Journal of New Materials for Electrochemical Systems 13, 349-354 (2010)
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Electrochemical Behavior of Resorcinol at a Gold Nanoparticle/ Carbon Nanotube Composite Modified Glassy Carbon Electrode

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Received: July 18, 2010, Accepted: November 19, 2010, Available online: December 07, 2010

Abstract: *A Gold nanoparticle/carbon nanotube composite modified glassy carbon electrode was fabricated by simple casting method and was used to study the electrochemical behavior of resorcinol in neutral pH condition. The modified electrode exhibited synergistic electrochemical catalytic effects of carbon nanotube and gold nanoparticles on the electrochemical reactions of resorcinol. The intensity of oxidation peak of resorcinol on the modified electrode was enhanced about 10-times compared with that on the bare electrode. The electrochemical reaction was mainly controlled by diffusion process. The layers of composite, pH, electrolytes could influence electrochemical signal of resorcinol. The stability and reproducibility of the modified electrode is good. The oxidation peak current was proportional to resorcinol concentration in the range of* 1×10^{-5} *to* 1×10^{-3} *mol/L and the detection limit of resorcinol was* 5.0×10^{-6} *mol/L, demonstrating that it is promising for the detection of resorcinol using the gold nanoparticle/carbon nanotube modified glassy carbon electrode.*

Keywords: gold nanoparticle, carbon nanotube, resorcinol, modified electrode, glassy carbon electrode

1. INTRODUCTION

Electrochemical detection of analyte is a very elegant method in analytical chemistry. The interest in developing electrochemical-sensing devices for use in environmental monitoring, clinical assays or process control is growing rapidly. Electrochemical sensors satisfy many of the requirements for such tasks particularly owing to their inherent specificity, speed of response, sensitivity and simplicity of preparation. Glassy carbon electrode is one of the most commonly used electrodes in fabrication of electrochemical sensors. However, a bare glassy carbon electrode often suffered from low sensitivity, large values of concentration as detection limit, and electrode fouling. To overcome these limitations, the modification of electrode surface with nanomaterials is a good choice. In the past two decades, nanomaterials including metal nanoparticles and carbon nanotube (CNT) have become the focus of scientific researchers because of their unique electronic, optical and catalytic properties [1]. Since their discovery, carbon nanotubes have become one of the most exciting and well investigated nanoscale materials. CNT-modified electrodes have been used frequently for the development of biosensors and have been proved to have excellent electroanalytical properties such as wide potential windows, low background current and good biocompatibility [2-5]. In addition to enhanced electrochemical reactivity, CNT modified electrode have also been shown useful to accumulate important biomolecules and to alleviate surface fouling effects. Metal nanoparticle is another kind of attractive materials in fabricating modified electrode because of its high surface-to-volume ratio and high surface energy. They frequently display unusual physical and chemical properties, depending on their size, shape, and stabilizing agents [6-8]. Even though the electrocatalytic activity of CNTs and metal nanoparticle films individually shows good results, some of the biochemical compounds do not undergo electrocatalysis. To overcome this difficulty, new studies have been developed for the preparation of composite films composed of both CNTs and metal nanoparticles. Noble metals such as Au [9], Pt [10] Ru [11], have been immobilized on CNTs surface by different methods to form nanohybid films. These new hybrid nanomaterials have been shown to exhibit excellent catalytic activity, electrical conductivity and photonic properties. Among these nanocomposites, of particular interest are nanocomposites involving gold nanoparticles, due to the combination of the unique electronic properties of carbon nanotube and their ease of surface

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modification, along with the biocompatibility of gold nanoparticles. Resultant composite materials have provided physicists, chemists and biologists vast opportunities to develop unique catalysis and light harvesting and sensing systems [12-17].

As one kind of polyphenolic compounds, resorcinol is widely used as industrial intermediates for the manufacture of drugs, pesticides, dyestuffs and so on. Resorcinol could impact environment and human health seriously once it was discharged into the receiving water systems with industrial waste streams. Therefore, to develop a highly sensitive, selective and simple method for the low level detection of resorcinol is of significance. Up to date, the technology involved in the detection of resorcinol limited to chromatographic [18-21], spectrophotometric [22-24], and chemiluminescence [25,26] etc. There has seldom report about the detection of resorcinol with electrochemical methods, which is partly due to the weak signal of resorcinol obtained at traditional electrodes, such as gold electrode and glassy carbon electrode. In recent years, many electrochemical inactive species obtained satisfied electrochemical signals at various nanoparticle modified electrodes. Therefore, it is necessary to study electrochemical behaviors of resorcinol at nanoparticle modified electrodes to develop more sensitive methods in detecting resorcinol. In this paper, a gold nanoparticle/carbon nanotube modified glassy carbon electrode was fabricated by a simple casting method for its simplicity, controllability and versatility. The electrochemical responses of resorcinol at the modified glassy carbon electrode were studied. The results revealed that resorcinol exhibited excellent electrochemical response at the modified electrode, which make it possible to detect resorcinol by electrochemical method. The effect of layers of composite, pH, potential scan rate and electrolytes, as well as linear range of resorcinol were also studied in detail.

2. EXPERIMENTAL

2.1. Reagents

Multi-walled carbon nanotubes were purchased from Shenzhen Nanotech Port Co., Ltd (Shenzhen, China). Chloroauric acid ($HAuCl_4{\cdot}3H_2O$) was obtained from Shanghai Reagent (Shanghai, China). A 1.0 g/L $HAuCl_4$ stock solution was prepared by dissolving 1 g of $HAuCl_4$ in 1 L of redistilled water and stored at 4 ^{o}C. Resorcinol was purchase from Shanghai Reagent (Shanghai, China). Resorcinol working solutions were prepared by dissolving resorcinol in 0.1 mol/L phosphate buffer solutions (PBS) of different pH before each electrochemical measurement. All the other reagents used in the experiment were of analytical grade and double-distilled water was used throughout.

2.2. Synthesis of gold nanoparticles

Gold colloids with diameter of 16 nm were prepared according to the literature [27] and our previous work [28]. The process is as follows: A 50 mL portion of $HAuCl_4$ (10^{-2}% w/w) solution was heated to boiling. While stirring vigorously, 1 mL of trisodium citrate (1 wt %) was added rapidly. The solution was maintained at the boiling point for 15 min, during which time a color change from gray to blue to purple was observed before a wine-red color was reached. The heating source was removed, and the colloid was kept at room temperature for 15 min and then stored at 4 ^{o}C. The average diameter of synthesis gold nanoparticles was ~16 nm [28].

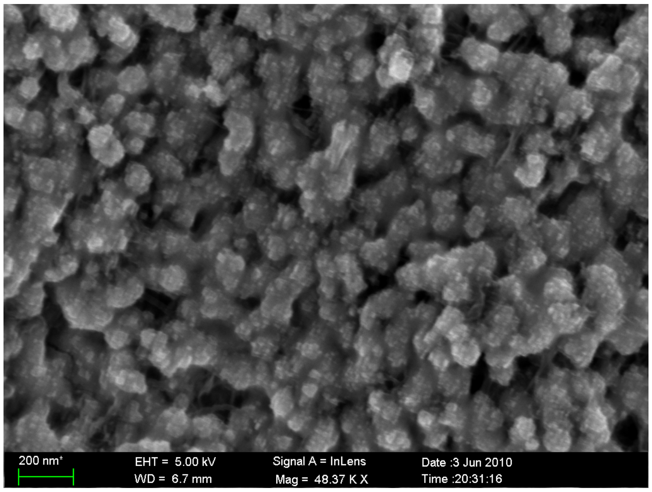

Figure 1. SEM image of GNP/CNT modified glassy carbon electrode.

2.3. Fabrication of gold nanoparticle/carbon nanotube composite modified electrode

The CNT suspension was prepared by dispersing 10 mg CNT in 10 mL DMF solvent with sufficient ultrasonication for about 1 h until a relatively uniform CNT suspension was obtained. Prior to modification, a glassy carbon electrode (3 mm in diameter) was polished to a mirror with polish paper and alumina pastes of 0.5 μm, and cleaned thoroughly in an ultrasonic cleaner with alcohol and water successively. Multi-walled carbon nanotube modified glassy carbon electrode (denoted as CNT/GCE) was prepared by coating 10 μL MWNTs suspension on the surface of bare electrode and allowed to evaporate liquid at room temperature in the air. Then, 10μL gold colloid solution was coated on CNT/GCE and dried at room temperature in the air to form gold nanoparticle/carbon nanotube modified glassy carbon electrode (denoted as GNP/CNT/GCE). The surface state of the GNP/CNT/GCE was characterized by scanning electron microscopy (SEM) (JEOL JSM-6700F, Japan).

2.4. Equipment and electrochemical methods

A LK2005A instrument (lanlike Co. Ltd, China) is employed for the electrochemical measurement. The working electrode is GNP/CNT/GCE. A Pt plate and a saturated calomel electrode (SCE) are used as the counter and reference electrode, respectively. All potentials in this study are reported with respect to saturated calomel electrode (SCE). Electrochemical impedance spectroscopy (EIS) was recorded at an amplitude of 10 mV in the frequency range from 2 kHz to 0.1 Hz. Complex impedance plots were obtained in $K_3[Fe(CN)_6]$ solution. The working solution is deaerated with high purity nitrogen gas for 10 min prior to the measurement.

3. RESULTS AND DISCUSSION

3.1. Surface state of a GNP/CNT/GCE

The surface state of the electrode modified with GNP/CNT composite film was characterized by SEM as shown in Fig. 1. It was found that gold nanoparticles were uniformly distributed in the

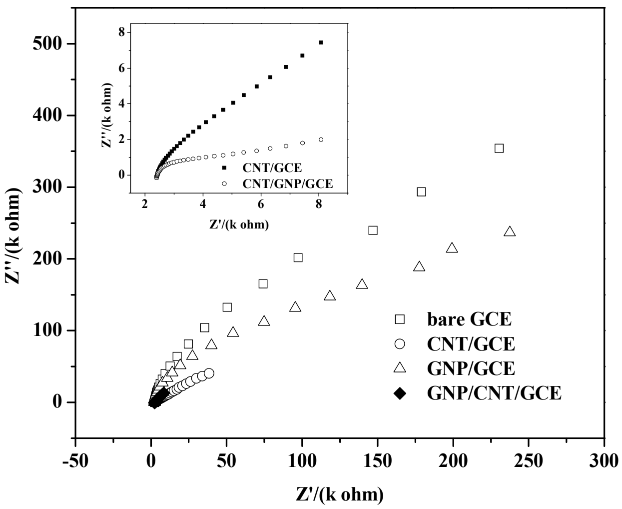

Figure 2. Electrochemical impedance spectroscopy of a bare glassy carbon electrode, of a gold nanoparticles modified glassy carbon electrode, of a carbon nanotube modified glassy carbon electrode and of a gold nanoparticle/carbon nanotube modified glassy carbon electrode. $K_3Fe(CN)_6$, 1.0×10^{-3} mol/L; KCl, 0.1 mol/L.

upper layer of the composite film. Carbon nanotube could be found through the seam of gold nanoparticle film, suggesting that gold nanoparticles were deposited on the carbon nanotube film to form multi-layer modified electrode.

3.2. Electrochemical Impedance Spectroscopy

It is well-known that EIS is an effective tool for studying the interface properties of surface modified electrodes [29-31]. To better understand the electrocatalytic properties of nanoparticle modified electrode, EIS was recorded as shown in Fig. 2.

The impedance spectrum of a bare glassy carbon electrode was a semicircle in all frequency domains, indicating that the electrode process was controlled only by electron transfer. When gold nanoparticles were assembled on the glassy carbon electrode, the impedance spectrum was still a semicircle but the diameter of the semicircle is diminished, suggesting that electron transfer became facile for the existing of gold nanoparticles. When carbon nanotubes were assembled on the bare electrode, the diameter of the semicircle was reduced greatly, demonstrating that the excellent conductivity of carbon nanotubes make it more facile for the electron transfer through carbon nanotube film. When gold nanoparticles were assembled on carbon nanotube film, the diameter of semicircle was further reduced. Therefore, gold nanoparticle/carbon nanotube composite exhibited a synergetic enhancing effect toward electron transfer resulting from gold nanoparticles and carbon nanotube, which might be the main reason for the excellent electrocatalytic effect of gold nanoparticle/carbon nanotube modified electrode to the electrochemical reaction of resorcinol which will be reported in the following text.

3.3. Cyclic voltammograms of resorcinol

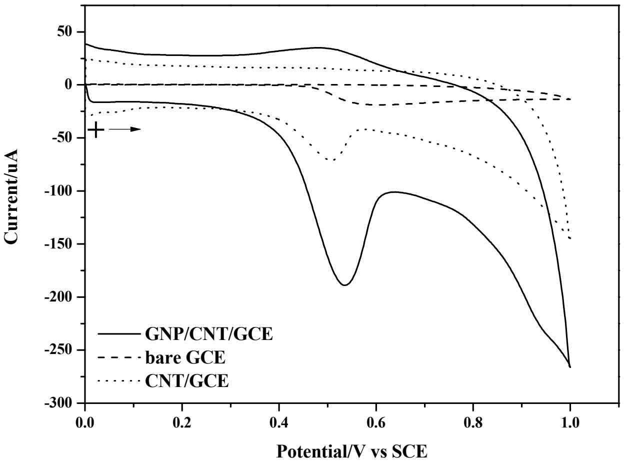

Figure 3. CV curves of resorcinolol at a bare GCE (solid line), a CNT/GCE (dotted line) and a GNP/CNT/GCE (dashed line) under N_2-saturated conditions, resorcinol, 1×10^{-3} mol/L; PBS, 0.1 mol/L; pH, 7; scan rate 50 mV/s.

In order to further elucidate the fascinating properties and potential of the GNP/CNT/GCE in the determination of resorcinol, the electrochemical behavior of resorcinol at three different working electrodes, such as a bare glassy carbon electrode (GCE), a carbon nanotube modified glassy carbon electrode (CNT/GCE) and a gold nanoparticle/carbon nanotube composite modified glassy carbon electrode (GNP/CNT/GCE), in phosphate buffer solution of pH 7.0 were comparatively studied by cyclic voltammetry (CV) and the results were shown in Fig. 3.

It demonstrated that only one oxidation peak can be seen at three electrodes in the potential range from 0 to 1.00 V (vs SCE) in the positive potential scan, which could be assigned to the oxidation process of resorcinol. A weak reduction peak located at 0.48 V was observed at the GNP/CNT/GCE during the reversal potential scan, which could be assigned to the reduction of gold nanoparticles because this reduction peak could not be observed at the bare GCE and the CNT/GCE [29]. Therefore, the electrochemical reaction of resorcinol is a totally irreversible process at all electrodes. At a bare GCE, oxidation peak is broad and weak due to slow electron transfer, and a poorly defined oxidation peak with very low current was observed at 0.59 V on the positive scan. The intensity of the oxidation peak was 16.89 μA. Because the electrochemical signal of resorcinol on the bare GCE was extremely weak, the detection of resorcinol with electrochemical techniques was impossible. However, under identical conditions, the oxidation peak current of resorcinol at a CNT/GCE increased significantly. The intensity of the oxidation peak reached 70.83 μA, increasing about 5-times compared with that on the bare electrode. The peak shape was well-defined and the peak potential located at 0.51 V concurrently shifts negatively in comparison with that of the bare GCE. Both the remarkable peak current enhancement and the negative shift of oxidation peak potential are undoubtedly attributed to the unique characteristics of CNTs. It is well-known that gold nanoparticles could exhibit excellent electrocatalysis behavior in many electrochemical reactions. Therefore, in this study, gold nanoparticles were deposited on the carbon nanotube modified glassy carbon electrode to

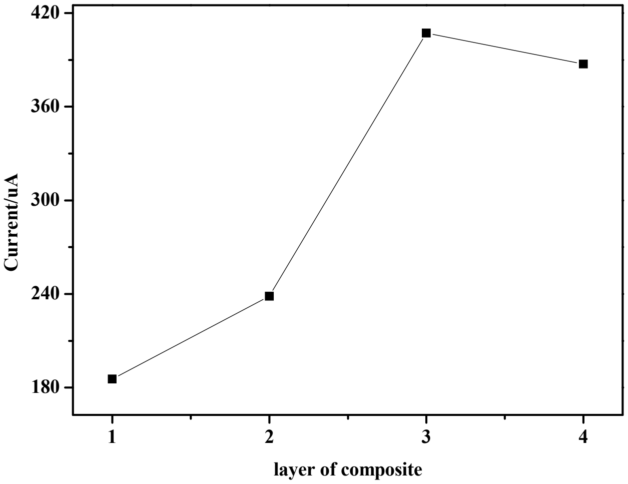

Figure 4. Effect of GNP/CNT composite film thickness on electrochemical signal of resorcinol, resorcinol, 1×10^{-3} mol/L; PBS, 0.1 mol/L; pH, 7; scan rate 50 mV/s.

fabricate a GNP/CNT/GCE, and then, the electrochemical behavior of resorcinol was also investigated at the GNP/CNT/GCE under the same condition. It could be found from Fig. 3 that the peak potential of resorcinol obtained at the GNP/CNT/GCE is 0.53 V, which is slightly shifted to positive potential compared with that of CNT/GCE. Even the peak potential of resorcinol at the GNP/CNT/GCE is slightly positive than that at the CNT/GCE, the beginning potential of the oxidation peak of resorcinol located at 0.32 V at the GNP/CNT/GCE which is more negative than that at the CNT/GCE (0.40V). Therefore, it could be deduced that GNP/CNT/GCE exhibited more efficient electroanalytical effect on the oxidation of resorcinol. The intensity of the oxidation peak reached 188.50 μA at the GNP/CNT/GCE, increasing about 2-times compared with the CNT/GCE. The increase in the intensity of oxidation peak of resorcinol is probable due to the increase in the surface area as well as the electrocatalytical effect of GNP/CNT composite. Therefore, gold nanoparticle/carbon nanotube composite modified electrode fabricated by simple casting method could not only withhold the merits from gold nanoparticles and carbon nanotube, but also show synergistic electrocatalytical effect on the electrochemical reaction of resorcinol. Well-defined and strong oxidation peak of resorcinol at the GNP/CNT/GCE make it possible for the detection of resorcinol with electrochemical methods.

3.4. Effects of GNP/CNT composite film thickness

The thickness of gold nanoparticle/carbon nanotube composite film was investigated and the results were shown in Fig. 4.

It could be found that the intensity of oxidation peak of resorcinol increased with the increase of the thickness of composites. When the composite film reaches three layers, the electrochemical signal exhibits maximum values. However, further increase in film thickness, signal decreased. During the experiment, it was found that when thickness of composite film increased, the stability of the modified electrode decreased. When the layers of composite exceeded three, the film is flexible to be broken off. In order to obtained stable electrochemical signal, one layer of composite was chosen to modify glassy carbon electrode.

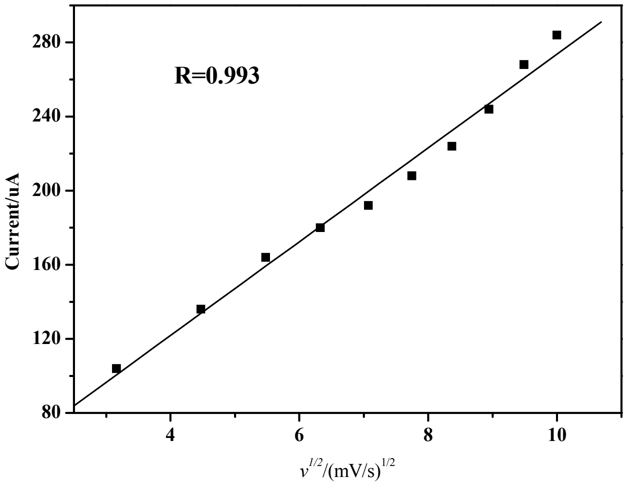

Figure 5. Effect of potential scan rate on electrochemical signal of resorcinol, resorcinol, 1×10^{-3} mol/L; PBS, 0.1 mol/L; pH, 7.

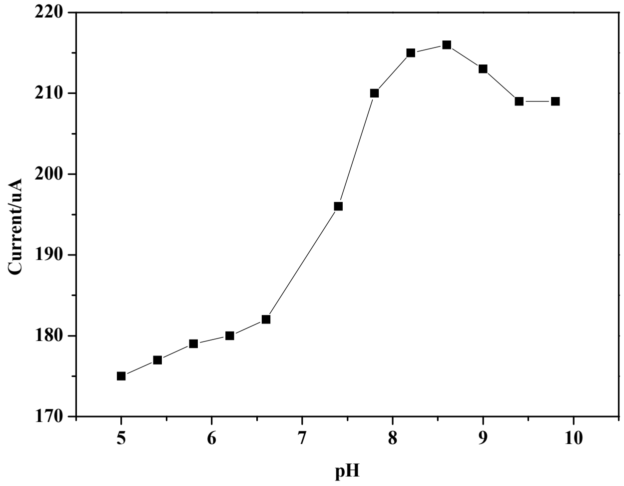

Figure 6. Effect of pH on electrochemical signal of resorcinol, resorcinol, 1×10^{-3} mol/L; PBS, 0.1 mol/L; scan rate 50 mV/s.

3.5. Effects of potential scan rate

The effect of potential scan rate on electrochemical response of resorcinol was studied with the scan rate increasing from 10 to 100mV/s and the results were shown in Fig. 5.

A linear relationship with a correlation coefficient of R=0.993 was observed between the peak current and the square root of scan rate ,which revealed that the oxidation of resorcinol was rather a diffusion-controlled process than an adsorption-controlled step. Only an oxidation peak was observed even at low scan rate (10 mV/s), suggesting that the electrode reaction of resorcinol under these conditions was totally irreversible.

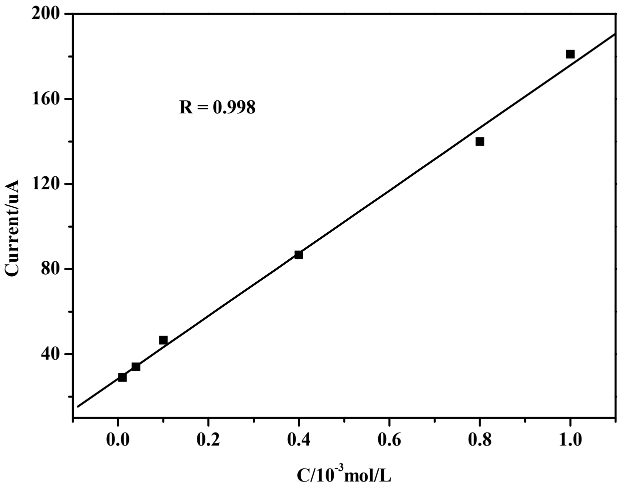

Figure 7. Calibration curve for resorcinol under CV conditions, pH, 8.4; PBS, 0.1mol/L; scan rate, 50 mV/s.

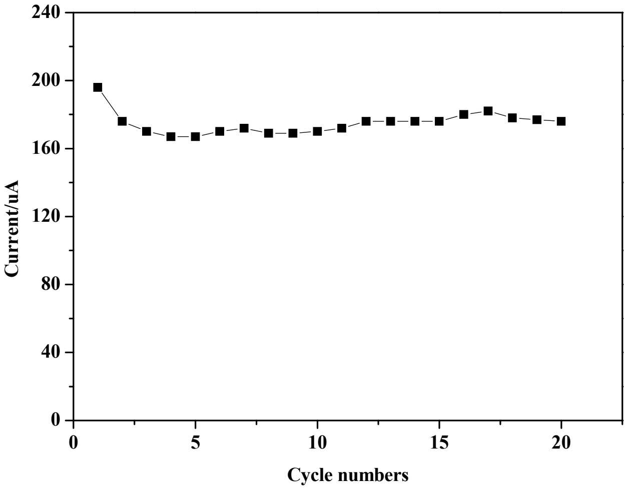

Figure 8. Stability of GNP/CNT/GCE in resorcinol solution, resorcinol, 1×10^{-3} mol/L; PBS, 0.1 mol/L; pH, 7; scan rate 50 mV/s.

3.6. Effects of pH

The pH value of the working solution has a significant influence on the oxidation of resorcinol at the GNP/CNT/GCE, by altering both the peak current and the peak potential. To optimize the electrocatalytic response of the GNP/CNT/GCE for resorcinol oxidation, the pH effect was studied between pH 5.0 and 10.0. The pH values were adjusted by changing the ratio of Na_2HPO_4 and NaH_2PO_4 in PBS with the whole concentration maintaining at 0.1 mol/L. The result was shown in Fig. 6.

The largest oxidation peak current of resorcinol was obtained at pH 8.4. Hence, the solution pH of 8.4 was selected in the following experiments. The experiments also showed that the trend of the peak potential shifts linearly towards negative potentials with an increase in pH, indicating that protons were directly involve in the oxidation of resorcinol.

3.7. Calibration curve and detection limit

The calibration curve for resorcinol was measured by CV and shown in Fig. 7.

Under the optimum detection conditions, the oxidation peak current was proportional to resorcinol concentration in the range of 1×10^{-3} to 1×10^{-5} mol/L. The linear regression equations were expressed as I_p (μA) = 28.4825 + 147.4064 C (C in mM) and correlation coefficient (R) was 0.998. The detection limit of resorcinol was 5.0×10^{-6} mol/L in terms of the role of signal to noise ratio of 3:1.

As a practical use, the GNP/CNT/GCE was used to detect resorcinol in tap water samples. The recovery of resorcinol is determined by standard addition and the result is 102 %, suggesting that the modified electrode is reliable in the determination of resorcinol.

Table 1. Effect of electrolytes on electrochemical signal of resorcin in neutral pH solution, PBS, 0.1 mol/L; NaAc-HAc, 0.1 mol/L; KCl, 0.1 mol/L; KNO_3, 0.1 mol/L.

electrolytes	NaH_2PO_4-Na_2HPO_4	NaAc-HAc	KNO_3	KCl
I_p/μA	121.13	123.37	109.82	103.11
E_p/V	0.52	0.89	0.96	0.96

3.8. Effects of electrolytes

The highest sensitivity of resorcinolol was obtained in the 0.1 mol/L phosphate buffer of pH 7.0. Other supporting electrolytes, such as HAc-NaAc, KCl, KNO_3, were also tested and the results were shown in Table 1.

Under the same pH value, all of them were not as favorable as PBS for the determination.

3.9. Stability and reproducibility of the modified electrode

For the practical applications, long-term stability of the electrode is an important feature. The long-term stability of a GNP/CNT/GCE was investigated in $1\cdot10^{-3}$ mol/L resorcinol solution and the results were shown in Fig.8.

The electrochemical signal of resorcinol was the strongest in the first cycle and then decreased about 10% and varied slightly in the following cycles. The decrease in the electrochemical signal may result from the adsorption of resorcinol on the electrode surface, which is the main reason for the weak electrochemical signal of resorcinol at a bare glassy carbon electrode. Therefore, the GNP/CNT/GCE could sufficiently alleviate electrode fouling in resorcinol compared with that at a bare glassy carbon electrode. The reproducibility of different modified electrodes was also investigated. The results show that relative standard deviation (RSD) of the electrochemical signals of 10 modified electrodes is 5.3%, suggesting the reproducibility of the modified electrode is good.

4. CONCLUSIONS

Gold nanoparticle/carbon nanotube modified electrode exhibited synergistic catalytic effects on the electrochemical reaction of resorcinol from the gold nanoparticles and carbon nanotube, respectively. The intensity of oxidation peak of resorcinol was enhanced about 10-times at a GNP/CNT/GCE compared with that at a bare GCE. The stability and reproducibility of the modified electrode is good and can be used in the determination of resorcinol. Under the optimum detection conditions, the oxidation peak current was proportional to resorcinol concentration in the range of 1×10^{-3} to 1×10^{-5} mol/L and the detection limit of resorcinol reached 5.0×10^{-6} mol/L. The results provided us a potential application of such a composite modified electrode in electrochemical detection of resorcinol.

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