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A sensitive and selective pyrosine sensor based on palygorskite-graphene modified electrode

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ABSTRACT

Palygorskite–graphene composite was obtained by the electrochemical reduction of palygorskite–graphene oxide (GO), and the resulted palygorskite–graphene modified glassy carbon electrode (GCE) was used as the amperometric sensor for pyrosine determination. Compared to the graphene modified GCE, the detecting sensitivity of pyrosine was greatly improved at the palygorskite–graphene modified GCE. This was mainly attributed to the high adsorption capability of palygorskite. The effect of the mass ratio of GO to palygorskite was investigated, and the optimum mass ratio of GO to palygorskite was chosen as 2:1. The calibration curve was linear for pyrosine concentration from 21 to 598 μ M, and the detection limit was as low as 5.98 nM (signal-to-noise ratio of 3). The palygorskite–graphene modified GCE also had satisfactory fabrication reproducibility, good determination precision and high detecting selectivity for pyrosine.

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1. Introduction

Pyrosine, an important synthetic pigment, has been widely used in the food industry for improvement and maintenance of color appearance in foods. However, inappropriate intake of pyrosine to human body will result in serious diseases such as hyperthyroidism (Al-Degs et al., 2012). Many techniques, such as high performance liquid chromatography (Kirschbaum et al., 2003; Kiseleva et al., 2003; Minioti et al., 2007), ion chromatography (Chen et al., 1998), spectrophotometry (Nevado et al., 1999; Vidotti et al., 2005), thin layer chromatography (Oka et al., 1987) and capillary electrophoresis (Huang et al., 2002; Prado et al., 2006), have been developed for the detection of synthetic pigment. To the best of our knowledge, however, no work on the direct detection of pyrosine has been reported.

Electrochemical sensor shows great potential in the detection of synthetic pigments owing to its simple instrumentation, simplicity to use, and speed to arrive at a result (Gan et al., 2012; Zhang et al., 2010). Modified electrodes play an important role in the construction of electrochemical sensors, and it has been reported that montmorillonite modified electrode shows strong electrocatalytic activity to the oxidation of catechol due to high adsorption efficiency of montmorillonite (Kong et al., 2012).

Palygorskite is a hydrated octahedral layered magnesium aluminum silicate mineral with large surface area with excellent stability and high adsorption (Fan et al., 2008; Yao et al., 2012). Owing to its extraordinary adsorption ability, it has been used as the electrode material for the detection of phenolic compounds, and improved sensitivity was obtained (Kong et al., 2010, 2011).

In the present work, palygorskite–graphene oxide (GO) was used to modify glassy carbon electrode (GCE), and then it was reduced electrochemically to palygorskite–graphene. Electrochemical detection of pyrosine was firstly reported based on the palygorskite– graphene modified GCE, and a sensitive and selective detection of pyrosine was achieved successfully.

2. Experimental

2.1. Reagents and apparatus

Palygorskite was obtained from Jiangsu NDZ Technology Company (China) and graphite powder was purchased from Shanghai colloid chemical plant (China). Pyrosine, quinoline yellow and brilliant blue were from Jiangsu Provincial Center for Disease Prevention and Control (China). Other chemicals were of analytical grade and used without further purification. All solutions were prepared with doubly distilled water. A CHI 660D electrochemical workstation (China) was used for all the electrochemical experiments.



Note





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2.2. Preparation of the palygorskite-graphene modified GCE

A GCE (3 mm in diameter) was polished with alumina slurry of 0.05 µm diameter on a polishing cloth and then sonicated in distilled water for 10 min before use. GO was prepared from graphite powder by a modified Hummer's method (Hummers and Offeman, 1958; Qin et al., 2012; Xu et al., 2008). In brief, 3 g graphite powder was put into a solution containing 12 mL H_2SO4, 2.5 g K_2S_2O8, and 2.5 g P_2O5. The mixture was kept at 80 °C for 4.5 h. Then, the mixture was cooled to room temperature and diluted with 0.5 L of deionized water and left overnight. The pretreated graphite powder was put into 120 mL cold concentrated H₂SO₄. Successively, KMnO₄ was added gradually and the temperature was kept below 20 °C. 20 mL H_2O_2 (30%) was added to the mixture, and the mixture was filtered and washed with 1:10 HCl aqueous solution followed by 1 L deionized water. The resulting solid was dried and diluted to make GO dispersion. Aqueous dispersion of GO and palygorskite at a mass ratio of 2:1 was prepared by sonicating for 60 min. A 10 µL dispersion of GO and palygorskite was dropped on the GCE which was then allowed to dry at room temperature to form palygorskite-GO. The palygorskite-GO modified GCE was then reduced at -1.0 V for 90 min in 0.3 M phosphate buffer solution (PBS) of pH 4.3 to form palygorskitegraphene modified GCE, which was denoted as palygorskite-graphene A modified GCE. The graphene modified GCE was prepared by a similar procedure except the addition of palygorskite in the dispersion. For a comparison purpose, palygorskite-graphene B modified GCE was prepared by a layer-by-layer assembly described as follows: firstly, a 5 µL dispersion of palygorskite was dropped on the GCE that was allowed to dry at room temperature. Secondly, another 5 µL dispersion of GO was dropped on the palygorskite modified GCE followed by an electrochemical reduction at -1.0 V for 90 min in 0.3 M PBS.

2.3. Analytical procedure

A traditional three-electrode, consisting of a palygorskite– graphene A or a palygorskite–graphene B working electrode, a platinum foil counter electrode and a saturated calomel reference electrode (SCE), was used for the differential pulse voltammetry. The differential pulse voltammograms (DPV) of 0.1 mM pyrosine were recorded in 0.1 M HCl at a scan rate of 50 mV s⁻¹. All experimental solutions were deaerated by bubbling nitrogen for 10 min.

3. Results and discussion

3.1. Characterization of the palygorskite-graphene A modified GCE

The cyclic voltammograms of the palygorskite–GO modified GCE and the palygorskite–graphene A modified GCE in 0.3 M PBS of pH 4.3 were shown in Fig. 1. The current of the palygorskite–GO modified GCE was rather low (curve a), indicating a poor conductivity of palygorskite–GO. However, the current of the palygorskite–graphene A modified GCE was significantly improved (curve b). This was mainly attributed to the high conductivity of graphene (its mobility is $1.5 \times 104 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) (Novoselov et al., 2004), which played a key role in enhancing the beginning electrolytic current after the onset of the electrolysis (Chen and Mu, 2011).

3.2. DPV of pyrosine at palygorskite–graphene A and palygorskite–graphene B

The electrochemical response of pyrosine in 0.1 M HCl was recorded by using differential pulse voltammetry. The DPV of 0.1 mM pyrosine at the graphene modified GCE, the palygorskite–graphene A modified GCE and the palygorskite–graphene B modified GCE were shown in Fig. 2. An obvious oxidation peak appeared at about 0.27 V for all the three electrodes, however, the current



Fig. 1. Cyclic voltammograms of the palygorskite-GO modified GCE (a) and the palygorskite-graphene A modified GCE (b) in N₂-saturated 0.3 M PBS of pH 4.3 at a scan rate of 50 mV s⁻¹.

intensity on the different modified GCE was quite different. The peak current of pyrosine at the palygorskite–graphene A modified GCE (218 μ A) was much higher than that at the graphene modified GCE (132 μ A), indicating that the presence of palygorskite in the modified GCE could remarkably promote the electrode reaction of pyrosine. The electrocatalytic oxidation of pyrosine at the palygorskite–graphene A modified GCE was mainly caused by the large surface area of palygorskite, which exhibited high accumulation efficiency to pyrosine in the solution.

It was noteworthy that at the palygorskite–graphene B modified GCE, the peak current of pyrosine (65 μ A) was even lower than that at the graphene modified GCE. This result was unexpected and might be attributed to the layer-by-layer assembly for the electrode preparation. In this preparation method, palygorskite acted as the inner layer and graphene as the outer layer. Since palygorskite was nonconducting, the inner layer of palygorskite certainly hindered the charge transfer on the electrode-solution interface and therefore the peak current of pyrosine decreased at the palygorskite–graphene B modified GCE.

Since the palygorskite–graphene A modified GCE greatly improved the sensitivity of pyrosine detection compared to the palygorskite– graphene B modified GCE and the graphene modified GCE, it was used in the following experiments.



Fig. 2. Differential pulse voltammograms of 0.1 mM pyrosine in 0.1 M HCl at the palygorskite–graphene A modified GCE (a), the graphene modified GCE (b), and the palygorskite–graphene B modified GCE (c), respectively.

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