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Research paper

Simultaneous electrochemical sensing of hydroquinone and catechol using nanocomposite based on palygorskite and nitrogen doped graphene

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ABSTRACT

A novel electrochemical sensor based on nitrogen doped graphene (NGE) and palygorskite (Pal) for the simultaneous detection of hydroquinone (HQ) and catechol (CT) has been proposed. Pal is particularly pointed out for its appreciable specific surface area and reactive-OH groups on its surface. Acid treatment Pal demonstrated better physico-chemical properties, which are propitious to electrochemical sensor construction. The introduction of NGE not only improved the poor conductivity of Pal but also served as an excellent adherent matrix. The modified electrode demonstrated the enhanced redox peak currents of HQ and CT with good discrimination. Under optimized conditions, the linear ranges for HQ and CT were 2–50 μM and 1–50 μM, with detection limit (LOD) of 0.8 μM and 0.13 μM, respectively. The result designates that the Pal/NGE composite promises to be a new eco-friendly modified material for sensor fabrication.

1. Introduction

Various kinds of clay minerals are scattered throughout in the environment and our daily life. The utilization of clay minerals can be traced back to the primeval times when our ancestors mainly used them for pottery and ceramics making (Jyh-Myng Zen, 2004). In the context of economy and green chemistry, one can find diverse clay minerals that can fit into a desired application, be it environmental governance (Yang et al., 2016), material processing (Mu et al., 2013) medical application (Li et al., 2014; Yufei et al., 2009) and scientific research. Palygorskite (Pal) is a natural fibrillar nano-clay with porous and large specific area (Al-Futaisi et al., 2007). It is a kind of phyllosilicate which is different from other sheet silicate family in absence of continuous octahedral sheets. There are plenty of reactive hydroxide groups exist on the surface of palygorskite, which can act as catalytic active sites thereby making it suitable for catalytic application (Lu et al., 2015; Mu and Wang, 2015; Xie et al., 2016). In order to exploit the merits of Pal ulteriorly, its physico-chemical performances can be regulated either by heating, acid pre-treatment or surface modification (Barrios et al., 1995; Xue et al., 2011). All of the advantages of Pal, such as excellent salt and alkali resistance, appreciable specific surface area, abundant in nature and eco-friendly, make it a promising choice for electrochemical sensor fabrication (Luo et al., 2016). Zhang et al. proposed a nanohybrid sensor based on carboxyl functionalized graphene dispersed palygorskite for niclosamide determination and a low LOD of 4.6 nM was acquired (Zhang et al., 2017).

However, poor conductivity of Pal is a fatal obstacle to its further application. A suitable conductive matrix may be introduced into Pal to broaden its application in electrochemistry. Among various conductive matrix, NGE has been emerged greatly in scientific research due to its excellent conductivity and catalysis (Lee et al., 2010). For example, Wen et al. developed a carboxymethyl cellulose, Pal and nitrogen doped graphene (NGE) nanocomposite modified electrode for simultaneous analysis of uric acid, xanthine and hypoxanthine (Wen et al., 2017).

The usage of dihydroxybenzene isomers seeps into various aspects of our lives. They are important intermediates of the pharmaceutical industry, extensively used in preservatives, dye, stabilizer, antioxidants and so on (Wang et al., 2003). However, they take a significant toll on the environment due to their toxity and low degradability (Yin et al., 2011). The similar structure and property of dihydroxybenzene isomers makes them difficult to be detected at the same time, especially catechol (CT) and hydroquinone (HQ). Therefore, it is crucial to draw a distinction between CT and HQ. Traditional analytical methods of dihydroxybenzene isomers, such as chromatography (Foglia et al., 2005), spectrophotometry (Nagaraja et al., 2001) and synchronous fluorescence (Pistonesi et al., 2006) usually require sophisticated instruments and expert operators, which result in high cost analysis. By contrast, it is a rapid and economical method to detect dihydroxybenzene isomers

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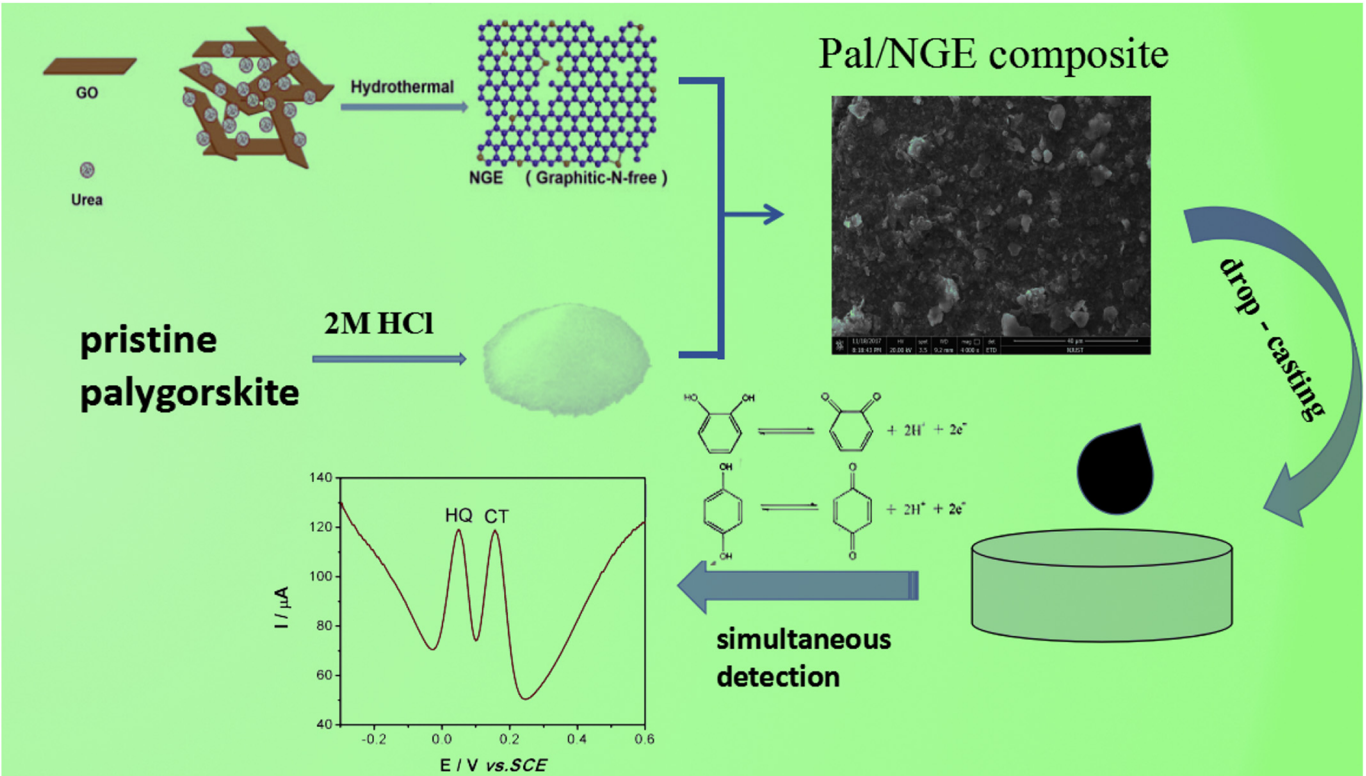

Scheme 1. Schematic representation of Pal/NGE/GCE preparation and HQ and CT simultaneous detection.

by electrochemical modified electrodes (Si et al., 2014; Yao et al., 2014)

Herein, a novel electrochemical sensor based on Pal and NGE for the simultaneous analysis of HQ and CT was developed. Palygorskite presented better physico-chemical properties after acid treatment, making it more suitable for sensor construction. The introduction of NGE not more than served as an excellent adherent matrix but also improved the poor conductivity of Pal significantly (Borowiec et al., 2013; Wu et al., 2008). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were used so as to evaluate the sensing performance of the redox of HQ and CT at Pal/NGE/GCE. The peak currents enhanced remarkably with good discrimination between HQ and CT compared to the bare GCE, NGE/GCE and Pal/GCE.

2. Experimental

2.1. Material and chemicals

Graphite powder was purchased from Shanghai Carbon Co.,Ltd. Pristine Pal (3000 mesh) was obtained from Jiangsu Jiuchuan Clay Company (Xuyi, China). Citric acid monchydrate, urea, disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4{\cdot}12H_2O$), Potassium ferricyanide ($K_3[Fe(CN)_6]$), KCl and *N*,*N*-dimethylformamide (DMF) were purchased from Chengdu Kelong Chemical Co.,Ltd. Potassium ferricyanide ($K_4[Fe(CN)_6]$) was purchased from Shanghai Lingfeng Chemical Reagent Co.,Ltd. Catechol was purchased from Sinopharm Chemical Reagent Co.,Ltd., and hydroquinone was obtained from Guangzhou Jinhuada Chemical Reagent Co.,Ltd. All the chemicals were analytical grade and used as received without any purification. 0.1 M citric acid phosphate buffer solution (CPS) was prepared from citric acid monchydrate and $Na_2HPO_4{\cdot}12H_2O$.

2.2. Apparatus

CHI660D electrochemical workstation (Shanghai Chenhua Instrument Company, China) was used for all electrochemical measurements. Traditional three electrodes system was exploited for electrochemical measurements, bare glassy carbon electrode (GCE) or modified electrodes as the working electrode, saturated calomel electrode (SCE) as the reference electrode, while platinum wire electrode acts as the counter electrode. Precision acidity meter PHS-2C (Shanghai Dapu Instrument Co., Ltd) was used to adjust the pH value of electrolyte solution. The X-ray diffraction (XRD) patterns were acquired by Advance X (Bruck AXS GmbH) with a Cu target. Fourier transform infrared spectroscopy (FTIR) was recorded on Nicolet islo (ThermoFisher) with Ever G10 optical source. The BET measurement was performed by TriStar II 3020 Version 3.02 (Micromeritics Instrument Corporation).

2.3. Preparation of NGE

Graphene oxide (GO) was prepared from graphite powder by Hummers method (Borowiec et al., 2013; Wu et al., 2008). Urea was used as nitrogen source during the preparation process of NGE (Lei et al., 2012; Xia et al., 2013). In brief, 150 mL GO solution (0.5 mg/mL) was adjusted to pH 8.0 by diluted $NH_3{\cdot}H_2O$. Then, urea (5.0 g) was added into above GO solution with violent stirring in 95 °C,maintained the temperature and refluxed for 30 h. The final black product was obtained by filter, washed several times by deionized water and ethanol, finally was freeze-dried.

2.4. Preparation of modified electrodes

Pristine Pal was pretreated by 2 M HCl for 60 h in room temperature. The precipitate was collected by filter, washed several times with distilled water and then freeze-dried. The product was stored in a sealed condition in room temperature. A certain mass of Pal was added into 0.5 mg/mL NGE (DMF), ultrasonication for 6 h to obtain homogeneous black suspension. Four microliters of this solution were drop-casting onto the surface of glassy carbon electrode and dried in dryer for further used. For comparison, Pal and NGE modified electrodes were prepared by the same method. The electrochemical sensing process was