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Electrochemical sensor for simultaneous detection of ascorbic acid, uric acid and xanthine based on the surface enhancement effect of mesoporous silica

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ABSTRACT

The measurement of ascorbic acid (AA), uric acid (UA) and xanthine (XA) is very important in the clinical diagnosis because many diseases have been found to be associated with their concentrations. Herein, an electrochemical sensor using mesoporous SiO_2 as sensing material was firstly developed for the simultaneous detection of AA, UA and XA. With distinctive properties such as uniform porous networks, large surface area and high sorption ability, the mesoporous SiO_2 sensor exhibits remarkable surface enhancement effect, and greatly increases the response signals of AA, UA and XA. In addition, the electrochemical responses of coexistence of AA, UA and XA were studied, and three well-shaped oxidation peaks were observed at 0.00, 0.25 and 0.63 V. Further studies suggest that their oxidation takes place independently and has no mutual interference. This sensor possesses high sensitivity, and the limit of detections are 3.0×10^{-6} mol L^{-1}, 1.0×10^{-7} mol L^{-1} and 7.5×10^{-7} mol L^{-1} for AA, UA and XA. Finally, the mesoporous SiO_2 sensor was successfully employed to detect AA, UA and XA in the urine and blood serum samples.

1. Introduction

Ascorbic acid (AA), uric acid (UA) and xanthine (XA) are important biomicromolecules. Studies have proven that many diseases are associated with their concentrations. For example, AA is a powerful antioxidant that is effective against the superoxide radical ion, the hydroxyl radical as well as the singlet oxygen. Thus, the content of AA in biological fluids can be used to access the amount of oxidation stress, which is linked to cancer, diabetes and hepatic disease. UA, the final product of purine metabolism, has been found to be associated with many diseases such as gout, cardiovascular disease, hypertension and obesity since the 19th century [1]. In addition, high concentrations of UA in blood cause deposition of urate crystals, which could ultimately result in chronic joint inflammation, renal impairment and high risk factors for atherosclerosis [2,3]. XA is usually considered as a stable lesion in DNA under physiological conditions, indicating the need for repair [4,5]. Therefore, the measurement of AA, UA and XA is very important in the clinical diagnosis.

Due to their excellent sensitivity, rapid response, low cost, in vivo detection as well as good convenience, electrochemical sensor has obtained wide applications in biomedical monitoring. AA, UA and XA contain electrochemical active groups (see Fig. 1), which can be oxidized at different potentials. So, various electrochemical sensors were reported for their analysis. For instance, a polycalconcarboxylic acid-modified glassy carbon electrode (GCE) [6], a poly (Evans Blue) modified-GCE [7], a gold nanoparticles modified-GCE [8], a palladium nanoparticle-loaded carbon nanofibers modified carbon paste electrode [9], an ordered mesoporous carbon/Nafion composite film modified-GCE [10], a $LaFeO_3$ nanoparticles modified-GCE [11], an electrospun carbon nanofibers modified electrode [12] and a methylene blue adsorbed phosphorylated zirconia–silica composite electrode [13], have been published for the simultaneous determination of AA and UA. Besides, different electrochemical sensors, including a xanthine oxidase immobilized carbon based screen-printed electrode [14], a preanodized nontronite-coated screen-printed electrode [15] and a multi-wall carbon nanotubes modified-GCE [16], were reported for the simultaneous detection of UA and XA. However, to the best of our knowledge, simultaneous detection of AA, UA and XA using electrochemical sensor is very limited.

Since the discovery of ordered mesoporous silica molecular sieves [17], the interest in this research field has expanded all over the world. With distinctive properties such as specific porous networks, large surface area, narrow pore-size distribution and tunable pore sizes over a wide range, mesoporous silica has obtained much attention and broad applications in catalysis [18], drug delivery [19], sorption and separation [20,21], and so on. From the point of electrochemical sensing, these unique

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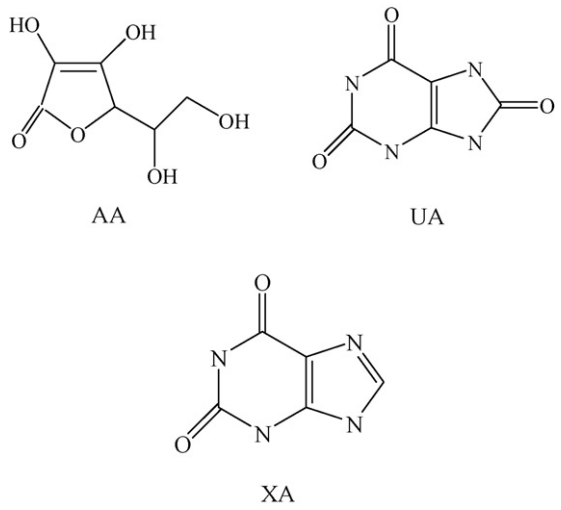

Fig. 1. Chemical structures of AA, UA and XA.

properties strongly indicate that mesoporous silica is an excellent sensing material to prepare electrochemical sensor. Thus, different mesoporous silica-based electrochemical sensors have been developed for heavy metal ions [22], nitroaromatic compounds [23], epinephrine [24] and bisphenol A [25].

Herein, a kind of mesoporous silica (denoted as MCM-41) was synthesized, and used to modify the surface of carbon paste electrode, resulting in a MCM-41 electrochemical sensor. Owing to its large surface area and considerable surface enhancement effect, MCM-41 sensor greatly increases the oxidation peak currents of AA, UA and XA. In addition, the electrochemical responses of coexistence of AA, UA and XA were studied. At the graphite sensor, the oxidation peaks of AA and UA are overlapped, and the peak currents are low. However, the oxidation peak currents remarkably increase, and the oxidation peaks of AA and UA are largely separated at the MCM-41 sensor. The potential mutual interferences of AA, UA and XA were examined, suggesting that their oxidations take place independently at MCM-41 sensor. Therefore, the MCM-41 sensor is very suitable for the sensitive and simultaneous detection of AA, UA and XA.

2. Experimental

2.1. Reagent

All the chemicals were analytical grade and used directly without further purification. Cetyltrimethylammonium bromide (CTAB, purity >99.0%), tetraethyl orthosicate (TEOS, SiO_2 purity >28.4%), graphite powder and paraffin oil were purchased from the Sinopharm Group Chemical Reagent Co., Ltd., China. AA was purchased from Sigma and dissolved into re-distilled water to prepare 0.10 mol L^{-1} standard solution. UA (Sigma) and XA (Sigma) were dissolving into 0.01 mol L^{-1} NaOH to prepare 0.01 mol L^{-1} standard solution, respectively. All the standard solutions were stored at 277 K.

2.2. Instruments

Electrochemical measurements were carried out using CHI 610B electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) in a conventional three-electrode system. The working electrode is MCM-41 sensor, the reference electrode is saturated calomel electrode (SCE), and the auxiliary electrode is platinum wire.

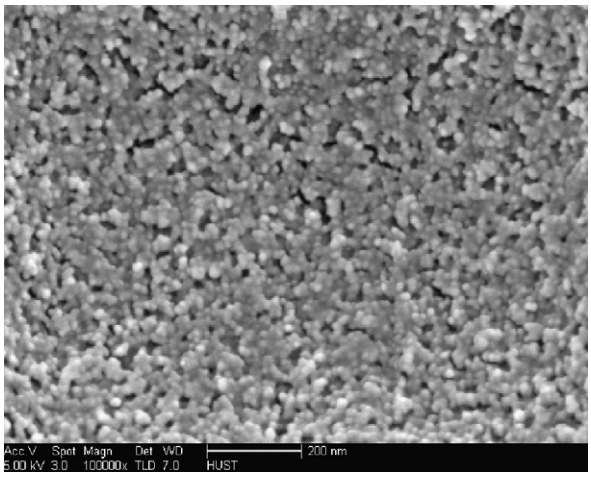

Fig. 2. SEM of MCM-41.

Scanning electron microscopy (SEM) was performed with Sirion 200 microscope (FEI Company, Netherlands).

2.3. Synthesis of MCM-41

MCM-41 was synthesized as the reported method [26] using CTAB as the template. A solution of CTAB in NaOH was prepared and stirred at 298 K. After that, TEOS was added into the solution under stirring to give a gel mixture with following molar compositions: 1 SiO_2/0.25 NaOH/0.1 CTAB/100 H_2O. After 30 min of stirring, the mixture was sealed and then heated at 343 K for 24 h under static conditions. The resulting solid precipitate was recovered by filtration, then washed with re-distilled water and dried at 353 K overnight. Finally, the dried solid precipitate was calcined at 823 K for 6 h to remove CTAB and form mesopores. The morphology of synthesized MCM-41 was characterized using SEM, which shown in Fig. 2. From the SEM image, it is apparent that the synthesized MCM-41 is composed of well-dispersed spherical nanoparticles.

2.4. Preparation of MCM-41 sensor

The synthesized MCM-41 (0.15 g) was mixed with graphite powder (0.85 g) and paraffin oil (0.3 mL) in a carnelian mortar to give a homogenous MCM-41 modified graphite paste. After that, the resulting paste was tightly pressed into the end cavity (3 mm in diameter) of sensor body. Finally, the sensor surface was polished on a smooth paper, and washed with re-distilled water. On the other hand, the unmodified electrode (i.e. graphite sensor) was also prepared by the same procedure but without MCM-41.

2.5. Analytical procedure

Unless otherwise stated, pH 7.0 phosphate buffer (0.1 mol L^{-1}) was used as the determining medium for AA, UA and XA. The differential pulse voltammetry (DPV) curves were recorded from −0.30 to 0.70 V, and the oxidation peak currents were individually measured at 0.00, 0.25 and 0.63 V.

3. Results and discussion

3.1. Electrochemical behaviors of AA, UA and XA

The electrochemical behaviors of AA at graphite sensor and MCM-41 sensor were studied using cyclic voltammetry (CV). Fig. 3 depicts the CVs of 2.0×10^{-4} mol L^{-1} AA in pH 7.0 phosphate buffer. During the cyclic sweep from −0.20 to 0.80 V, an oxidation