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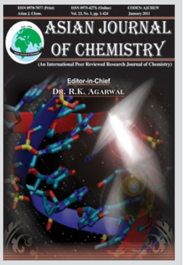

Study of Chitosan-TiO$_2$ Nanoparticles Composite Film Modified Electrode for the Electrochemical Oxidation Behaviour of Nitrite

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An electrochemical sensor for sensitive and convenient determination of nitrite, which was based on the nano-TiO$_2$/chitosan composite film modified electrode, was developed. Owing to the unique properties of nano-TiO$_2$ such as huge surface area, strong adsorptive ability and subtle electronic properties, the electrochemical oxidation signal of nitrite significantly increases at the nano-TiO$_2$/chitosan based electrochemical sensor, suggesting that the nano-TiO$_2$ exhibits obvious enhancement effect to the determination of nitrite. Based on this, a sensitive and convenient electrochemical method was developed for the determination of nitrite. The oxidation current was linearly related to nitrite concentration over the range of 5.0×10^{-6}-1.0×10^{-3} M, with a detection limit of 1.28×10^{-6} M. The results indicate that the nano-TiO$_2$/chitosan composite film modified electrode is an attractive thin film for the development of fast, simple and sensitive sensors.

Key Words: Nitrite, Chitosan, TiO$_2$ nanoparticles, Electrochemistry.

INTRODUCTION

Nitrite is ubiquitous within environmental, food and bio-resources. Nitrite ions can interact with amines to form carcinogenic N-nitrosamines[1] and it has well-documented toxicity to animals[2]. Therefore, determination of trace nitrite is necessary for environmental reason and public health. Many analytical methods have been developed for nitrite determination in recent years, for example, chromatography[3,4], spectrophotometry[5,6], flow injection analysis[7] and capillary electrophoresis[8]. However, it is noticed that the most of above methods need complicated process and expensive instruments. In addition to these methods, owing to the rapid response, cheaper and simple use, electrochemical approaches are favourable for nitrite determination[9-15]. Among the electrochemical modified electrode methods for the detection of nitrite, nanoparticles composite film modified electrodes have been used extensively, because of its high sensitivity and selectivity, strong adherence to electrode surface and chemical stability of the film[9,10,16].

Chitosan is the (β-1,4)-linked glucosamine derivative of chitin,which occurs widely as a naturally occurring biopolymer in the exoskeleton of crustaceans, in fungal cell walls and in other biological material. And the pKa values[17] of chitosan is *ca.* 6.3, when the pH is below the pKa, most of the amino groups would be protonated and the chitosan would take positive charges. The protonated chitosan could adsorb anions in acidic solution to the electrode surface, which could greatly enhance the electrochemical signals. Besides this, chitosan have excellent membrane-forming ability, good adhesion, non-toxicity and high mechanical strength[18]. With the rapid development of biopolymer film modified electrodes, chitosan has been widely used as an immobilization matrix for electrochemical sensor[10,19-23]. On the other hand, it is well known that nanoparticulate metal oxides exhibit intrinsic surface reactivity and high surface areas, which could strongly chemisorb many substances[24]. TiO$_2$ nanoparticles has been drawning increasing attentions for its large surface area, good dispersing properties, fast electron transfer ability and allowing for the applications of various biochemical sensors[22,25,26].

In this work, a simple method for fabricating a chitosan film containing TiO$_2$ nanoparticles was established. The electrochemical behaviour of nitrite on the nano-TiO$_2$/chitosan composite film modified gold electrode was investigated in details, which revealing that the film possesses the ability of adsorptive accumulation for nitrite. Therefore, a simple, rapid and sensitive electrochemical method for the determination of nitrite was developed.

EXPERIMENTAL

Cyclic voltammetry (CV) experiments were performed on Electrochemical Workstation LK2005 (LANLIK Instruments company, Tainjin, China). A conventional three-electrode system was equipped. The working electrode was a gold disk electrode (5 mm diameter)which would be used as the basal electrode for fabrication. A saturated calomel electrode (SCE) and a platinum wire served as reference and auxiliary electrode, respectively. A Model pHS-23 acidity meter (Shanghai Second Analytical Instruments, China) was used for pH determination.

A 1.0×10^{-2} mol/L stock solution of nitrite was prepared by direct dissolution of sodium nitrite in water and store in a cool dark area. chitosan (85-95 % deacetylation) and nano-TiO_2 (average particle size 20 nm) were obtained from Shanghai Chemical Reagents (Shanghai, China). Other reagent, such as acetic acid, anhydrous ethanol *etc*., were analytical reagent and were used without further purification. Moreover, double distilled water was used throughout. The supporting electrolyte was 0.1 M sodium nitrate solutions, whose pH value adjusted by sodium hydroxide solution or hydrogen chloride.

Preparation of nano-TiO_2/chitosan composite film modified gold electrode: To prepare nano-TiO_2/chitosan mixture solution, 0.2 g chitosan flakes was dissolved in 10 mL of 0.1 M acetic acid solution, then 0.3 g nano-TiO_2 was added in chitosan solution by sonicating for 1 h at room temperature. Prior to modification, the basal gold electrode was polished with an aqueous suspension of 0.5 mm Al_2O_3 slurry. After polishing, it was rinsed with doubly distilled water and ultrasoniced in ethanol and doubly distilled water about 5 min, in order to remove adsorbed substances on the electrode surface. Finally, a 8.0 μL of nano-TiO_2/chitosan mixture solution spread uniformly on gold electrode substrate for film formation by spin coating and drying at room temperature.

Measurement: The electrochemical behaviour of the nano-TiO_2/chitosan composite film modified gold electrod was carried out in 0.1 M sodium nitrate solutions at pH = 2.6 in the potential range between 0.5 and 1.0 V. Application of the electrode for the determination of nitrite was evaluated by running the cyclic voltammetric in 0.1 M sodium nitrate solutions in the potential range between 0.5 and 1.0 V at the scan rate of 50 mV/s. The high-purity nitrogen was used for deaeration of the prepared aqueous solutions during the measurements.

RESULTS AND DISCUSSION

Effect of the supporting electrolyte and solution pH: As an important factor, pH values have a great effect to the oxidation peak current of nitrite. The effect of pH on the voltammetric response of the modified electrode was studied in four different electrolytes. 0.1 M phosphate buffer solution, 0.1 M acetate buffer solution, 0.1 M sodium nitrate solution and B-R buffer solution as the supporting electrolyte which contain 1.5×10^{-4} M nitrite. It was found that the anodic peak current of nitrite in 0.1 M sodium nitrate solution was more sensitive and its shape was more preferable than the other three supporting electrolyte solutions. Thus, the effect of pH on the voltammetric response of nitrite was studied in 0.1 M sodium nitrate solution in the pH range of 1.0-6.0. The highest oxidation peak current of nitrite was observed in pH 2.6. So, the following experiments were used with the pH 2.6 sodium nitrate solution. According to the previous workers[27-29], it is learned that the observed oxidation peak was attributed to the conversion of NO_2^- to NO_3^- through the oxidation process of a two-electron and the electrode reaction involved proton.

Electroxidation behaviour of nitrite on the nano-TiO_2/chitosan composite film modified gold electrode: The cyclic voltammograms of nitrite at the bare gold electrode, chitosan/gold electrode and nano-TiO_2/chitosan composite film modified gold electrode,were shown in Fig. 1.

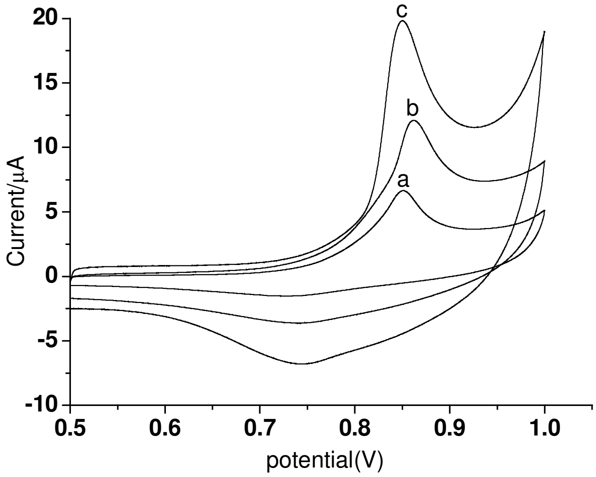

Fig. 1. Cyclic voltammogram of 1.5×10^{-4} M nitrite at gold electrode (a), chitosan film (b) and nano-TiO_2/chitosan composite film modified gold electrode (c), in $NaNO_3$ solutions (0.1 M, pH 2.6) at 50 mV s^{-1} scan rate

At bare [curve (a)], chitosan film [curve (b)] modified and nano-TiO_2/chitosan composite film modified gold electrode [curve (c)], scanning in the reverse direction did not produce a cathodic peak which indicate the irreversibility of the oxidation process. And, the nano-TiO_2/chitosan composite film modified gold electrode [curve (c)] showed 1.8-fold increased anodic current response relative to that at chitosan/gold electrode [curve (b)] and about 3-fold to that at bare gold electrode [curve (a)]. The changes in peak currents show that nano-TiO_2/chitosan composite film modified gold electrode held the properties that was favourable to the oxidation of nitrite.

The effect of scan rate on the oxidation of nitrite was studied at the nano-TiO_2/chitosan composite film modified electrode was shown in Fig. 2.

The oxidation peak current of nitrite increased linearly whith increasing the scan rate and the peak potentials shift positively. At low scan rate, the peak current Ipa of nitrite oxidation increases palinearly with V, as expected for a adsorption reaction of the slope of the straight line (R = 0.996). The results were shown in inset of Fig. 2, they were characteristics of surface-confined thin-layer electrochemical behaviours.

Further studies were performed to investigate the effect of the nitrite on the response of the modified composite film.

First, the effect of the chitosan concentration and the amount of chitosan modifier on the properties of the nanocomposite films are studied. Chitosan is derived from chitin by deacetylation and it has many active groups such as amino groups and hydroxy groups, which has high reactivity to several function groups[17]. In acidic solution, chitosan in solution is protonated and attracts negatively charged ions such as NO_2^-. The process of protonation and electrochemical reaction could be expressed as follows:

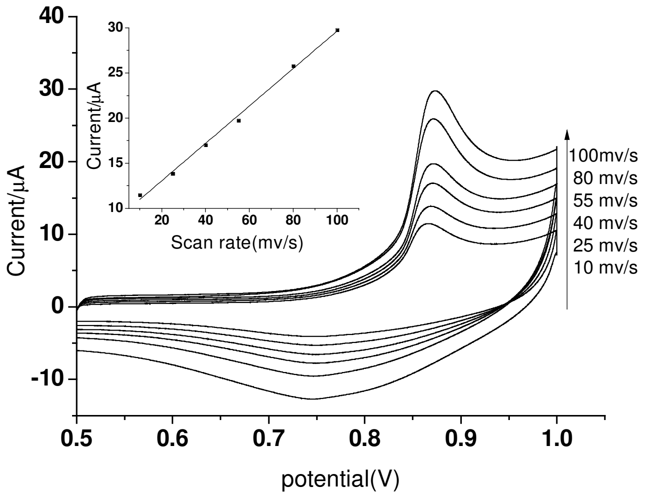

Fig. 2. Cyclic voltammogram of 1.0×10^{-4} M nitrite at nano-TiO_2/chitosan composite film modified gold electrode in $NaNO_3$ solutions (0.1 M, pH 2.6) at scan rate from 10-100 mV s^{-1}, (insert) the linear relationships of the anodic peak current (I_p) *versus* the scan rate (v) in $NaNO_3$ solutions (0.1 M, pH 2.6)

Bare electrode: $NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2e^-$

The modified electrode of chitosan film are shown in Fig. 3. With the increase of either the chitosan concentration or the amount of chitosan modifier, the thickness of the nanocomposite films increased and the response of the resulting electrodes to nitrite also increased in theory. However, too thick a nanocomposite film will result in large noise and slow response of sensors. So, the chitosan concentration of 2.0 wt % and the amount of 8.0 μL chitosan mixtures were selected.

Second, the effect of addition of nano-TiO_2 into chitosan mixtures was explored. Compared with the electrodes modified with mono-component, it can be seen that the response of the gold electrode modified with nano-TiO_2/chitosan composite film is much larger than that of the electrodes modified with only chitosan. It indicates that when there is no nano-TiO_2, the chitosan film only adsorb a small quantity of NO_2^- and results in a small response to nitrite. In other words, the advantages of the nano-TiO_2/chitosan composite film is that the electrochemically generated nano-TiO_2 is stabilized by chitosan and evenly dispersed within the chitosan film, which forms an excellent platform for response to nitrite. It was indicated that the addition of nano-TiO_2 in chitosan can increase porosity on film surface, this could be due to nano-TiO_2 particles possibly holding chitosan molecules against centrifugal forces applied during spin coating process. And nano-TiO_2 added chitosan can enhance the peak current, that may be due to higher probability of hydrogen and covalent binding between -OH group in chitosan molecules and Ti-O-Ti[30].

Amperometric detection of nitrite: From Fig. 4, it can be seen that a series of standard solutions of nitrites were determined by cyclic voltammetry. The oxidation current was linearly related to nitrite concentration over the range 5.0×10^{-6}-1.0×10^{-3} M, which suggested a stable and efficient catalytic property through the nano-TiO_2/chitosan composite film. And, the detection limit was 1.28×10^{-6} M. The linear regression equation was $Ip_a = 12.0160 + 0.0439C$. The stability of the modified electrode was also investigated. The modified electrode was evaluated by examining the cyclic voltammetric peak currents, no obvious changes of cyclic voltammetric response of the electrode can be observed after the nano-TiO_2/chitosan composite film modified gold electrode was stored at room temperature for 3 weeks, which suggested that the modified electrode had an excellent stability.

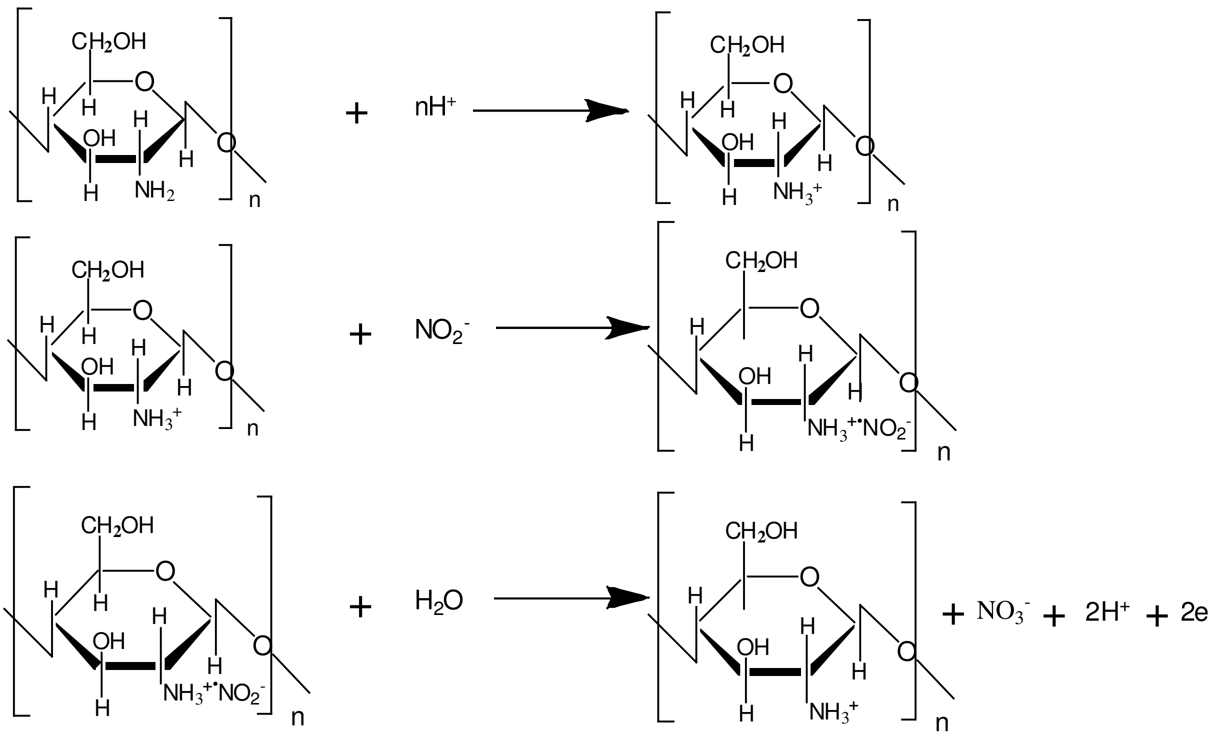

Fig. 3. Modified electrode of chitosan film

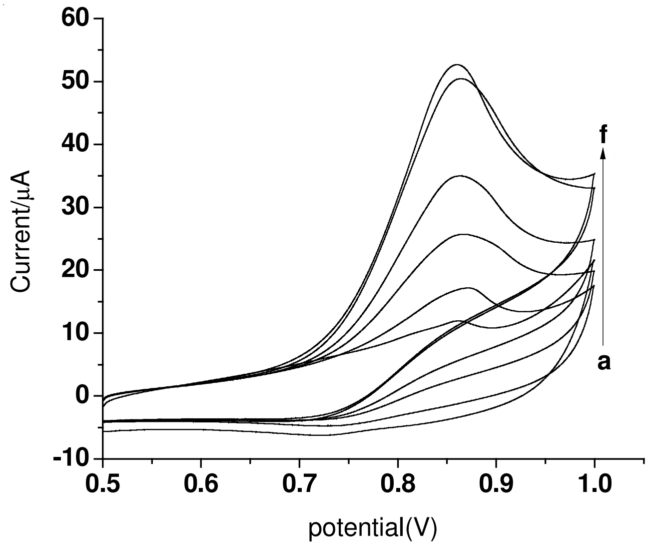

Fig. 4. Cyclic voltammograms of nano-TiO_2/chitosan composite film modified gold electrode in $NaNO_3$ solutions (0.1 M, pH 2.6) with (a) 5, (b) 100, (c) 300, (d) 500, (e) 800 and (f) 1000 μM nitrite. Scan rate, 50 mV s^{-1}

Interference: The influence of various foreign species on the determination of 1.0×10^{-4} M nitrite was investigated. The results showed that most of the ions, such as K^+, Na^+, Ca^{2+}, Mg^{2+}, Pb^{2+}, NH^{4+}, Zn^{2+}, Ba^{2+}, SO_4^{2-}, SO_3^{2-}, Ac^-, $H_2PO_4^-$, NO_3^- and PO_4^{3-} did not interfere with the determination. Some foreign species such as Br^-, I^- and $S_2O_3^{2-}$ also show no interference if their concentrations were within 10 times of nitrite concentration. Therefore, these results demonstrated the modified electrode have good selectivity for nitrite.

Conclusion

In this paper, a blending method was described for preparing a nano-TiO_2/chitosan composite film modified gold electrodes. The nano-TiO_2/chitosan composite film modified gold electrodes was used as the basal electrode for the investigation of direct electrochemistry of nitrite at room temperature. A rapid and sensitive mehod for the determination of nitrite was established by using cyclic voltammogram technique. The linear range was 5.0×10^{-6}-1.0×10^{-3} M and the detection limit was 1.28×10^{-6} M. These results suggest that nano-TiO_2/chitosan composite film are superior electrode modified material and it can be used as an electrochemical sensor to detect nitrite with satisfactory results.

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