J.Wang, B.A.Freiha; Bioelectrochem.Bioenerg., **12**, 225 **(1984)**.

[8] X.Cai; K.Kalcher, C.Neuhold, B.Ogorevc; Talanta, **41**, 407 **(1994)**.

[9] V.S.Eswara Dutt, H.A.Mottola; Anal.Chem., **46**, 1777 **(1974)**.

[10] F.Gonzalez, F.Parient, E.Lorenzo, L.Hernandez; Anal.Chim.Acta, **67**, 242 **(1991)**.

[11] J.A.Stanford, J.B.Justice; Anal.Chem., **69**, 359A **(1996)**.

[12] T.Tatsuma, T.Watanabe; Anal.Chim.Acta, **85**, 242 **(1991)**.

[13] E.Miland, A.J.Orderes, P.T.Blanco, M.R.Smyth, C.O.Fagain; Talanta, **43**, 785 **(1996)**.

[14] T.Nakaminami, S.Ito, S.Kuwabata, H.Yoneyama; Anal.Chem., **71**, 4278 **(1999)**.

[15] A.M.Yu, H.L.Zhang, H.Y.Chen; Analyst., **122**, 839 **(1997)**.

[16] L.Zhang, X.Q.Lin; Analyst., **126**, 367 **(2001)**.

[17] L.Z.Zheng, S.G.Wu, X.Q.Lin, L.Nie, L.Rui; Electroanalysis., **13**, 1351 **(2001)**.

[18] J.M.Zen, J.J.Jou, G.Ilangovan; Analyst., **123**, 1345 **(1998)**.

[19] J.M.Zen, P.J.Chen; Anal.Chem., **69**, 5087 **(1997)**.

[20] J.M.Zen, C.T.Hsu; Talanta, **46**, 1363 **(1998)**.

[21] E.Popa, Y.Kubota, D.A.Tryk; Anal.Chem., **72**, 1724 **(2000)**.

[22] Lin Mei Niu, Hong Qun Luo, Nian Bing Li; Instrumentation Science and Technology., **35**, 59 **(2007)**.

[23] Zhongua Wang, Yiming Wang, Guoan Luo; The Analyst., **127**, 1353 **(2002)**.

[24] Yongxin Li, Xiangquin Lin; Sensors and Actuators B: Chemical., **115**, 134 **(2006)**.

[25] T.Selvaraju, R.Ramaraj; J.Appl.Electrochemistry, **33**, 759 **(2003)**.

[26] E.Niranjana, R.Raghavendra Naik, B.E.Kumara Swamy, B.S.Sherigara, H.Jayadevappa; INt.J. Electrochem.Sci., **2**, 923 **(2007)**.

[27] Zonghua Wang, Yiming Wanga, Guoan Luoa; Analyst., **127**, 1353 **(2002)**.

[28] J.Oseryoung, J.J.O· Dea, A.J.Bard, Macel Deker; 'Elctcroanalytical Chemistry', New York, **14**, 86 **(1988)**.