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Original Research Article

Electrochemical determination of Uric acid by persian blue modified electrode with sol gel method

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ABSTRACT

An Au electrode modified with Persian blue (PB), has been applied to the electrocatalytic oxidation of uric acid, which reduced the overpotential by about 165 mV with obviously increased current response. The cyclic voltammetry method was employed to characterize the electrochemical behavior of the chemically modified electrode. The electrocatalytic efficiency of the modified electrode towards uric acid oxidation process depends on the solution pH value, and the optimum pH value for the oxidation of uric acid is 7.0. The overall number of electrons involved in the catalytic oxidation of uric acid and the number of electrons involved in the rate-determining steps are 2, respectively. And diffusion coefficient of the uric acid compound was estimated using the chronoamperometry technique. The proposed method is simple and rapid with excellent selectivity and sensitivity within the linear range of 0.2-2 mM uric acid with a detection limit of M and correlation coefficient $R^2 = 0.9913$.

Keywords: carbon ceramic electrode, Persian blue, electrocatalytic oxidation, uric acid

Introduction

Electrocatalysis of slow electron transfer reactions (CMEs) is one of the most important features of chemically modified electrodes. By reducing the overpotential in the related reaction, the rate of electron transfers in such electrodes increases. Therefore, for a poor kinetic reaction, at a

potential close to the equilibrium potential, such a high current density (i.e., enhanced sensitivity) is enabled by such electrocatalysts. Uric acid [2,6,8-trihydroxypurine] is one of the important nitrogen compounds in the product of purine metabolism, and urine in the human body. Uric acid (UA) is an important biochemical compound that plays an essential role in the renal, central nervous systems, and human metabolism. Abnormal levels of UA in the human body can be caused by various diseases such as Lesch-Nyan syndrome, hyperuricemia, gout, cardiovascular and chronic renal diseases. Therefore, it seems necessary to detect UA to prevent the increase of its abnormal levels in the body; otherwise it can lead to various diseases [1]. The presence of ascorbic acid (AA) as an interfering factor is one of the significant problems in detecting UA by the electrochemical method. The oxidation potential of AA is close to that of UA, and therefore, the bare electrode often suffers effects such as the sedimentation process [2]. Electrochemical methods were considered because they are less time-consuming and more selective than methods based on spectrophotometric or colorimetric. Electrochemical oxidation of UA has widely been used for its determination. Polymer modified/pretreatment electrodes were successfully used and investigated for UA determination. To sensitive determination of UA, different electrochemical biosensors and sensors, such as chemically modified electrodes, ion-exchange membrane coated electrodes [3], poly N, N-dimethyl aniline film coated GC electrodes [4], enzyme-modified electrodes [5], Glassy carbon electrode coated have been developed with ionic liquids and multi-walled carbon nanotube paste, etc. For electrochemical studies, the variety of Sol-gel technology is great in tailoring the matrix [6-8]. This issue has led to intensive and applied research in this field, especially concerning biosensing and sensing. Lev, s and his colleagues, for the first time prepared carbon ceramic electrodes (Aus) using sol-gel technology, which are part of a new class of composite electrodes. One of the important features of gold is the potential to produce high-volume modified electrodes for electro catalytic applications, electroanalytical, and surface-renewable. Aus preparation instructions allow other compounds to be incorporated into its preparation step and as a result, can be modified in bulk. Another benefit is that it is possible to manipulate the electrochemically active and wetted surface of the electrode by judicious selection of the monomers compound applied for the silicate synthesis matrix in aqueous solutions. Due to its versatility, simplicity, versatility, porosity, transparency, efficient flexibility, physical rigidity, and encapsulation in the fabrication process, Sol-gel chemistry presents novel possibilities and methods in the field of chemical biosensors

and sensors [8-11]. Recently, to fabricate effective electrochemical sensors, sol-gel (Aus)-derived ceramic carbon composite electrodes have been significantly applied. [12]. Composite electrodes are synthesized by mixing silicates modified by compounds with an organic structure (ormosil) with carbon, and the prepared mixture is packed on a spread suitable surface or into a tube. Therefore, the ceramic composite can be doped with various types of catalysts or reagents to produce the required sensing material compounds [13-15]. Considering that the sol-gel technique was used to make the chemically modified electrode containing PB, it is used for the electrocatalytic oxidation of uric acid. According to our knowledge, several groups used terpyridine derivatives to modify electrodes. Also, the voltammetry response of electrodes modified by sol-gel technique has been investigated by several research groups. [16-25]. But so far, limited chemically modified electrodes containing PB synthesized by the sol-gel method have not been reported. In this study, we applied an electrode for electro catalytic oxidation of uric acid, which was synthesized through a practical and simple sol-gel preparation technique.

Experimental

Methyltrimethoxysilane (MTMOS), Uric acid, HCl, and methanol has been supplied by Merck. Deionized water was used to prepare all solutions. Graphite powder with high purity properties was purchased from Merck and used. The background electrolyte solution was obtained and prepared from potassium chloride. Phosphate buffer was used to adjust the pH value of the solutions to 7. The ligand of $\text{Fe}_4(\text{III})[\text{Fe}(\text{II})(\text{CN})_6]_3$ (Figure.1) was prepared, and characterized as reported.

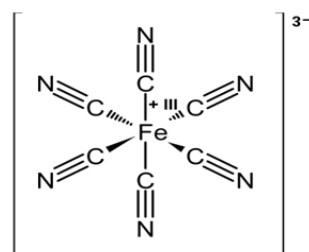


Figure 1. Molecular structure of $[\text{Fe}(\text{II})\text{CN}_6]^{3-}$

To investigate the effect of pH on the process, a universal buffer solution (0.1 M) with different pH values of acetic acid, boric acid, phosphoric acid, and sodium hydroxide was prepared. A three-electrode cell consisting of a saturated Ag/AgCl (saturated KCl) acted as the reference electrode, an Au modified with PB-complex as a working electrode, and all potentials in the text

refer to it. A system was run on a pc using GPES 4.9 software and electrochemical measurements were performed with an Autolab potentiostat/galvanostat model PGSTAT 30 (Metrohm, Utrecht, Netherlands). A personal computer was used for data storage and processing. The pH measurements were made with a Metrohm 632 pH meter using a combined glass electrode. The morphology of AUs modified with PB surface was investigated using a scanning electron microscope (SEM) from SERON technology AIS-2100. All experiments related to the electrochemical process were performed at room temperature (25 ± 0.5 °C).

Preparation of bare and PB modified Au

Carbon ceramic (Aus) electrodes were synthesized in accordance with the method presented by Lev et al. [25]. The fabrication of carbon ceramic electrodes modified with PB is briefly as follows. First, 5 mg of PB was dissolved in 1 ml of methanol and sonicated for 10 minutes to obtain a homogeneous and clear solution. Then, 0.9 ml of resulted solution was mixed with 0.1 ml of hydrochloric acid (0.1 M) and 0.6 ml (MTMOS), and stirred for 5 min to obtain a homogeneous gel solution. In the second step, the obtained mixture was well mixed with 4 mg of PB and 600 mg of graphite powder for 5 minutes and added to Teflon tubes (with 2 mm inner diameter, 3 cm length, and the length of composite material was about 0.5 cm). In addition, a little extra mixture was needed to keep it on top of the electrodes, and the mixture inside the tubes was pressed with a copper stick onto the flat plastic paper through the back. After drying for 48 h at 25 °C, to remove excess composite material, the electrode was first polished with emery paper and then gently wiped with weighing paper to obtain a shiny surface. To make electrical contact a copper wire was inserted from the opposite end. The resulting modified electrode was repeatedly washed with deionized water and used for electrochemical studies. The same method was applied to prepare ceramic carbon electrode activated by PB and bare ceramic carbon electrode.

Results and discussion

Electrochemical behavior of the modified electrode

Using cyclic voltammetry, the electrochemical properties of the ceramic carbon electrode modified with PB were investigated using the sol-gel technique. Figure 2 shows the typical

cyclic voltammogram of bare ceramic carbon electrode modified with PB in 0.1M KCl solutions in phosphate buffered electrolyte solution by sol-gel techniques at a scan rate of 20 mV s^{-1} and a pH value of 7. This clearly indicates that the oxidation peak areas of the modified PB electrode are much larger than those of the bare electrode. A small anodic peak current is observed with uric acid oxidation, while no cathodic peak is obtained, indicating that irreversible heterogeneous charge transfer occurs in this process.

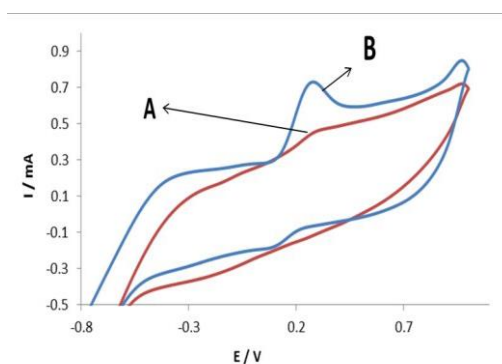


Figure 2. Cyclic voltammograms of the (a) bare Au and (b) PB modified Au in 0.1M KCl solutions in phosphate buffer electrolyte solution (pH = 7) at scan rate 20 mV s^{-1}

Electrocatalytic oxidation of uric acid

To evaluate the oxidation activity of uric acid toward PB-modified Au electrocatalytic, voltammograms were obtained comparing PB-activated carbon ceramic electrode and bare Au electrode in 0.1 M phosphate buffer solutions in the presence of 1 mM uric acid. (pH 7). At the bare carbon ceramic electrode, a larger peak current was seen at about 255 mV, a small oxidation peak current was observed at about 320 mV, and a sharp catalytic oxidation peak is well formed at around 155 mV was seen in PB modified Au. Therefore, compared to the activated carbon ceramic electrode with PB and bare Au, a decrease in the overpotential of uric acid and an increase in peak current in the PB-modified electrode were observed. This indicates an efficient uric acid oxidation reaction on the PB-modified carbon ceramic electrode. By using PB in the carbon ceramic electrode as an electron mediator, the rate of the heterogeneous electron transfer

is increased, and the obtained overpotential for the anodic oxidation of uric acid is significantly reduced.

PB-modified carbon ceramic electrode Characterization

Scanning Electron Microscope (SEM), which has been an essential tool to describe the physical properties of the adsorbent base and surface morphology, the carbon ceramic electrode modified with PB was characterized by it. A typical SEM image of the carbon ceramic electrode, and PB-modified Au are shown in Figure 3.

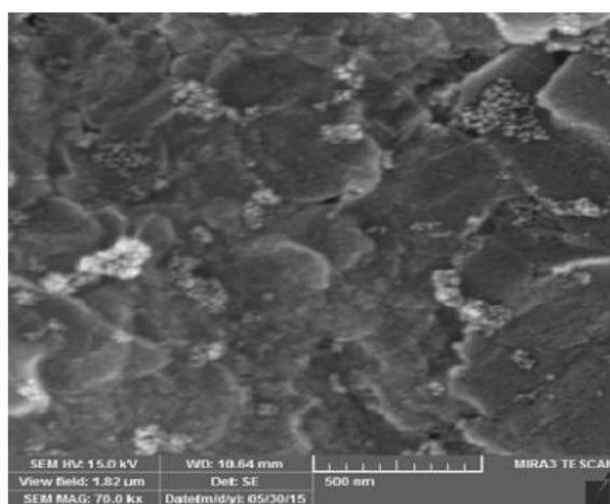


Figure 3. SEM image of PB- modified carbon ceramic electrode

The effect of pH

The oxidation of uric acid is influenced by the pH of the environment, so the pH should be optimized to determine its catalytic properties. Therefore, we investigated the electrochemical behavior of uric acid with different pH values of 2-11 in buffer solutions. (Figure. 4). It can be concluded that catalytic oxidation is more favored at neutral pH values, and for the oxidation of 1 mM uric acid, the anodic peak potential changes to more negative potential values with increasing pH. Therefore, it can be concluded that in a basic solution with a pH equal to 7, the electrocatalytic activity of PB has more suitable conditions for the oxidation of uric acid, and the sensitivity increases at this pH value where the current is maximum. Protonation or deprotonation

of uric acid can lead to a decrease in current at pH below and above 7 where Au significantly causes a change in the formal potential of uric acid.

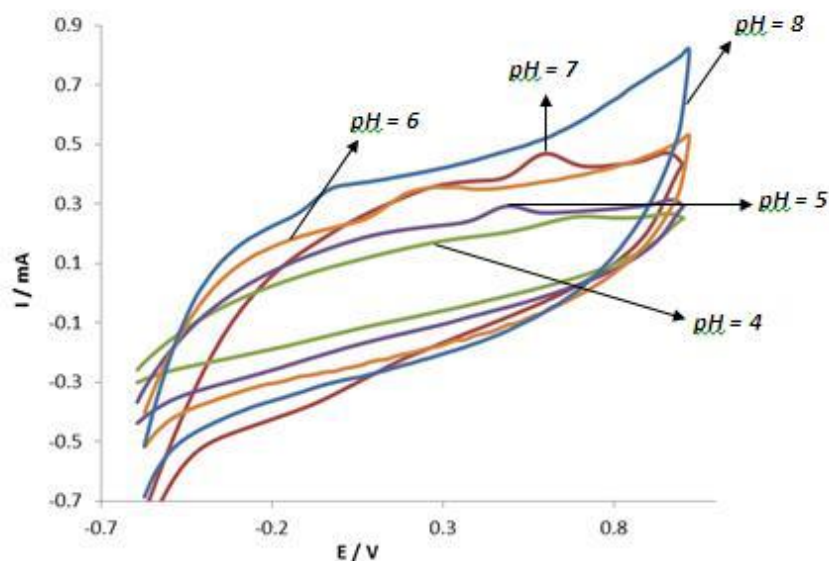


Figure 4. Cyclic voltammograms of PB modified Au in 1mM uric acid solutions with different buffered pHs. Scan rate was 50 mV s^{-1} . Inset shows dependence of the oxidation current of uric acid on pH values.

Cyclic voltammograms of a PB-modified carbon ceramic electrode in 0.1 M phosphate buffer solutions (pH 7) containing 1.0 mM uric acid at different scan rates are shown in Figure 5. The square root of the scan rate is proportional to the peak current for the anodic oxidation of uric acid (figure. 5.) The relevant reaction process involves mass transfer. From Figure 4B, it can be noted that the peak potential shifts and anodic currents increase as the scan rate increases. when peak current values were plotted against $v^{1/2}$, the following linear relationship was resulted (Figure. 3B):

$$I_p = 1 \times 10^{-4} v^{1/2} - 2 \times 10^{-4} \text{ (mV}^{1/2} \text{ s}^{1/2}), R^2 = 0.9752 \quad (1)$$

This behavior indicates that diffusion controls the oxidation process.

Also, a plot of the sweep rate-normalized current ($i_p/v^{1/2}$) vs. sweep rate (Figure.6 inset B) indicates the characteristic shape of an electrochemical-chemical (EC') catalytic process.

The slope of I_p versus $v^{1/2}$ is $17 \mu\text{A}/(\text{mV s}^{-1})^{1/2}$. Therefore, based on the following equation for a, the diffusion is completely irreversible:

$$I_p = 3.01 \times 10^5 n [(1-\alpha) n \alpha]^{1/2} A c D^{1/2} v^{1/2} \quad (2)$$

And considering $(1-\alpha)n\alpha = 0.55$ (see below), $D = 5.49 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (see chronoamperometric studies), $A = 0.118 \text{ cm}^2$, In the anodic oxidation of uric acid, the total number of electrons required is estimated to be $n \approx 2$.

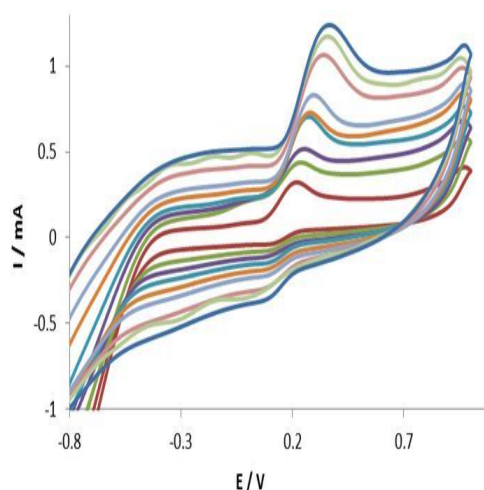


Figure 5. Cyclic voltammograms of modified Au electrode in 0.1M KCl solutions in phosphate buffer electrolyte solution (pH 7) containing 1 mM uric acid at scan rates of a-l: (a) 10, (b) 15, (c) 20, (d) 25, (e) 30, (f) 40, (g) 50, (h) 60, (i) 80, (j) 100, (k) 150, (l) 200 mV s^{-1}

To get useful information about the rate determining step, E_p , is proportional to $\log v$, as could be clearly illustrated in Fig.6A. The slope of E_p versus $\log v$ is 112 mV. The Tafel slope may be estimated based on the equation for a completely irreversible diffusion-controlled process:

$$E_p = (b \log v)/2 + \text{constant} \quad (3)$$

So, $b = 224$ mV. This result is similar to that inferred from polarization measurements. This slope shows a transfer of an electron to be rate limiting assuming a transfer coefficient of $\alpha = 0.73$. Another method can be used to obtain the TOEFL slope, b . A Tafel plot was drawn (Figure.6B). At a scan rate of 10 mV s^{-1} , results derived from data of the incremental section of the current-voltage curve, a slope of $107 \text{ mV decade}^{-1}$ is achieved which shows that the rate limiting step can be attributed to the transfer of one electron to be rate limiting assuming a transfer coefficient of $\alpha = 0.72$. In other words, the rate-determining step is a one electron transfer to obtain N_2 as the final product, followed by a three-electron process. Based on the results and findings, for the oxidation of UA at NiHCF/CPE, the most probable reaction mechanism is shown below:

Figure. 7A shows cyclic voltammograms at different concentrations of uric acid. As a function of the concentration, a plot of the peak current values was plotted. In the concentration range of 0.2-2.0 mM uric acid, the plot was completely linear.

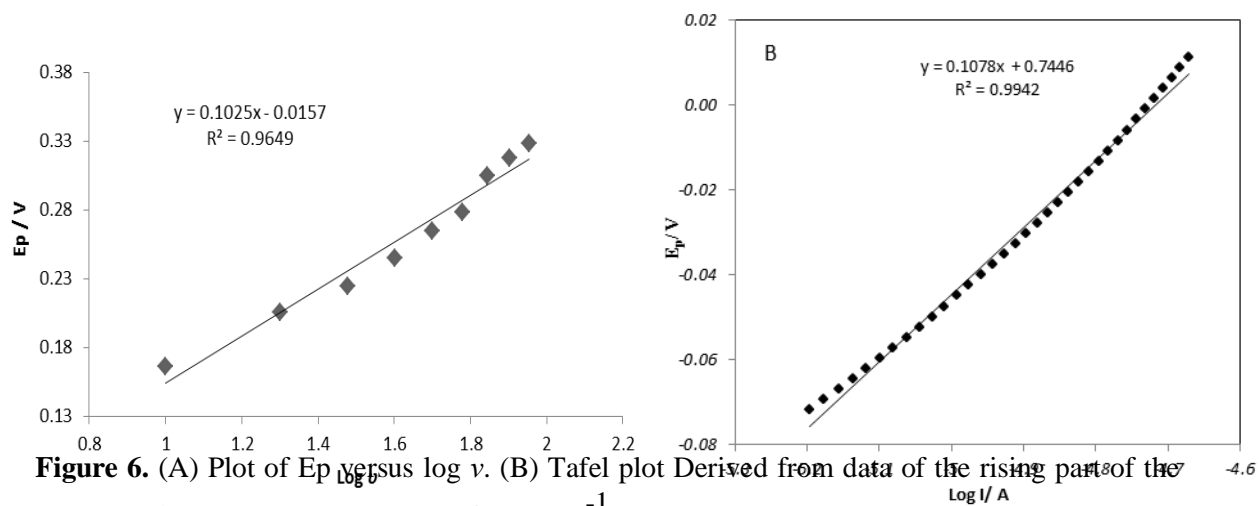


Figure 6. (A) Plot of E_p versus $\log v$. (B) Tafel plot Derived from data of the rising part of the current-voltage curve at a scan rate of 10 mV s^{-1}

Chronoamperometric studies

The oxidation of uric acid was investigated by the electrocatalytic method in carbon ceramic electrode modified with PB by chronoamperometric technique. As shown in Figure 7, the chronoamperograms were obtained with different concentrations for a series of uric acid solutions. Increasing uric acid concentration was associated with increasing anodic currents obtained for a potential step of 400 mV versus SCE. Furthermore, the level of Cottrell current increases with increasing uric acid concentration in the range of 0.2 to 2 mM measured for 60 seconds. In chronoamperometric studies, it is possible to determine the diffusion coefficient of uric acid in the modified electrode. Cottrell's equation justifies the relationship between time and current:

$$I = n F A D^{1/2} c / \pi^{1/2} t^{1/2} \quad (4)$$

Where c is the bulk concentration (mol cm^{-3}), and D is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$). From the slope, the value of D can be obtained and the plot of I versus $t^{-1/2}$ will be linear. Figure 6 B shows experimental plots of the obtained straight line plotted against uric acid concentration (Figure.6 B, inset), from which the diffusion coefficient $D = 3.31 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ for uric acid was calculated.

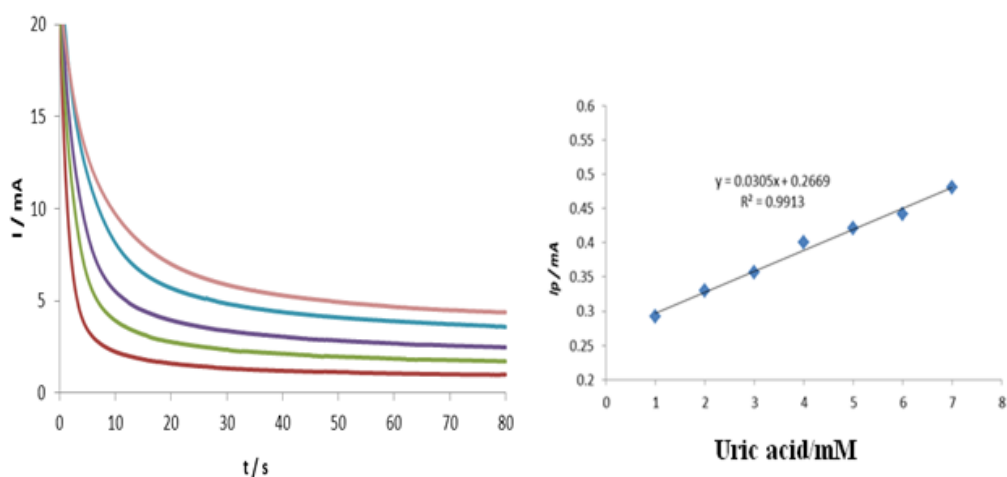


Figure 7. (A) Chronoamperometric response of a PB modified AU in 0.1 M phosphate buffer solution (pH 7.0) containing different concentrations of uric acid for a potential step of 400 mV vs. SCE, in the range of 0.2, 0.4, 0.6, 0.8, 1.2, 1.6 and 2 mM. (B) Plot of plot of I versus $t^{-1/2}$ obtained from chronoamperometric experiments.

Inset shows the relationship between the slope of the linear segments and the uric acid concentration.

Conclusions

In order to oxidation of uric acid, the PB-modified Au electrode act as an electrocatalyst. In an aqueous solution of phosphate buffer containing KCl salt as a supporting electrolyte, this electrode toward uric acid oxidation exhibits excellent electrocatalytic behavior.

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