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Preparation and characterization of a novel hybrid hydrogel composite of chitin stabilized graphite: Application for selective and simultaneous electrochemical detection of dihydroxybenzene isomers in water

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ABSTRACT

The development of new and robust sensors for real-time monitoring of environmental pollutants have received much attention. Therefore, in the present work, we have fabricated a simple and robust electrochemical sensor for the simultaneous electrochemical determination of dihydroxybenzene isomers using chitin (CHI) stabilized graphite (GR) hydrogel composite modified electrode. The GR-CHI hydrogel composite was prepared by a simple sonication of raw GR in CHI solution and the as-prepared materials were characterized by range of physicochemical methods. Compared with CHI and GR modified electrodes, the GR-CHI hydrogel composite modified electrode shows an excellent electron transfer ability and enhanced electrocatalytic activity towards hydroquinone (HQ), catechol (CC) and resorcinol (RC). Differential pulse voltammetry was used for the simultaneous determination of HQ, CC and RC. Under optimized conditions, the fabricated electrode detects the HQ, CC and RC in the linear response from 0.2 to 110.6 μM, 0.3 to 110.6 μM and 1.3 to 133.4 μM, respectively. The detection limit for HQ, CC and RC were 0.065 μM, 0.085 μM and 0.35 μM, respectively. The sensor shows its appropriate practicality towards the determination of HQ, CC and RC in different water samples.

1. Introduction

In recent years, development of cost-effective and robust sensors for real-time monitoring of environmental pollutants has received much attention in the scientific community [1]. In particular, the simultaneous determination of dihydroxybenzene isomers such as hydroquinone (HQ), catechol (CC) and resorcinol (RC) has received sustainable interest due to their significant role in the industries [2]. For example, the HQ, CC and RC has been continually used as important chemicals in various industrial sectors, including pesticide, cosmetics, dyes, medicine, tanning, photography and pharmaceutical applications [3,4]. The U.S. Environmental Protection Agency (EPA) and the European Union (EU) has revealed that HQ, CC and RC as toxic environmental pollutant due to their high toxicity and poor degradability in the biological environment [2]. Different analytical methods have been reported so far for the simultaneous determination of HQ, CC and RC [3,5–9]. Compared to high-performance liquid chromatography, spectrometry, fluorescence and chemiluminescence methods, the electrochemical methods are found to be a simple and inexpensive for the simultaneous determination of dihydroxybenzene isomers [3,10]. However, the simultaneous determination of HQ, CC and RC is quite challenging on unmodified carbon electrodes such as glassy and screen-printed carbon due to their poor selectivity and electrode fouling [11]. Hence, the chemically modified electrodes have been widely used for simultaneous determination of HQ, CC and RC owing to their high conductivity, high stability and wide potential window [12].

Carbon nanomaterials and its composites have received significant interest in the electroanalytical community due to their higher surface area, wide potential window and extreme stability [13–15]. For example, carbon nanotubes, graphene oxide and reduced graphene oxide or their composites have been widely used for the simultaneous determination of HQ, CC and RC [3,10,16–19]. Carbon nanomaterials modified electrodes exhibited good electroanalytical performance for a range of analytes, including dihydroxybenzene isomers, yet the synthesis of carbon nanomaterials is quite-time consuming and expensive. Hence, simple and cost-effective nanomaterials with improved analytical performance for the simultaneous determination of HQ, CC and RC is of interest to the analytical community. Our recent studies revealed

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that the carbohydrate polymers entrapped graphite (GR) exhibited an enhanced electron transfer ability towards dopamine and the analytical performances have been found analogous to carbohydrate polymers entrapped graphene [20,21].

In the present work, we prepared a highly stable chitin (CHI) stabilized GR hydrogel composite by a simple sonication of GR in CHI solution for the first time. Compared to graphene and other carbon nanomaterials modified electrodes, the GR/CHI hydrogel composite is less expensive, environmentally friendly and can be prepared in a short time (45 min). It is well-known that CHI is a low-cost carbohydrate biopolymer with excellent biocompatibility, biodegradability, low toxicity and high mechanical stability [22,23]. The unique properties of CHI are often more promising in various applications such as protein sorption, water remediation, food wrapping, tissue engineering, wound dressings and drug delivery [24–26]. To the best of our knowledge, we have for the first time, we have prepared GR-CHI hydrogel composite and its potential application in electroanalysis. As a proof, the as-prepared GR-CHI hydrogel composite is used for the simultaneous determination of HQ, CC and RC and the analytical characteristics were compared with graphene-CHI hydrogel composite modified electrode. The strong hydrogen bonding between dihydroxybenzene isomers with CHI and large edge plane defects of exfoliated GR sheets in the composite are result into the enhanced electrocatalytic activity of dihydroxybenzene isomers. The electrochemical behavior of HQ, CC and RC was studied and the analytical performance of the GR-CHI hydrogel composite modified electrode was compared with previously reported carbon nanomaterials modified electrodes (see Table 1).

2. Experimental details

2.1. Materials and method

Chitin (from crab shells) and raw graphite powder (average diameter > 20 μm) were purchased from Sigma-Aldrich and used without purification. Hydroquinone, catechol and resorcinol were obtained from Wako Pure Chemical Industries, Ltd. and used as received. Phosphate buffer with pH 7 (PBS) was used as a supporting electrolyte, and prepared using 0.1 M Na_2HPO_4 and NaH_2PO_4. The chemical solutions were prepared using Millipore water without purification.

CHI 750a Electrochemical analyzer (CH instruments) was used for the cyclic voltammetry and differential pulse voltammetry (DPV) measurements. The DPV was operated under the pulse width = 0.05 s, sampling width = 0.0167 s, amplitude = 0.05 V, and pulse period = 0.2 s. Hitachi S-3000 H scanning electron microscope was used to evaluate the surface morphological studies. Thermo SCIENTIFIC Nicolet iS10 instrument was used for the Fourier transform infrared spectroscopy (FTIR) measurements. Electrochemical impedance spectroscopy (EIS) was performed using IM6ex ZAHNER (Kronach, Germany). Typical three electrode system was used for electrochemical experiments, in which modified glassy carbon electrode (GCE), Sat. Ag/AgCl and platinum wire were used as a working, reference and counter electrodes, respectively. The electrochemical measurements were carried out at room temperature in absence of oxygen.

2.2. Preparation of GR-CHI hydrogel

To prepare GR-CHI hydrogel, first the CHI solution was prepared by dissolving 20 mg of CHI into the 5% acetic acid for 30 min sonication. Then, the raw GR (5 mg mL^{-1}) was added into the CHI solution and sonicated continuously for 45 min. After the successful sonication, the clear GR-CHI hydrogel was obtained. The schematic representation of the preparation of GR-CHI hydrogel composite is shown in Scheme 1.

About 8 μL of the GR-CHI hydrogel (optimum concentration) composite was drop casted on the pre-cleaned GCE and dried at room temperature. The obtained GR-CHI hydrogel composite modified electrode was further used for electrochemical experiments. The CHI modified electrode was prepared by drop coating of CHI solution without GR. Consequently, the GR modified electrode was prepared without CHI and GR dispersion was prepared by similar procedure as reported previously [21]. For comparison, the graphene-CHI hydrogel composite was prepared by similar method using graphene instead of GR. The modified electrodes were stored at room temperature under dry condition when not in use.

3. Results and discussion

3.1. Characterizations

The surface morphology of the as-prepared materials was characterized by SEM. Fig. 1 shows the SEM images of GR (A), CHI (B) and GR-CHI hydrogel composite in lower (C) and higher (D) magnification. The SEM image of GR shows flake sheet morphology with the association of bundle of micro graphitic sheets. The SEM of CHI shows the dense pore structure morphology where CHI microfibers are interlinked each other. Whereas, the uniform distribution of CHI in GR layers was observed in the SEM image of GR-CHI hydrogel composite. The strong

Table 1

Comparison of analytical performance of the as-prepared GR-CHI hydrogel composite modified electrode with the previously reported modified electrodes for the simultaneous determination of HQ, CC and RC.

Electrode	Linear response range (μM)			LOD (μM)			Ref.
	HQ	CC	RC	HQ	CC	RC	
GR/CHI/GCE	1.0–400.0	1.0–550.0	1.0–300.0	0.75	0.75	0.75	[3]
Poly-*p*-ABSA/GCE	1.2–600.0	2.0–900.0	NR	0.4	0.5	NR	[9]
GR–La$(OH)_3$/GCE	5.0–300.0	5.0–300.0	NR	0.05	0.01	NR	[11]
CNF/GCE	6.0–200.0	2.0–200.0	NR	0.25	0.1	NR	[12]
MOF/CHI-ERGO/GCE	5.0–400.0	2.0–200.0	1.0–200.0	0.41	0.44	0.33	[13]
MWNTs-IL/GCE	0.2–35.0	0.18–35.0	NR	0.07	0.06	NR	[17]
ERGO/GCE	6.0–200.0	1.0–200.0	NR	0.2	0.1	NR	[18]
RGO-CuNPs/GCE	3.0–350.0	3.0–350.0	12.0–200.0	0.03	0.03	0.09	[19]
CdSe nanosheets/GCE	0.6–1500.0	0.2–300.0	NR	0.011	0.06	NR	[27]
Fe_3O_4/NH_2-CNTs/FTO	1.0–260.0	NR	NR	0.5	NR	NR	[30]
PANI/MnO_2/GCE	0.2–100.0	0.2–100.0	0.2–100.0	0.13	0.16	0.09	[31]
ECF-CPE	1.0–200.0	1.0–200.0	NR	0.4	0.2	NR	[32]
NCNT@CNF/GCE	0.1–425.0	0.08–350.0	NR	0.05	0.02	NR	[33]
GR-CHI/GCE	0.2–110.6	0.3–110.6	1.3–133.4	0.065	0.085	0.35	This work

Abbreviations:

LOD – limit of detection; GR – graphene; CHI – chitosan; GCE – glassy carbon electrode; Poly-*p*-ABSA – poly (*p*-aminobenzoic acid); NR – not reported; CNF – carbon nano-fragment; MOF – metal organic framework; ERGO – electrochemically reduced graphene oxide; MWCNTs – multiwalled carbon nanotubes; IL – ionic liquid; CNTs – carbon nanotubes; FTO – fluorine-doped tin oxide; PANI – polyaniline; ECF – electrospun carbon nanofiber; CPE – carbon paste electrode; NCNT – *N*-doped carbon nanotube; CNF – electrospun carbon nano-fiber.