



# The influencing mechanism of acidity on the oxidation peak currents of guanine and uric acid: hydrogen bond catalysis and degree of auxiliary electrode reduction reaction



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## ABSTRACT

In this paper, a pre-anodized inlaying ultrathin carbon paste electrode with 316L stainless steel as a matrix (316L-PAIUCPE) was constructed by a simple and fast electrochemical method. Taking uric acid (UA) and guanine (G) as the target compounds, it was discussed in detail to illustrate the dependent of the peak currents intensity of ( $i_p$ ) of UA and G upon the pH on the basis of the charge properties of the electrode surface active groups, the formation and catalysis of hydrogen bond, the molecular configuration of target, the degree of oxygen reduction reaction at the auxiliary electrode, the oxidation peak potential, distribution coefficient of both UA and G, and so on. A new mechanism was proposed that decreasing of the  $i_p$  of UA and G with the increasing of pH might result from the degree of oxygen reduction reaction at the auxiliary electrode, although the oxidation peak potential shifted negatively. Moreover, in pH = 5.00 phosphate buffer solution, a linear relationship between oxidation peak current and concentration of UA and G was obtained in the range of  $5.0 \times 10^{-7}$  to  $2.2 \times 10^{-4}$  mol·L<sup>-1</sup> and  $2.0 \times 10^{-7}$  to  $1.5 \times 10^{-4}$  mol·L<sup>-1</sup> with a detection limit of  $8.2 \times 10^{-8}$  and  $3.4 \times 10^{-8}$  mol·L<sup>-1</sup>, respectively. The constructed electrode exhibited excellent reproducibility and stability. Finally, this technique was employed for simultaneous determination of UA and G in human urine with satisfactory results.

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## 1. Introduction

Different electrode materials influence the reaction rate and selectivity of electroactive species at electrode [1–3]. Therefore, developing a novel electrode material was one of the hot spots in electroanalytical chemistry. Glassy carbon electrodes get more and more attention owing to the advantages of good conductivity, high stability, hard texture, wide potential range and could be used for the matrix of different chemical modified electrodes with variety functions [4–6]. But the preparation of glassy carbon material was complex, and the price was relatively expensive. There were many applications of carbon paste electrode (CPE) due to the features of its simple preparation, easy to update surface, wide range of potential [7,8] and so on. But the resistance of CPE would usually vary with the changes of condition of its preparation, and electroactive species are easier to diffuse toward the interior of carbon paste electrode, so that the reproducibility would be affected [9].

In order to minimize the diffusion extent of electroactive species from electrode surface to the interior and achieve good reproducibility, an inlaying ultrathin (about thickness of 100 nm) carbon paste electrode (IUCPE) which adopted nichrome as a substrate was developed by Wang et al. [10], whose advantages was easier to make, low cost, high stability and good electrochemical response to Ag<sup>+</sup> on account of the thickness of carbon paste which embedded in the substrate surface was only about 100 nm. However, so far the research using 316L stainless steel as electrode substrate material had not been reported yet. Owing to its commendable biocompatibility and corrosion resistance in the biological environment, 316L was often used as femoral shaft [11]. The superiorities such as strength, hardness, wear resistance, toughness, oxidation resistance and corrosion resistance etc [12,13], made 316L stainless steel (316L) superior to the common steel. A pre-anodized inlaying ultrathin carbon paste electrode (316L-PAIUCPE) was constructed using the industry leftover 316L as a matrix in this paper. The 316L could not be used as working electrode directly because there was no electrochemical response to the template molecule of K<sub>4</sub>[Fe(CN)<sub>6</sub>]. But after a ultrathin carbon paste was modified in its surface, a good electrochemical response was obtained for the K<sub>4</sub>[Fe(CN)<sub>6</sub>], and excellent results were presented for simultaneous determination

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of UA and G. Compared to the literatures [14–18], the electrode was simple to prepare, low cost and do not need complex modification, and so on. Therefore, it was easier to popularize in conventional laboratory and has a wide application prospect in the future.

Although the acidity of solution had an important influence on the intensity and position of peak current, which were considered as the preferential research conditions in the optimization, it was seldom discussed in the previous reported, especially for the electrode, in which protons could be released in the process of electrode reaction. In fact, so far it had been not reported in detail to understand the mechanism for the effects of acidity on the size of peak current. For example, it was reported that the contents of UA and G were determined under a certain pH value, but it failed to give the reason why was the oxidation peak current influenced by pH had not been discussed [19,20]. For the electrode reaction of which proton could be released at the anode (working electrode) [21–24], the oxidation potential always shifted negatively with the pH increasing, indicating that the reducing ability of electroactive species was improved with increasing pH value. Moreover, in different pH conditions, the shift of the oxidation peak current varies as different electroactive species was employed. Although oxidation potential generally shifted negatively with the rise of pH, in the electrode reaction to lose proton, the dependence of the oxidation peak currents on pH value varied a lot in different reports. Therefore, it is significant to figure out the mechanism of the pH impact on the size of peak current.

In this paper, it was discussed in detail that how the size of oxidation peak current ( $i_p$ ) of UA and G varied with the pH value from the aspects of the degree of oxygen reduction reaction at the auxiliary electrode, the oxidation peak potential and distribution coefficient of UA and G, the charge properties of electrode surface, the formation and catalysis of hydrogen bond, molecular configuration *and so on*. It was shown that the losing electrons abilities for different acid-base species of UA and G at electrode surface could be one of the primary reasons in influencing the size of oxidation peak current. Moreover, it was put forward that the degree of oxygen reduction reaction at auxiliary electrode decreased with the increase of pH, which might be the other reason that led to the variation of the oxidation peak current. On this basis, it was also proposed to a new point of view that the  $H^+$  which released in reaction layer for the oxidization of UA and G migrated to cathode along a concentration gradient to make up for the consumption of cathode reaction for its, which could not only supply the energy for the transport of UA and G from the diffusion layer to the reaction layer, but also promoted the degree of oxidation reaction for UA and G at working electrode. Namely,  $i_p$  of UA and G were enlarged along with the  $H^+$  released in reaction layer migrating from anode toward cathode. Accordingly, the diagram that the size of  $i_p$  for UA and G varied with the pH values could obtain a detailed explanation on the basis of subsequent discussion, and the theoretical foundation could be provided to select the optimal pH value for electroanalytical experiment. Therefore, the research was of great theoretical significance and practical value.

## 2. Experimental

### 2.1. Apparatus and Reagents

Scanning electron microscopy (SEM) images were obtained with a JEOL JSM-7500F scanning electron microscope. All electrochemical experiments were performed with a CHI 832 C electrochemical workstation (Shanghai Chenhua Instrument Company, China) controlled by a microcomputer with CHI 832 C software. A PFS-80 digital pH meter (Shanghai Dazhong Analysis Instrument Company, China) was used for the preparation of buffer solutions. A

conventional three-electrode system was used for all electrochemical experiments, which consisted of a platinum wire as counter electrode, a saturated calomel electrode (SCE,  $Hg/Hg_2Cl_2/3\text{ mol}\cdot L^{-1}\text{ KCl}$ ) as reference electrode, a self-made 316L-PAIUCPE (2.5 mm diameter) as working electrode.

All reagents were of analytical reagent grade and used without further purification. All solutions were prepared with double distilled water.  $1.00 \times 10^{-2}\text{ mol}\cdot L^{-1}$  stock UA (A.R, Kamai Shu Biotechnology (shanghai) Co., Ltd. CAS: 69-93-2) and G (New Jersey, USA, CAS: 73-40-5) standard solutions containing  $0.10\text{ mol}\cdot L^{-1}$  of NaOH were respectively prepared for use, and kept at  $4^\circ\text{C}$ , shielding from light. Urine sample was taken from healthy adult. Graphite powder (the purity is 99.85%, purchased from Shanghai, China) and paraffin oil (C.P. purchased from Xinxiang, China) were used as binding agents for the graphite pastes. The supporting electrolyte used for all experiments was  $0.10\text{ mol}\cdot L^{-1}$  PBS ( $KH_2PO_4-K_2HPO_4$ ) in the pH range of 2.00–10.00.

### 2.2. Fabrication of the pre-anodized inlaying ultrathin carbon paste electrode of 316L stainless steel (316L-PAIUCPE)

An industry leftover 316L stainless steel rod with 2.5 mm diameter and a known length was sealed in a plastic tube of matching length. One end of the rod was used as the electrode connection held out of the plastic tube and the other one as the working electrode surface. Prior to use, the surface of the working electrode was polished with 0.05 mm alumina slurry for 8–10 min, washed with 1: 1 nitric acid, absolute ethanol and double distilled water in an ultrasonic bath for 5 min, respectively, and allowed to dry in air. A 7: 3(w/w) mixture of graphite powder and paraffin was blended in an agate mortar and ground for 20 mins until a homogeneous paste was obtained. Then the pretreated 316L substrate was rubbed in the carbon paste to fabricate the 316L-IUCPE with a layer thickness of carbon paste film in the range of a few tens of nanometers to several micrometers.

The as-prepared 316L-IUCPE was anodized by successive scan for 30 cycles from 0 V to +1.2 V with a scan rate of  $100\text{ mV}\cdot s^{-1}$  in  $0.20\text{ mol}\cdot L^{-1}$  of NaOH solution. After pre-anodization, it was thoroughly rinsed with double distilled deionized water and dried in air, and then the 316L-PAIUCPE was fabricated for subsequent tests.

### 2.3. Experimental procedures

A certain volume of UA and G standard solution was transferred into a 10 mL colorimetric tube and diluted to degree scale with buffer solution of PBS (pH=5.00), and the three-electrode system was installed in the cell. The voltammetric behaviors of UA and G were studied in  $0.10\text{ mol}\cdot L^{-1}$  PBS (pH=5.00) at the surface of 316L-PAIUCPE between 0 V and +1.2 V at a scan rate of  $100\text{ mV}\cdot s^{-1}$  by linear sweep voltammetry. All experiments were accomplished at room temperature.

## 3. Results and discussion

### 3.1. The morphology characteristic of different electrode surfaces

The morphology of the bare 316L electrode surface was characterized by a scanning electron microscope (SEM). Grooves with several micrometers in width could be estimated on the surface of the bare 316L electrode (Fig. 1a), and its depth was approximately in the range of a few tens of nanometers to several micrometers. It was enough for the inlay of the carbon paste to form a layer of an inlaying ultrathin carbon paste which had the film thickness of nanometer level, then an inlaying ultrathin carbon paste electrode was constructed with the bare 316L as the matrix (316L-IUCPE, Fig. 1b). The surface of 316L-IUCPE was flake graphite which

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