



Copper nanoparticles modified nitrogen doped reduced graphene oxide 3-D superstructure for simultaneous determination of dihydroxybenzene isomers



Haifeng Zhou^a, Tingting Huang^b, Dejian Chen^c, Shunxing Li^{b,*}, Huiwu Yu^b, Yuhui Li^b, Qijun Song^{a,*}

^a The Key Lab of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, Jiangsu 214122, People's Republic of China

^b Department of Chemistry and Environment, Minnan Normal University, Zhangzhou, Fujian 363000, People's Republic of China

^c State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

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ABSTRACT

Copper nanoparticles modified nitrogen doped reduced graphene oxide 3-D superstructure was successfully prepared via a two-step reaction. Polydopamine was used as nitrogen source for the fabrication of nitrogen doped reduced graphene oxide and reducing agent for in-situ reduction of CuCl₂. After calcination under nitrogen protection, the conductivity, electron transfer ability and electrocatalytic activity of nanocomposites were substantially improved. The enhanced redox property could be attributed to the difference in the electronegativity of carbon and nitrogen atoms of the 3-D superstructure. By using this composite material, an electrochemical sensor was constructed for the detection of dihydroxybenzene isomers, which exhibited excellent sensitivity (with limit of detection at 81–131 nmol L⁻¹ levels), wide linear ranges (0.5–720 μmol L⁻¹) and good selectivity. Hence it was directly applied for the simultaneous determination of dihydroxybenzene isomers in contaminated samples (e.g., waste waters).

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1. Introduction

Dihydroxybenzene, substituted phenolic isomers, i.e., hydroquinone (HQ), catechol (CC), resorcinol (RC) are classified as priority toxic pollutants by the United States Environmental Protection Agency and the European Union. They often coexist in wastewater or natural water, and exhibit low degradability in the ecological system. Therefore, rapid and simultaneous determination of these compounds is of significant importance for the environment monitoring and protection. To date, several analytical technologies have been developed to quantify dihydroxybenzene isomers, including capillary electrophoresis [1], gas chromatography–mass spectrometry [2], high performance liquid chromatography [3], and synchronous fluorescence [4]. However, these methods are not quite suitable for in-situ monitoring application, due to the requirement of expensive instrument, complicated and time-consuming

pretreatment processes, etc. Due to the advantageous features such as high sensitivity and selectivity, low detection limit, simple operation and low cost, the electrochemical methods have showed great potential for such applications. Specially, nanomaterial modified electrode could endow electrochemical sensors with improved performance [5]. A variety of nanomaterials, such as carbon nanotubes [6], metal sulfides [7], Metal-Organic Framework Materials (MOFs) [8], quantum dots [9], and graphene [10], have been used as the sensor materials for simultaneous determination of these isomer compounds (HQ, CC and RC). These materials made great contributions in the development of the sensors for the detection of HQ, CC and RC. Unfortunately, the complicated synthesis approach, high toxicity, and/or poor analytical performance hindered their wide applications. Therefore, the development of robust and convenient sensing platform for the simultaneous determination of dihydroxybenzene isomers is urgently needed. This may be achievable by the construction of the nanomaterials based sensor with superb electrochemical performance.

In this regard, copper nanoparticles (Cu NPs) could be an ideal candidate, because they have excellent redox, catalytic, antifungal, and antifouling properties. In addition, they can be prepared

* Corresponding authors.

E-mail addresses: lishunxing@mnnu.edu.cn, shunxing.li@aliyun.com (S. Li), qsong@jiangnan.edu.cn (Q. Song).

conveniently and cost effectively in comparison with the noble metal nanoparticles. The electrochemical sensors fabricated with composite of Cu NPs and carbon based materials have shown excellent redox properties [11–15]. The synthesis process, however, was relatively complex and required additional reducing agent. The synthesis process may be substantially simplified by utilizing the multifunctional property of dopamine. On the one hand, dopamine can undergoes self-polymerization and functionalization in the presence of dissolved oxygen under alkaline conditions [16] and the resultant polydopamine (PDA) can be deposited spontaneously on the surfaces of various substrates. On the other hand, the functional groups (N–H, –OH, C–O, and C–N) possessed by PDA can absorb and reduce metal ions into metal/metallic oxide nanoparticles [17–20]. This unique approach would open up a new path for the synthesis of Cu NPs. Carbon substrates play a vital role in electrode materials due to the electron transfer requirement of a complete channel. Graphene is a real two-dimensional material, which show charming application in electrochemical sensors due to its unique physical and chemical properties [21]. Hu et al. [22] developed a synergistically integrated graphene-based ternary composite (rG-Cu) consisting of uniform PDA-functionalized graphene sheets and well-dispersed Cu NPs, which show high catalytic activity and good reusability for catalytic reductions. However, they ignored the strong reducibility and adsorption properties of PDA, i.e., hydrazine, a highly toxic and hazardous material was used as reducing agent in reaction process. Moreover, PDA can be used as a rich source of nitrogen [23–26]. Typically, N-doped graphene exhibits rich free charge-carrier densities, outstanding conductivities [27,28], excellent electron transfer rate and high catalytic activity, hence it has been used to develop electrochemical analysis platform. The composite materials of graphene modified with metal nanoparticles have been confirmed to greatly increase the conductivity, electrocatalytic and redox properties [29]. After the pyrolysis of PDA modified graphene oxide, we can obtain the nitrogen doped graphene with a convenient and green synthesis method.

Thus a simple protocol was proposed in present work for green synthesis of Cu NPs and the fabrication of in-situ nitrogen doped reduced graphene 3-D superstructure. The new method can not only synthesize Cu NPs and nitrogen doped graphene with an environment-friendly approach, but more importantly, the resultant the copper nanoparticles and nitrogen doped graphene exhibited a synergistic effect, which substantially improved electrochemical performance of the composite material modified electrode. The electrochemical sensor developed in this work was successfully applied to the simultaneous determination of dihydroxybenzene isomers, which displays wide detection range, low detection limit, high sensitivity and good selectivity (Scheme 1).

2. Experimental

2.1. Materials

2-Amino-2-hydroxymethylpropane-1,3-diol (Tris), cupric chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), and graphite powder were purchased from Sinopharm Chemistry Reagent Co., Ltd. (Shanghai, China). HQ, CC, RC and dopamine hydrochloride were purchased from Aladdin (Shanghai, China). Ethanol, sulphuric acid (98%), potassium permanganate, and sodium nitrate were obtained from Xilong Chemical Co., Ltd. (Guangdong, China). All of the chemicals were analytical grade and used directly without further purification. Deionized water was purified by a Millipore-Q system (Millipore Co., USA) and used as a solvent with a resistivity of $18.2 \text{ M}\Omega$.

Standard stock solutions (50 mmol L^{-1}) of CC, HQ, and RC were prepared and stored under low temperature (4°C) in the dark conditions. Desired concentrations of HQ, CC and RC should be further

diluted by water immediately before used. As the supporting electrolyte, phosphate buffer saline (PBS, 0.1 mol L^{-1} , pH 4.0–9.0) was kept at room temperature in the dark conditions.

2.2. Preparation of GO, GO-PDA, GO-PDA- CuO_x and GR-CN-Cu microspheres

In a typical procedure, GO was synthesized according to a modified Hummers method [30], and the details could be found in Supporting information (SI). GO-PDA was prepared according to our previous work [20]. Briefly, GO (50 mg) was suspended in deionized water (100 mL) by sonication, then Tris (0.121 g) and dopamine hydrochloride (50 mg) were successively added and the mixture was stirred for 24 h at room temperature. The resultant products (i.e., GO-PDA) were separated, rinsed with deionized water three times, and dried at 60°C under vacuum for 8 h.

The above prepared GO-PDA (100 mg) was suspended in deionized water (100 mL) by sonication. Then a certain amount CuCl_2 (3, 5 and 8 mmol L^{-1}) was added into the suspension solution and the mixture was stirred for 24 h at room temperature. The products (i.e., GO-PDA- CuO_x -3, GO-PDA- CuO_x -5, GO-PDA- CuO_x -8) were centrifugally separated, rinsed with deionized water three times. In the end, they were dried in a 60°C vacuum oven.

For GR-CN-Cu preparation, GO-PDA- CuO_x was placed in a porcelain crucible and heated at 500 – 800°C for 2 h with a heating rate of 2°C min^{-1} in a N_2 atmosphere. After cooling to ambient temperature, the final product was labeled as GR-CN-Cu.

2.3. Preparation of modified electrodes

Prior to modification, the bare GCE was polished to a mirror-finish with $1 \mu\text{m}$, $0.3 \mu\text{m}$, and $0.05 \mu\text{m}$ alumina slurry successively, then sonicated successively with anhydrous alcohol and double-distilled deionized water, and dried under N_2 blowing. An amount of 2 mg GR-CN-Cu was dispersed in the mixed solution containing $50 \mu\text{L}$ water, $50 \mu\text{L}$ ethanol, and 0.05 wt% nafion. Then, the as-prepared GR-CN-Cu solution (0.1 mg mL^{-1} , $10 \mu\text{L}$) was casted onto the pretreated GCE surface and dried under room temperature. The obtained electrode was noted as GR-CN-Cu/GCE. The GO-PDA/GCE, GO-PDA- CuO_x /GCE and GR-CN/GCE were also prepared with the above method but GR-CN-Cu was replaced by GO-PDA, GO-PDA- CuO_x or GR-CN respectively.

2.4. Electrochemical measurements

Differential pulse voltammetry (DPV) and cyclic voltammetry (CV) experiments were performed with an Electrochemical Workstation (CHI 660E, Shanghai Chenhua Instrument Co., Shanghai, China) at room temperature. The modified GCE, platinum wire, and Ag/AgCl/KCl (saturated) were served as working, counter and reference electrode, respectively. The DPV and CV measurements were conducted from 0 to 0.8 V with a pulse amplitude of 100 mV s^{-1} and a pulse width of 50 ms.

3. Results and discussion

3.1. Characterization of GO-PDA, GR-CN, GO-PDA- CuO_x and GR-CN-Cu

The materials were characterized by the scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectra, and the experimental details were given in Supporting information. The SEM and TEM results for the samples (GO-PDA, GR-CN, GO-PDA- CuO_x and GR-CN-Cu) obtained at each stage are shown in Figs. 1 and S1. The prepared GO-PDA and GR-CN

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