Simultaneous Determination of Dihydroxybenzene Isomers using Glass Carbon Electrode Modified with 3D CNT-graphene Decorated with Au Nanoparticles

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3D CNT-graphene decorated with Au nanoparticles was modified onto glassy carbon electrode (Au NPs/CNTs/graphene/GCE) surface through casting and subsequent electrodeposition method. Morphological characterization of Au NPs/CNTs/graphene/GCE was performed by scanning electron microscopy (SEM), and evenly distributed Au NPs were observed to be anchored onto porous and 3D CNTs/graphene hybrids. The resultant electrode is used as an electrochemical interface for simultaneous determination of dihydroxybenzene isomers of hydroquinone (HQ), catechol (CC) and resorcinol (RC). Three well-resolved and sensitive peak signals were observed from cyclic voltammetric results attributing to the unique porous 3D nanostructure and high electrical conductivity of Au NPs/CNTs/graphene. Differential pulse voltammetry was used to perform quantitative detection of the three isomers. It was found that good performance of Au NPs/CNTs/graphene/GCE for detection of dihydroxybenzene isomers was obtained, including wide linear range, high sensitivity and selectivity, low detection limit and excellent stability. In addition, the proposed method can be successfully used for the determination of dihydroxybenzene isomers in real water samples.

1. INTRODUCTION

As the members of carbon family, the nanomaterials of carbon nanotubes (CNTs) and graphene have stimulated intensive research interest in various fields, such as energy storage, materials science, transistor devices, electrocatalyst, and electrochemical sensors, due to their unique properties including huge surface area, excellent mechanical strength, rapid charge transfer, and prominent conductivity [1-8]. A lot of reports have been focused on the usage of single CNTs or graphene as support to load

active materials for versatile applications. Recently, the integration of 1D CNTs and 2D graphene to form 3D nanostructures has been shown to remarkably facilitate electron transfer from multiple dimensions and pathways, thus provide potentially enhanced performance [9-12]. Noncovalent interactions based on π-π stacking between CNTs and graphene is the simplest way to synthesize 3D CNTs/graphene hybrids. In this assembly process, the respective properties of CNTs and graphene can be well preserved to form hybrids.

Gold nanoparticles (Au NPs), as a famous active metal, has been widely applied in areas of fuel cells, catalyst and electrochemical sensors or biosensors [13-16], because of its outstanding catalytic activities, tunable particle size and good biocompatibility. However, Au NPs tend to aggregate together to lower its active sites. Therefore, a host of materials consisting of CNTs [17], carbon spheres [18] and graphene [19] have been used to disperse Au NPs. It is expected that CNTs/graphene hybrids would be an ideal support for homogeneous dispersion of Au NPs owing to its multi-dimensional electron transfer pathways and unique 3D nanostructures. The active Au NPs can further increase the active surface area of hybrids and enhance the charge transfer. Therefore, the resultant analytical devices are supposed to improve the detection sensitivity and selectivity for target species when used as a sensing platform.

Catechol (CT), hydroquinone (HQ) and resorcinol (RS) are three positional isomers of dihydroxybenzene, which are classified as highly toxic pollutants due to its toxicity to human beings and difficulty for degradation in ecological environment [20,21]. The three isomers have similar structure and often coexist in environmental samples, thus, it is always hardly to achieve their identification and simultaneous determination. Electrochemical method is a powerful technique for distinguishing isomers because of its cost effectiveness, simple device, high detection sensitivity and selectivity [22-24]. However, the three isomers with the same hydroxy groups usually exhibit overlapped redox peaks, resulting in interference from each other. To resolve this problem, various materials with high electrocatalytic activities has been used for electrode modifications to separate the peak signals of isomers [25-29]. So far, there is still an urgent need for developing novel nanomaterials to improve the detection sensitivity and selectivity of dihydroxybenzene isomers.

To get the goal of developing high performance sensing platform for identification and simultaneous determination of dihydroxybenzene isomers, in this work, 3D CNTs/graphene hybrids decorated with Au NPs (Au NPs/CNTs/graphene) has been synthesized using casting and subsequent electrodeposition method. SEM was used to characterize the morphology of the resultant 3D Au NPs/CNTs/graphene hybrids. The electrochemical experiments indicated that three well-resolved oxidation peaks corresponding to HQ, CC and RC can be distinguished. The excellent electrical conductivity and unique 3D nanostructure of Au NPs/CNTs/graphene hybrids greatly enhance the electrochemical oxidation peak currents of dihydroxybenzene, leading to a high detection sensitivity and low detection limit. In addition, the present method can be successfully used to determine dihydroxybenzene isomers in ecological water samples with good accuracy.

2. EXPERIMENTAL SECTION

2.1. Reagents and apparatus

$HAuCl_4 \cdot 3H_2O$ and cetyltrimethylammonium bromide (CTAB) were purchased from Sigma Aldrich. HQ, CC and RC were obtained from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). The electrolyte solutions for electrochemical detection of dihydroxybenzene isomers were prepared with acetate buffer solution (0.1 M ABS: pH 5.7). All of the above chemicals were of analytical reagent grade. Deionized water was prepared with a Milli-Q water purification system.

The surface morphology of modified electrodes were characterized by field-emission SEM (Hitachi SU-8010). Electrodeposition, cyclic voltammetric (CV) and differential pulse voltammetric (DPV) experiments were carried out on a CHI 660D electrochemical workstation with a conventional three-electrode system: a glassy carbon electrode (GCE, diameter of 3 mm) with or without modifications as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode.

2.2. Fabrication of Au NPs/CNTs/graphene hybrids modified electrode

CNTs and graphene oxide (GO) with a weight ratio of 1:1 was first mixed together to form a homogeneous dispersion with a concentration of 1 mg/mL under the help of ultrasonic shake. Then, 10 µL of the above dispersion was cast onto surface of GCE. After drying in air, the obtained CNTs/GO/GCE as working electrode was placed into 0.1 M KCl solution, and a CV technique was performed by scanning from -1.5 V to 0 V for 10 cycles using the above three electrode system. In this process, the GO was electrochemically reduced to graphene. Then, the resultant CNTs/Graphene/GCE was immersed into deposition solutions with 1.0 mM $HAuCl_4$ and 10 mM CTAB involved. Galvanostatic technique with a current density of 3.5 mA/cm^2 was applied for 300 s to electro-deposition of Au NPs. Through this step, Au NPs/CNTs/graphene hybrids modified electrode was fabricated. For comparison, Au NPs/GCE, Au NPs/CNT/GCE and Au NPs/graphene/GCE were also prepared according to the above corresponding procedures.

3. RESULTS AND DISCUSSION

3.1. Morphological characterizations

The SEM images of electrodes modified with nanomaterials of CNTs, CNTs/graphene and Au NPs/CNTs/graphene hybrids are shown in Fig.1. As observed, CNTs have a nanotubular structure with a diameter of less than 10 nm (a). For CNTs/graphene, the tangled nanotubes were seen to be wrapped by 2D graphene nanosheets under the π-π stacking interactions (b). When Au NPs were further electrodeposited, a lot of Au NPs with homogeneous dispersion was distributed onto surface of CNTs/graphene (c). The size of Au NPs is in the range of 20 to 50 nm (d). In addition, it can also be seen that the Au NPs/CNTs/graphene hybrids shows a typical 3D and porous structure due to the

presence of interpace for tangled CNTs/graphene. This structure is beneficial for electron transfer, and meanwhile, facilitate the transport of target species to exposed active sites of nanomaterials [12,30].
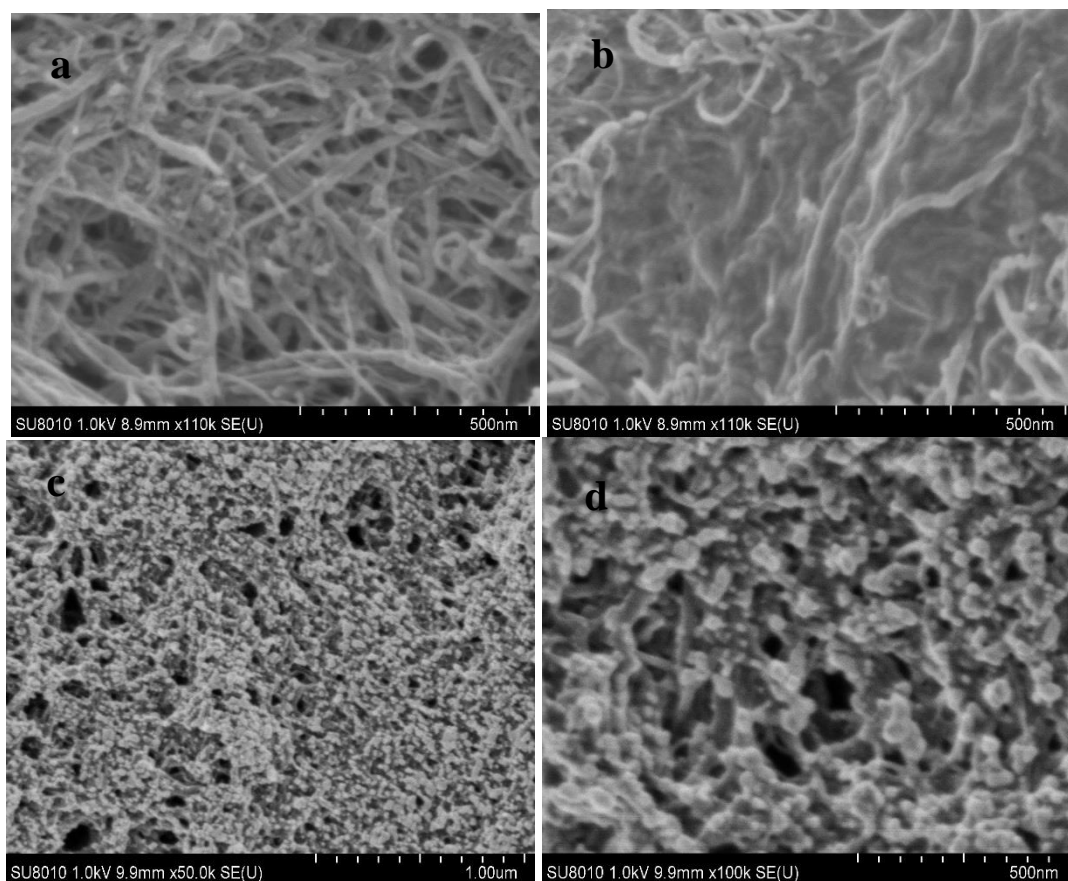

Figure 1. SEM images of electrodes modified with nanomaterials of CNTs (a), CNTs/graphene (b) and Au NPs/CNTs/graphene hybrids (c,d), respectively.

3.2. Electrochemical responses of dihydroxybenzene isomers at Au NPs/CNTs/graphene hybrids modified electrode

The electrochemical responses of dihydroxybenzene isomers at Au NPs/CNTs/graphene hybrids modified electrode was investigated, and the CV results were shown in Fig. 2. To exhibit the distinct advantages of the Au NPs/CNTs/graphene hybrids for dihydroxybenzene detection, the bare GCE, Au NPs/GCE, Au NPs/CNT/GCE and Au NPs/graphene/GCE were also compared. For the bare GCE, only two weak anodic peaks are observed. The anodic peak at potential of 0.36 V corresponds to oxidation of both HQ and CC, which indicates overlapped peak for HQ and CC oxidation. Therefore, it is unable to distinguish HQ and CC from their electrochemical signals at bare GCE. The anodic peak at 0.72 V is related with oxidation of RC. When the bare GCE was modified with nanomaterials such as Au NPs, Au NPs/CNT, Au NPs/graphene and Au NPs/CNTs/graphene, three separated and enhanced oxidation peaks are present. In addition, the oxidation peak potentials of HQ, CC and RC all shift to more negative values. Compared the anodic peak currents of isomers at these electrodes, it can

be found that the peak current height is in the following sequence: I(A u NPs) < I(Au NPs/CNT) < I(Au NPs/graphene) < I(Au NPs/CNTs/graphene). From these results, we can conclude that the introduction of CNTs or graphene both improve the electrocatalytic activities of Au NPs toward dihydroxybenzene due to the large surface area and excellent conductivity of these carbon nanomaterials. The integration of CNTs and graphene to form 3D CNTs/graphene nanostructure further enlarged the electrocatalytic activities of Au NPs to achieve the highest peak currents for oxidation of three isomers. At Au NPs/CNTs/graphene/GCE, the oxidation peak potentials of HQ, CC and RC is located at 0.15，0.26 and 0.65 V respectively, with the adjacent peak to peak separation of 0.11 and 0.39 V, suggesting the feasibility of Au NPs/CNTs/graphene hybrids for identification and simultaneous detection of the three isomers. For the cathodic curve, only two cathodic peak were observed, corresponding to reduction of HQ and CC respectively. There was no reduction peak of RC observed owning to the irreversible process for the electrochemical reaction of RC.
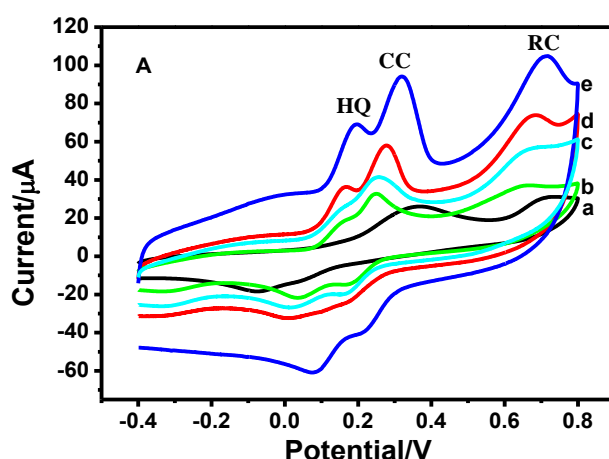

Figure 2. CV responses of 0.2 mM HQ, CC and RS in 0.1 M pH 5.7 ABS at GCE (curve a), Au NPs/GCE (curve b), Au NPs/CNT/GCE (curve c), Au NPs/graphene/GCE (curve d) and Au NPs/CNTs/graphene/GCE (curve e).

3.3. The effect of pH on electrochemical responses of dihydroxybenzene isomers

It is well known that the electrochemical oxidation of hydroxyl group in dihydroxybenzene isomers is accompanied by proton participation. Therefore, the influence of pH for 0.1 M electrolyte of ABS on anodic peak potentials of 0.2 mM HQ, CC and RC at Au NPs/CNTs/graphene/GCE was studied, the results of which is shown in Fig.3. The dihydroxybenzene isomers are prone to be oxidized in air at high pH conditions, thus, pH below 8.0 was used in this experiment. As seen from Fig.3, the oxidation peak potentials of dihydroxybenzene isomers shift negatively with the increase of pH with slope of -58.8 mV/pH，-61.8 mV/pH and -59.9 mV/pH for HQ, CC and RC, respectively. Based on Nerst equation, it is estimated that two electron accompanied by two proton are involved in the electrochemical oxidation of dihydroxybenzene isomers. This result is consistent with previously reported [26,29].
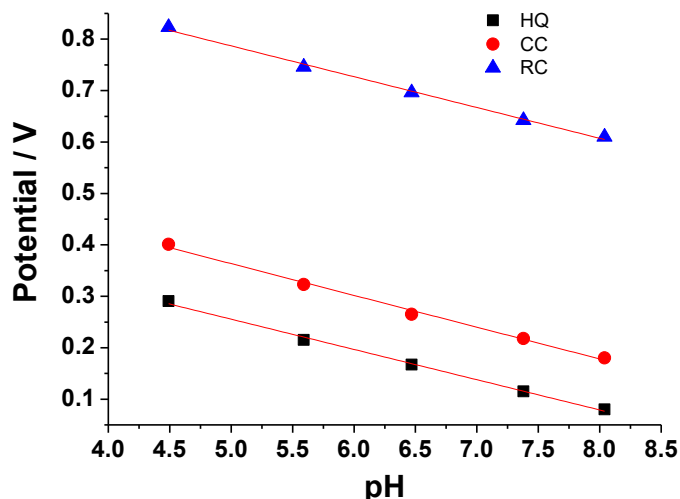
Figure 3. The influence of pH for 0.1 M electrolyte of ABS on anodic peak potentials of 0.2 mM HQ, CC and RC at Au NPs/CNTs/graphene/GCE.

3.4. Influence of the potential scan rate

Fig.4a shows CV responses of 0.2 mM HQ, CC and RC in 0.1 M pH 5.7 ABS at Au NPs/CNTs/graphene/GCE with different scan rates. Obviously, with the increase of scan rate, the oxidation peak currents of HQ, CC and RC increase accordingly, and a linear relationship between anodic peak currents and scan rates is obtained (Fig.4b), indicating a surface-controlled process for electrochemical reaction of HQ, CC and RC at Au NPs/CNTs/graphene/GCE. This imply that the adsorption of dihydroxybenzene isomers on Au NPs/CNTs/graphene hybrids dominates the process for electrochemical reaction.
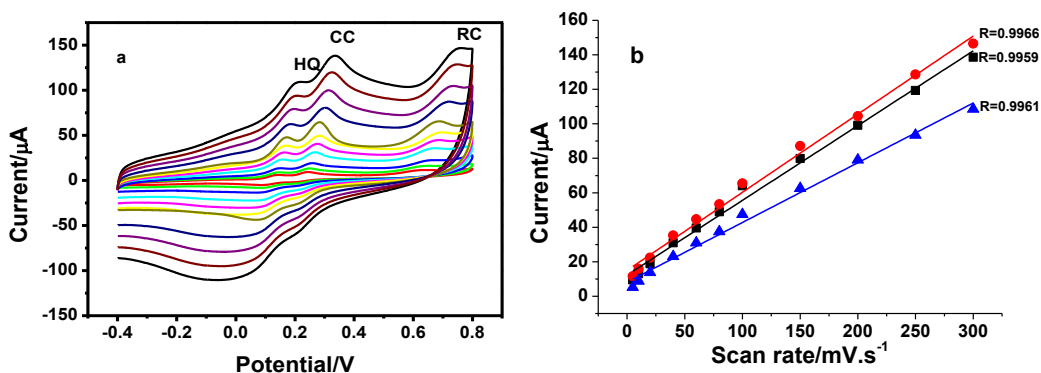

Figure 4. (a) CV responses of 0.2 mM HQ, CC and RC in 0.1 M pH 5.7 ABS at Au NPs/CNTs/graphene/GCE with different scan rates (from inner to outer:5, 10, 20, 40, 60, 80, 100, 150, 200, 250, 300 mV/s); (b) The relationship between peak currents of HQ, CC and RC and scan rate.

3.5. Differential pulse voltammetric results for simultaneous determination of dihydroxybenzene isomers

Differential pulse voltammetry (DPV) is proved to be a more sensitive method than traditional CV, therefore, it is exploited for quantitatively simultaneous determination of dihydroxybenzene isomers. Fig. 5 shows DPVs of Au NPs/CNTs/graphene/GCE in 0.1 M pH 5.7 ABS by stepwise additions of dihydroxybenzene isomers in the concentration range from 0 to 80 μM. Obviously, three significant oxidation peaks are observed at potentials of 0.04, 0.14 and 0.49 V, corresponding to HQ, CC and RC respectively, and the DPV peak to peak separation is 0.10 and 0.35 V, allowing for sensitive and simultaneous determination of the three isomers. The peak currents of HQ, CC and RC in DPV curves increase proportionaly to the concentration of dihydroxybenzene isomers in the range of 2~80 μM. The linear relationship between peak current and concentration for HQ, CC and RC can be expressed as I (μA)=11.6586+0.1826C(μM), I(μA)=9.5866+0.1643C(μM) and I(μA)=7.6535+0.0745C(μM), with corelation coefficient of 0.9940, 0.9917 and 0.9604 respectively. The limit of detection for HQ, CC and RC is estimated to be 0.8 μM、0.95 μM and 0.1 μM respectively. These results are comparable with those electrodes modified with electropolymerization of tetraruthenated oxovanadium porphyrin [31], poly-3-amino-5-mercapto-1,2,4-triazole-MWNTs film [32], electrospun carbon nanofibers [33], Fe_3O_4 functionalized graphene oxide-gold nanoparticle composite [34], but is inferior to multiwalled carbon nanotubes/polydopamine/gold nanoparticles composites modified electrode [35].
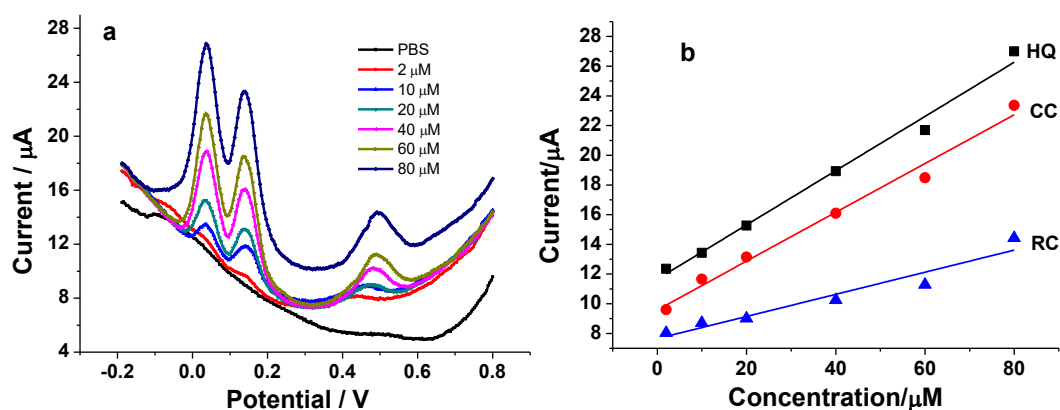

Figure 5. DPVs of Au NPs/CNTs/graphene/GCE in 0.1 M pH 5.7 ABS by stepwise addition of dihydroxybenzene isomers in the concentration range from 0 to 80 μM.

3.6. Stability and reproducibility of Au NPs/CNTs/graphene/GCE

Stability and reproducibility are vital factors for evaluating an electrochemical sensor. The electrochemical stability of the Au NPs/CNTs/graphene/GCE toward HQ (50 μM) detection was investigated over a month at intervals of 5 days. The results indicated that the modified electrode retained 95.1% of the initial current of HQ even for a storage time of a month, showing an excellent

storage stability. To study the reproducibility of the modified electrode, five Au NPs/CNTs/graphene modified electrodes were prepared according to the same fabrication method and its electrochemical response toward 50 μM HQ was monitored. It was found that only a relative standard deviation (RSD) of 3.2% was obtained for this five results, indicating a good fabrication reproducibility. Based on these results, the Au NPs/CNTs/graphene/GCE is appropriate for continuous analysis in real samples.

3.7. Interference studies

The interference of some possible interferents in water samples on the simultaneous determination of 50 μM HQ, CC, RC in ABS solution (0.1 M, pH 5.7) was tested. It is considered to have no interference when the current variation caused by interferents is less than 5%. The results demonstrates that 600-fold concentrations of Na^+, K^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Cl^-, Zn^{2+}, NO_3^- and SO_4^{2-} results in only a negligible interference. However, 5-fold concentrations of phenol, aminophenol and nitrophenol interfered seriously with the determination of dihydroxybenzene isomers.

3.8. Water sample analysis

Two kinds of water samples (tap water and river water) were checked to evaluate the performance of the fabricated electrode in real sample analysis. After filtered, the two water samples were diluted with 0.1 M pH 5.7 ABS. There was no dihydroxybenzene isomers found in this two samples, therefore, certain concentrations of standard solutions were spiked into water samples. The DPV responses of the samples were measured to obtain quantitative analysis from cablication curve. The obtained results are shown in Table 1. The recoveries are in the range of 95.7−104%, indicating good feasibility and reliability of the Au NPs/CNTs/graphene/GCE for identification and simultaneous detection of HQ, CC, and RC in water samples.

Table 1. Simultaneous determination of dihydroxybenzene isomers in real water samples.

Water samples	Added (μM)			Founded (μM)			Recovery (%)			RSD (%,n=4)		
	HQ	CC	RC	HQ	CC	RC	HQ	CC	RC	HQ	CC	RC
Tap water	10.0	10.0	10.0	10.2	9.83	9.57	102	98.3	95.7	4.5	5.2	3.8
	20.0	20.0	20.0	19.6	19.2	20.8	98.0	96.0	104	6.4	5.3	4.2
River water	5.0	5.0	5.0	5.2	5.3	4.8	104	106	96	3.3	2.8	5.7
	15.0	15.0	15.0	14.6	14.9	15.7	97.3	99.3	104	4.1	3.6	4.7

4. CONCLUSIONS

In this work, 3D CNT-graphene hybrid decorated with Au nanoparticles was prepared and used as electrode modifications for the identification and simultaneous determination of dihydroxybenzene

isomers including HQ, CC and RC. The Au NPs/CNTs/graphene/GCE showed three well-resolved voltammetric peaks with higher peak current and more negative peak potentials compared to the bare GCE. The observed electrocatalytic activities of Au NPs/CNTs/graphene hybrids toward dihydroxybenzene isomers is attributed to the superior conductivity, unique 3D nanostructure and large surface area. Good preformance of Au NPs/CNTs/graphene/GCE was obtained for simultaneous determination of HQ, CC and RC, such as high detection sensitivity, wide linear range, low detection limit and good reproducibility and stability. Furthermore, acceptable recoveries were obtained when the present method was used to determine the three dihydroxybenzene isomers in water samples.

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