Comparative Studies of Electrochemical Behaviors of Benzenediols at a Gold Nanoparticle/carbon Nanotube Composite Modified Glassy Carbon Electrode

Yong-Ping Dong[*], Qian-Feng Zhang and Taike Duan

School of chemistry and chemical engineering, Institution of molecular engineering and applied chemistry,
Anhui University of Technology, Maanshan, China, 243002

Abstract: *A gold nanoparticle/carbon nanotube composite modified glassy carbon electrode was fabricated and used to investigate electrochemical characteristics of hydroquinone, catechol, and resorcinol via cyclic voltammetric analysis under neutral pH conditions. The results imply that the gold nanoparticle/carbon nanotbue modified electrode exhibited a synergistic and excellent electrocatalytic effect of gold nanoparticles and carbon nanotube on the redox behaviors of benzenediols. The reversibility of electrochemical reaction was improved greatly and the peak currents were increased significantly compared with a bare electrode. Good linear relationships were obtained between the oxidation peak currents and the concentrations of catechol and resorcinol. The electrochemical process of catechol was controlled by surface adsorption process, while that of resorcinol was controlled by diffusion process. However, the peak current and the concentration of hydroquinone were not proportional in the whole concentration range, which is because the controlling process of electrochemical reactions was different in the different hydroquinone concentration. Benzenediols could be detected simultaneously at the modified electrode but not at the bare electrode. The stability of the modified electrode was excellent in the benzenediols solutions, which made it possible for the practical application of the modified electrode.*

Keywords: hydroquinone; catechol; resorcinol; gold nanoparticles; carbon nanotube

1. INSTRUCTION

Benzenediols are biologically and environmentally important phenolic compounds. They are widely used as industrial intermediates for the manufacture of drugs, photographic developer, rubber and food antioxidants, polymerization inhibitors, and so on. They are of particular interest due to its negative environmental and human healthy impacts once discharged into the receiving water system with industrial waste streams. Therefore, to develop a highly sensitive, selective and simple method for the low level detection is of significance for the study of toxicological analysis, foods inspection, and environmental concerns. Various methods are available for the determination of benzenediols, including chromatographic [1-4], spectrophotometric analyses [5-8] and chemiluminescent (CL) detection [9-11]. Spectrophotometric

methods are employed mainly for the determination of total amount of phenolic compounds. While chromatographic methods permit selective determination of individual phenolic compounds, however, lower sensitivity of the detector used are usually encountered and thereby greatly hamper their application from trace analysis. CL detection is proved to be much more sensitive and have advantages of wide dynamic range, simple instrumentation and rapidity in signal detection. Unfortunately, most of the methods reported can be used only for the determination of signal compound in simple matrices, while the determination for complex matrices, such as biological and environmental samples is almost impossible because phenolic congeners are often present together in these samples and similar CL reactions will lead to the interference from one to another. Electrochemical detection of analyte is a very elegant method in analytical chemistry particularly owing to their inherent specificity, speed of response, sensitivity and simplicity of preparation. However, low electrochemical signals of

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*To whom correspondence should be addressed: Email: dongyp@ahut.edu.cn
  Phone: :+86-555-2311807

benzenethiol on the traditional electrodes, such as gold and glassy carbon electrode, hamper the application of electrochemical methods in the detection of benzenediols. In order to sensitively detect polyphenol with electrochemical technology, it is necessary to develop a novel electrochemical biosensor.

In the past few decades, preparation of nanostructured electrode surface with various nanomaterials such as metal nanoparticles and carbon nanotubes (CNTs), for the design of electrochemical sensing devices has attracted much attention. Among them, carbon nanotubes have been extensively employed for the fabrication of electrochemical sensors and biosensors with noticeable features such as an excellent electrocatalytic activity towards the oxidation processes of various molecules and enhanced sensitivity for the detection of different substances [12-14]. 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 sizes, shapes, and stabilizing agents [15-17]. Even though the electrocatalytic activity of carbon nanotube 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 to possess properties of the individual components with a synergistic effect. Metal nanoparticles, such as Au, Ag, Pt, Ni, Pd and Cu, have been reported to coat or deposit onto the side walls of both single-walled carbon nanotubes and multi-walled carbon nanotubes [18-24] to fabricate nanohybrid films. These novel hybrid nanomaterials have been shown to exhibit excellent catalytic activity, electrical conductivity and photonic properties. For example, coupling CNTs with Pt nanoparticles resulted in remarkable improvement of the electroactivity of the composite materials toward H_2O_2 [25]. A glucose biosensor was reported based on electrodeposition of palladium nanoparticles and glucose oxidase (GOD) onto Nafion-solubilized carbon nanotube electrode [26]. Among these metal nanoparticles and carbon nanotube hybrid nanomatrials, of particular interest are nanocomposites involving gold nanoparticles (GNPs), due to the combination of the unique electronic properties of carbon nanotubes and their ease of surface modification, along with the biocompatibility of GNPs. This nano-composite modified electrode has already been utilized in many fields [27-30].

In this paper, a gold nanoparticle/carbon nanotube composite modified glassy carbon electrode was prepared by simple casting method and electrochemical responses of benzenediols such as hydroquinone, resorcinol, and catechol, at the modified glassy carbon electrode were comparatively studied. The potential for the simultaneously determine three benzenediols using electrochemical methods was also discussed.

2. EXPERIMENTAL

2.1. Reagents

Multi-walled carbon nanotubes (MWNTs) were purchased from Shenzhen Nanotech Port Co., Ltd (Shenzhen, China). Chloroauric acid (HAuCl$_4\cdot$3H$_2$O) was obtained from Shanghai Reagent (Shanghai, China). A 1.0 g/L HAuCl$_4$ stock solution was prepared by dissolving 1 g of HAuCl$_4$ in 1 L of redistilled water and stored at 4 °C. Hydroquinone, catechol and resorcinol were purchased

from Shanghai Reagent (Shanghai, China) Working solution was prepared by dissolving benzenediols in 0.1 mol/L pH=7 phosphate buffer solutions (PBS) before each electrochemical measurement. All the other reagents in the experiment were of analytical grade and double-distilled water was used throughout.

2.2. Synthesis of gold nanoparticles

Gold colloids with a diameter of 16 nm were prepared according to the literature [31] and our previous work [32]. The typical process is as follows: a 50 mL portion of HAuCl$_4$ (10^{-2}% w/w) solution was heated to boiling. While stirred 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 °C. The average diameter of synthesis gold nanoparticles was ~16 nm as reported in our previous work [32].

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 sequentially. 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).

2.4. Equipment and electrochemical methods

A LK2005A instrument was employed for the electrochemical measurement. The working electrode was GNP/CNT/GCE. A Pt plate and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All potentials in this study were reported with respect to 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 DISCUSSIONS

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 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.

It is well-known that EIS is an effective tool for studying the
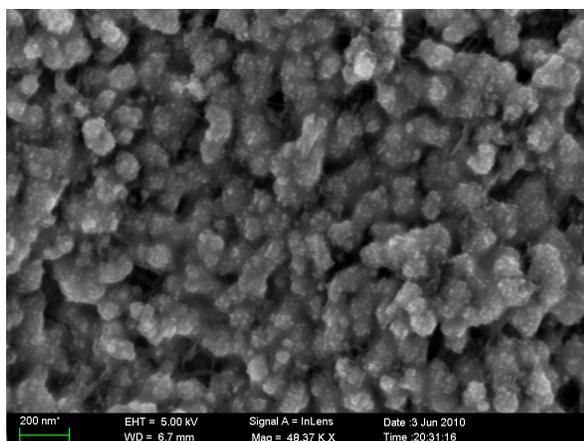
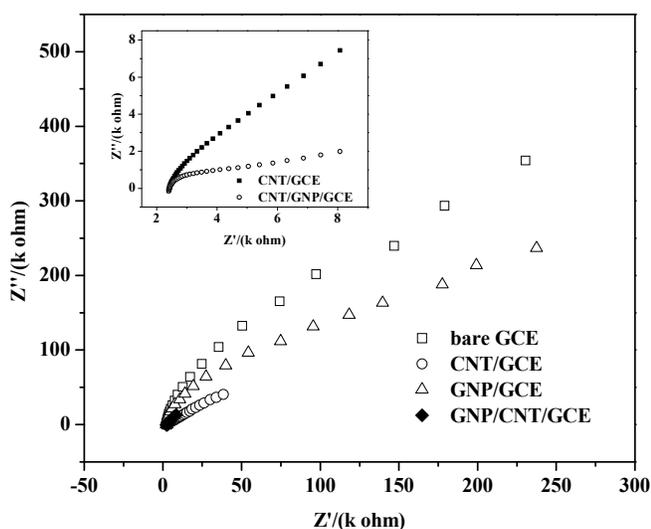Figure 1. SEM image of GNP/CNT modified glassy carbon electrode.

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.
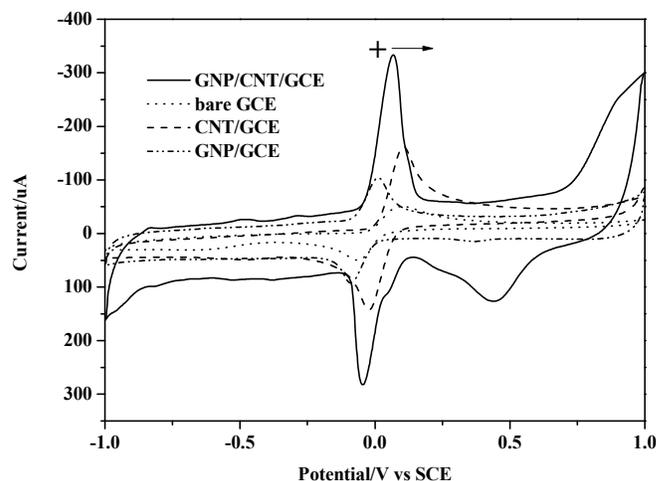

Figure 3. Electrochemical behavior of hydroquinone at a bare GCE, a GNP/GCE, a CNT/GCE and a GNP/CNT/GCE. hydroquinone, 1.0×10^{-3} mol/L; scan rate, 50mV/s; pH, 7.0; PBS, 0.1mol/L

strating that the excellent conductivity and large surface area of carbon nanotubes make it more facile for the charge transfer through carbon nanotube film. When gold nanoparticles were assembled on carbon nanotube film, the diameter of semicircle was further reduced. From the result of EIS, it could be found that the charge transfer becomes more facile when gold nanoparticles and carbon nanotubes were assembled on the electrode surface. To some extent, these EIS results might elucidate the significant enhancing effect of gold nanoparticles and carbon nanotube to the electrochemical signals of hydroquinone.

3.2. Electrochemical of benzenediols at a GNP/CNT/GCE

In order to further elucidate the fascinating properties and application potential of the GNP/CNT/GCE in the determination of benzenediols, the electrochemical behaviors of hydroquinone, resorcinol, and catechol, at 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.

3.2.1. Hydroquinone

Fig.3 shows the cyclic voltammograms of 1mM hydroquinone at different electrodes in the potential range from -1.00 to 1.00 V (vs SCE), at a scan rate of 50 mV/s. A pair of well-defined redox peaks assigned to hydroquinone was obtained in all conditions, suggesting that the electrochemical reactions of hydroquinone at those electrodes are a reversible process. At a bare GCE, an oxidation peak (Ep_a) was observed at ~0.10 mV in the positive potential scan and a reduction peak (Ep_c) was observed at ~ -0.06 mV in the reverse potential scan. The peak-to-peak separation between Ep_a and Ep_c is 160 mV. The intensity of oxidation peak and reduction peak is 51.22 and 50.51μA, respectively. It could be deduced that the

interface properties of surface modified electrodes [33-35]. 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 mainly by charge transfer process. When gold nanoparticles were assembled on the glassy carbon electrode, the impedance spectrum was still a near semicircle but the diameter of the semicircle is diminished, suggesting that charge transfer through electrode surface is facile for the existing of gold nanoparticles. When carbon nanotubes were assembled on the bare electrode, the diameter of the semicircle was reduced greatly, demon-
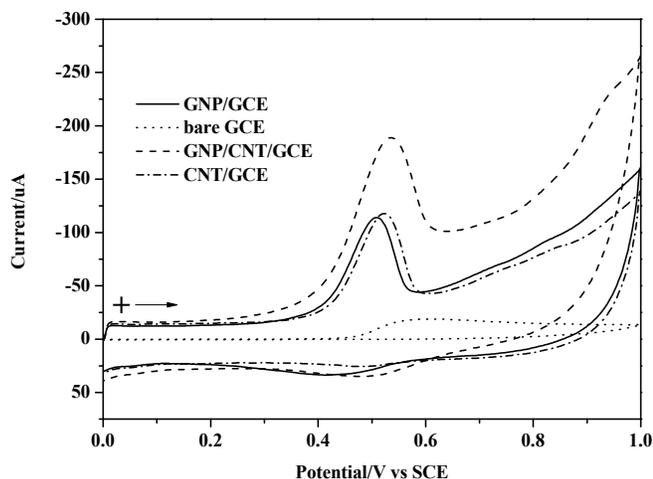
Figure 4. Electrochemical behavior of resorcinol at a bare GCE, a GNP/GCE, a CNT/GCE, and a GNP/CNT/GCE, resorcinol, 1.0×10^{-3} mol/L; scan rate, 50mV/s; pH, 7.0; PBS, 0.1mol/L

Figure 5. Electrochemical behavior of catechol at a bare GCE, a GNP/GCE, a CNT/GCE and a GNP/CNT/GCE, catechol, 1.0×10^{-3} mol/L; scan rate, 50mV/s; pH, 7.0; PBS, 0.1mol/L

reversibility of the electrochemical reaction of hydroquinone at the bare GCE is poor. At a GNP/GCE, the peak potential difference reduced to ~90 mV and the peak current doubled, suggesting that gold nanoparticles exhibit good electrocatalytic effect towards the electrochemical reaction of hydroquinone. At a CNT/GCE, the peak potential changed slightly compared with the bare electrode and the peak potential difference reduced to ~120 mV. The peak current is 3-times stronger than that of the bare electrode. The results suggest that the increase of electrochemical signal of hydroquinone at CNT/GCE is probable due to the large surface area and the electrocatalytica effect of carbon nanotubes. At the GNP/CNT/GCE, an oxidation peak and a reduction peak, which could not be observed at the CNT/GCE and the bare GCE, were observed at 0.80 V and 0.44 V respectively and could be attributed to the redox process of gold nanoparticle, suggesting that gold nanoparticles were fabricated on the electrode. The peak potential difference of hydroquinone reduced to 102 mV and the peak current increase 6-times compared with the bare GCE. The results reveal that the GNP/CNT composites exhibit more efficient electrocatalytic effect on the electrochemical reaction of hydroquinone compared with CNT film and gold nanoparticle film. Therefore, electrochemical reactions of hydroquinone are enhanced significantly at a GNP/CNT/GCE because of the excellent and synergistic electrocatalytic effect of gold nanoparticles and carbon nanotubes, which might make it more sensitive in the determination of hydroquinone by electrochemical methods.

3.2.2. Resorcinol

The electrochemical behaviors of resorcinol at three working electrodes were recorded in the identical condition and shown in Fig.4. It demonstrated that only one oxidation peak appeared at all electrodes in the potential range from 0 to 1.00 V (vs SCE) in the positive potential scan and no reduction peak was observed in the reverse potential scan, suggesting that the electrochemical reaction of resorcinol is a totally irreversible process. At a bare GCE, oxidation peak is broad and weak due to slow electron transfer, and a
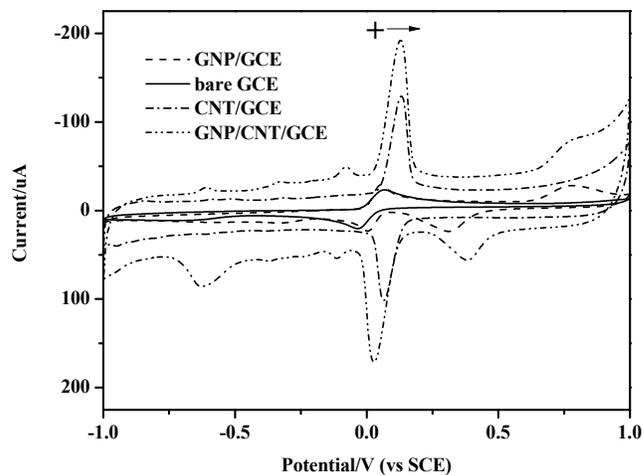
poorly defined oxidation peak with very low current was observed at 0.59 V, on the positive scan. The intensity of the oxidation was 18.20 μA. Because the electrochemical signal of resorcinol on the bare GCE was extremely weak, the detection of resorcinol using electrochemical techniques was impossible. Under the identical conditions, the oxidation peak current of resorcinol at a CNT/GCE and a GNP/GCE increased significantly. The intensity of the oxidation peak reached 116.87 μA, increasing about 10 times compared with that on the bare electrode. The peak shape was well-defined and the peak potential located at 0.50 V at the GNP/GCE and 0.52 V at the CNT/GCE respectively. Both the remarkable peak current enhancement and the negative shift of oxidation peak potential are undoubtedly attributed to the unique characteristics of CNTs. At the GNP/CNT/GCE, the peak potential was identical to that at the CNT/GCE and the intensity of the oxidation peak reached 188.50 μA, increasing about 60% compared with that at the CNT/GCE, suggesting that the GNP/CNT/GCE exhibited more efficient electroanalytical effect on the oxidation of resorcinol. Therefore, gold nanoparticle/carbon nanotube composite modified electrode fabricated by casting method could not only withhold the merits of 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.

3.2.3. Catechol

The electrochemical behavior of catechol were also recorded in the same condition and shown in Fig.5. Gold nanoparticles and carbon nanotube modified on the electrode exhibit a synergistic electrocatalytical effect on the electrochemical reactions of catechol either. At a GNP/CNT/GCE, the oxidation/reduction peaks of gold nanoparticles were also observed at 0.77 V and 0.38 V respectively. The electrochemical signals were increased at least 8-times and the peak potential difference was reduced from 100 to 90 mV compared with that at a bare GCE.
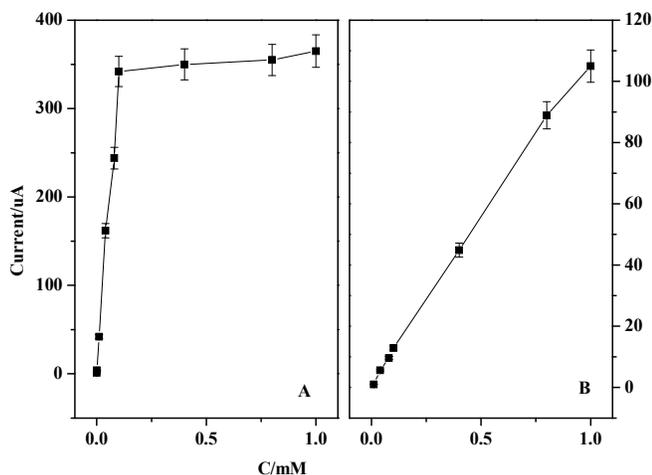
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Figure 6. Relationship between the oxidation peak current and the concentration of hydroquinone at a GNP/CNT./GCE (A) and a bare GCE (B), pH, 7.0; PBS, 0.1mol/L; scan rate, 50 mV/s

Figure 7. Simultaneous detection of hydroquinone, catechol and resorcinol at a bare GCE and a GNP/CNT/GCE, hydroquinone, $1.0×10^{-3}$ mol/L; resorcinol, $1.0×10^{-3}$ mol/L; catechol, $1.0×10^{-3}$ mol/L; scan rate, 50mV/s; pH, 7.0; PBS, 0.1mol/L

3.3. Effect of concentration of benzenediols and potential scan rate

The calibration curves for resorcinol, catechol, and hydroquinone were measured by CV. Under the optimum detection conditions, the oxidation peak current was proportional to resorcinol and catechol concentration in the range of $1.0×10^{-3}$ to $1.0×10^{-5}$ mol/L and $1.0×10^{-3}$ to $4.0×10^{-5}$ mol/L, respectively. The linear regression equations were expressed as I_p (μA) = 28.4825 + 147.4064 C (C in mM) to resorcinol and I_p (μA) = -1.4654 + 137.8553 C (C in mM) to catechol. The correlation coefficient (R) was 0.997 and 0.996, respectively. The detection limit of resorcinol and catechol was 5.0 $×10^{-6}$ mol/L and 1.0 $×10^{-5}$ mol/L, respectively, in terms of the role of signal to noise ratio of 3:1.

All the articles related to the determination of hydroquinone with electrochemical methods reported that the electrochemical signal of hydroquinone is proportional to its concentration in the certain concentration range. In this paper, the relationship between the electrochemical signals and concentration of hydroquinone at a GNP/CNT/GCE and a bare GCE were studied in the optimal condition. The results reveal that at a bare electrode, the oxidation peak current was proportional to hydroquinone concentration in the range of $1.0×10^{-3}$ to $1.0×10^{-5}$ mol/L. However, at the GNP/CNT/GCE, one relationship was obtained in the range of $1.0×10^{-3}$ to $1.0×10^{-4}$ mol/L and another relationship was obtained in the range of $1.0×10^{-4}$ to $1.0×10^{-6}$ mol/L as shown in Fig.6. In order to further investigate the reason for the difference, the effect of the potential scan rate on the oxidation current in the different concentration range was studied in $5.0×10^{-4}$ mol/L and $5.0×10^{-5}$ mol/L, respectively. The results reveals that the anodic peak current is proportional to the scan rate in $5.0×10^{-4}$ mol/L, demonstrating that the oxidation of hydroquinone at the GNP/CNT/GCE is controlled by surface adsorption. In $5.0×10^{-5}$ mol/L, the anodic peak current is proportional to the square root of scan rate, revealing that the oxidation of hydroquinone is controlled by diffusion process. It is well-known that carbon nanotubes exhibit excellent adsorption ability for some species in the solution. Therefore, we concluded
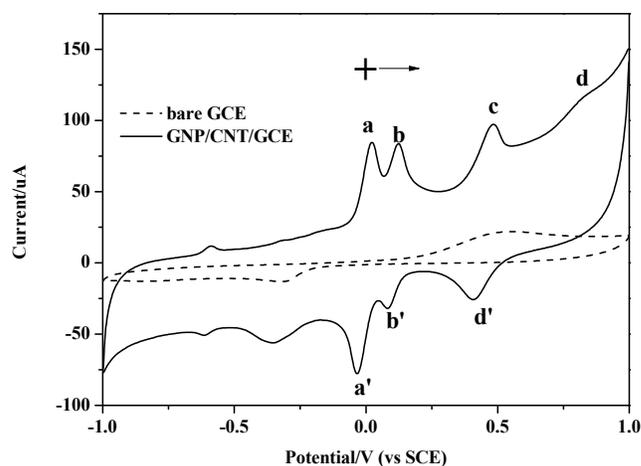
that a large amount of hydroquinone could be adsorbed on the electrode surface in the high concentration solution, as a result, the electrochemical was controlled by surface adsorption process. While in the lower concentration, the amount of adsorbed hydroquinone could not influence the electrochemical reactions of hydroquinone and the diffusion process turned to be the main reason for the controlling of the redox of hydroquinone.

The effect of scan rate on the anodic current of catechol and resorcinol was also studied in the potential scan rate range of 10 to 100 mV/s. The results show that the electrochemical reaction of catechol and resorcinol was controlled by surface adsorption process and diffusion controlling process, respectively. It could be found from CVs that the electrochemical process of hydroquinone and catechol is reversible. As a result, the adsorbed hydroquinone and catechol could react on the surface of electrode repeatedly and the electrochemical process was controlled by adsorption process. Whereas, the electrochemical process of resorcinol is irreversible and the adsorbed resorcinol might be oxidized rapidly, therefore, the electrochemical oxidation of resorcinol is controlled by diffusion process.

3.4. Simultaneous detection of three benzenediols

In order to investigate the potential of simultaneous determination of benezendiols at the GNP/CNT/GCE with electrochemical methods, the electrochemical signals of mixtures of hydroquinone, resorcinol, and catechol were obtained at the bare and modified electrode, respectively. The results are shown in Fig.7. It was demonstrated in the previous contents that the electrochemical signals of 1 mM hydroquinone, resorcinol, and catechol could be obtained at the bare glassy carbon electrode even the electrochemical signals was extremely weak. However, when three benezendiols with the same concentration were mixed, only one pair of extremely weak and broad oxidation and reduction peaks was observed at the bare GCE, GNP/GCE, and CNT/GCE, which could not be attributed exactly to any benezendiols. Therefore, the peak potentials for
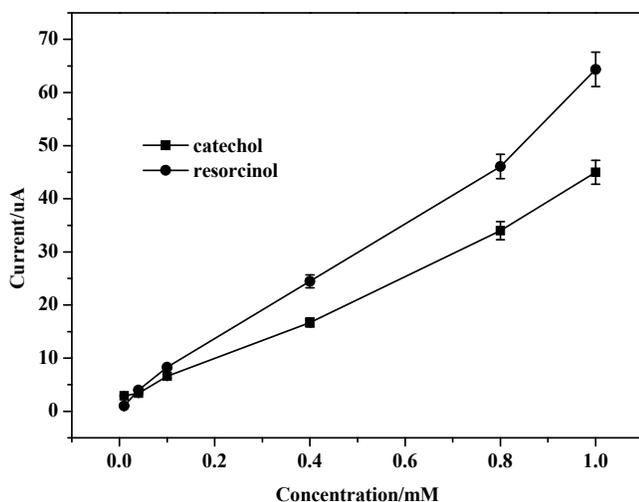
Figure 8. Detection of resorcinol and catechol respectively in the presence of same concentration of other benzenediols. hydroquinone, 1.0×10^{-3} mol/L; resorcinol, 1.0×10^{-3} mol/L; catechol, 1.0×10^{-3} mol/L;scan rate, 50mV/s; pH, 7.0; PBS, 0.1mol/L

Figure 9. Stability of a GNP/CNT/GCE. hydroquinone, 1.0×10^{-3} mol/L; resorcinol, 1.0×10^{-3} mol/L; catechol, 1.0×10^{-3} mol/L; scan rate, 50mV/s; pH, 7.0; PBS, 0.1mol/L

hydroquinone, catechol and resorcinol are indistinguishable and it is impossible to deduce any conclusion from broad voltammetric peak. But when the GNP/CNT/GCE was used under the identical conditions, the broad voltammetric peaks were splitted into several well-defined CV peaks as shown in Fig.7. Among them, peaks a-a' located at 0.02 and -0.03 V, b-b' located at 0.12 and 0.08 V, and c located at 0.48V, which are almost the same as the oxidation-reduction potentials of hydroquinone, catechol and resorcinol respectively. Therefore, it could be concluded that peaks a-a' corresponded to the electrochemical process of hydroquinone, b-b' corresponded to that of catechol and c corresponded to the oxidation of resorcinol. Peaks d and d' might be assigned to the oxidation/reduction of gold nanoparticles modified on the electrode. Those CV peaks of benezendiols were strong and could be separated significantly from each other, which make it possible for the determination of them simultaneously. In the optimal experimental condition, the electrochemical signal of catechol and resorcinol changed linearly with their concentration in the presence of other two benzenediols of the same concentration (Fig.8). The electrochemical signal of hydroquinone didn't change linearly with its concentration in the presence of catechol and resorcinol, therefore, the result was not shown in the paper.

3.4. Stability of the modified electrode

For the practical application, the long term stability of the GNP/CNT/GCE was investigated in 1 mM hydroquinone, resorcinol, and catechol respectively. It can be observed from Fig.9 that anodic current of three benzenodiols remains constant with increase of the scan number at a scan rate of 50 mV/s. The stability of the modified electrode can be attributed to the less poisoning of the electrode surface due to the modified carbon nanotubes.
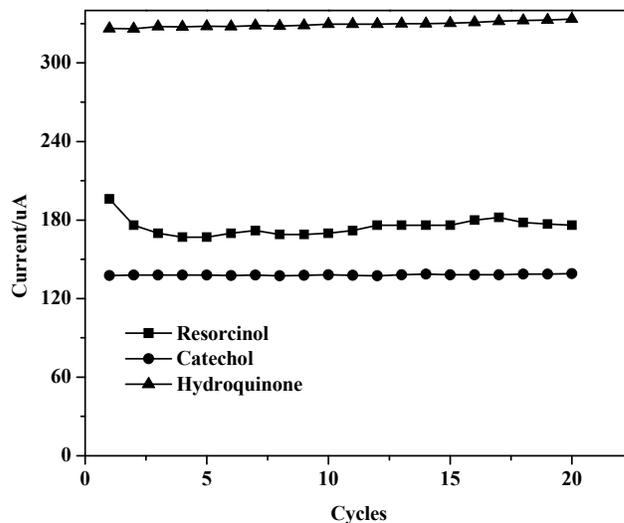
4. CONCLUSION

A novel gold nanoparticle/carbon nanotube film electrochemical sensor has been developed by using the glassy carbon electrode coated with carbon nanotubes and gold nanoparticels one after the other. The present study demonstrated that the electrochemical sensor exhibited excellent and synergistic electrocatalytic effect from gold nanoparticles and carbon nanotubes on the electrochemical reactions of hydroquinone, catechol, and resorcinol. The intensities of electrochemical currents were increased greatly, and the reversibility of electrochemical reactions was improved clearly. The modified electrode offered the possibility of simultaneously determination of benzenediols with electrochemical methods and could be used for a relatively long period.

5. ACKNOWLEDGEMENT

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