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Selective amperometric and flow injection analysis of 1,2-dihydroxy benzene isomer in presence of 1,3- and 1,4-dihydroxy benzene isomers using palladium nanoparticles-chitosan modified ITO electrode

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ABSTRACT

Amongst various isomers of dihydroxy benzene, 1,2-dihydroxy benzene (Catechol, CA) isomer and its derivative based natural compounds are considered to be the key functional group for various health benefits. In electrochemistry, pulse voltammetric techniques combined with chemically modified electrodes (CMEs) have been often reported for simultaneous detection of 1,2- (CA); 1,3- (Resorcinol, RE) and 1,4-dihydroxy benzene (hydroquinone, HQ) isomers at discreet potentials, ~0.1, ~0.2 and ~0.4 V vs Ag/AgCl, respectively, in a neutral pH condition. Indeed, the above technique and the reported CMEs were not suitable for selective amperometric i-t based detection of CA without interference from HQ and RE. In fact, at CA detection potential, ~0.2 V, HQ also got co-detected. Herein, we report a palladium nanoparticles-Chitosan indium tin oxide modified electrode (ITO/CHIT@Pd_{nano}) as a selective amperometric sensor system for CA isomer detection without any interference of HQ and RE. A specific interaction between Pd^{2+} and CA as {Pd^{2+}-CA complex} is proposed as a key factor for the selectivity achieved in this work. As a proof of concept, flow injection analysis of CA functional group in wine and tea real samples was demonstrated.

1. Introduction

Selective and sensitive determination of polyphenolic dihydroxy benzene isomers like 1,2-dihydroxy benzene (catechol, CA), 1,3-dihydroxy benzene (resorcinol, RE) and 1,4-dihydroxy benzene (hydroquinone, HQ) and its derivatives (dopamine, DA) is highly challenging research interest in the field of environmental, biochemical and medicinal chemistry [1,2]. Due to their structural similarities, isomers of polyphenolic compounds are coexisting as a mixture in many real samples [3,4]. For instance, a mixture of 1,2- and 1,3-dihydroxy benzene derivatives such as catechin, epicatechin, (−)-epicatechin-3-gallate, (−)-epigallocatechin and (−)-epigallocatechin-3-gallate exist in green tea and tanned wined samples [3]. Among these isomers, CA derivatives contain natural products like (−)-epigallocatechin-3-gallate is identified as a key compound for the human health benefits [3]. Thus, selective detection of the CA functional group without interferences from other isomers like HQ and RE and co-existing biochemicals such as ascorbic acid, glucose and cysteine is a highly demanding task in analytical chemistry. Herein, we report a simple, selective and sensitive amperometric *i-t* method for the detection of CA and its derivatives using palladium nanoparticles-chitosan chemically modified indium tin-oxide electrode (designated as ITO/CHIT@Pd_{nano}) in a neutral pH solution.

For the detection of dihydroxy benzene isomers, several analytical methods such as spectrophotometric [5], colorimetric [6], solid-phase extraction [7], GC–MS [8], HPLC [9,10] and electrochemical [11–15] techniques have been reported. In UV–visible spectroscopic technique, the specific reducing ability of this dihydroxy isomer by silver ions agglomerated gold nanoparticles and its distinct color changes appeared was referred as a quantitative tool for the isomers discrimination [6]. In the separation based techniques like GC–MS and HPLC, the analytes exposed to derivatization reagents to form an amenable compounds, was subjected to separation via expensive columns [8,9]. Meanwhile, differential pulse (DPV) and linear sweep voltammetric (LSV) techniques based electrochemical methods have been reported for the simultaneous

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detection of these isomers at three distinct redox potentials on solid carbon electrodes like carbon nanotubes [12,13], graphitized mesoporous carbon [3], graphene oxide [14] and reduced graphene oxide [15] modified glassy carbon electrode (GCE) and screen printed carbon electrode (SPE). Unfortunately, these electrodes have been suffered seriously by strong adsorption, passive surface film formation and **surface-fouling** problems. For example, CA gets strongly chemisorbed/adsorbed on activated carbons (GCE* or SPE*) and multiwalled carbon nanotubes (CA@MWCNT) via —C—C— hydrogen bonding and π–π interactions, respectively [16–18]. On the other hand, amperometric *i-t* technique based methodology under hydrodynamic condition favors adsorption-less and low analyte volume detection with excellent sensitivity and selectivity. Indeed, this technique was rarely reported for selective detection of CA in presence of other isomers. Since, co-electrochemical oxidations of these isomers occurred at a closer detection potentials, for example, HQ at ~0.1 V, CA at ~0.2 V, RE at 0.4 V vs Ag/AgCl in neutral pH, it is difficult to detect CA selectively by amperometric technique.

It is noteworthy that amperometric sensing of HQ without interference from CA and RE is feasible [11,19–24], if applied potential is fixed at around 0.1 V. Nevertheless, at an applied potential of 0.2 V, elimination of the CA interference is difficult. Thus, selective detection of CA without interference of HQ and RE is rarely reported in the literature [25]. Meanwhile, enzyme based systems such as tyrosinase, a binuclear copper-containing monoxygenase enzyme [26,27] or polyphenol oxidase [28] based biosensor systems were also reported for the detection of dihydroxy benzene isomers. Again, these biosensors are non-selective to 1,2-dihydroxy benzene, other isomers such as HQ, RE, phenol are also getting oxidized and detected [26–28]. Note that working with enzymatic systems is complicated, expensive, time consuming and several precautions should be taken to address the stability and temperature concerns. In this work, we show selective amperometric detection of CA without interference from HQ and RE on ITO/CHIT@Pd_{nano} modified electrode in neutral pH solution.

In electroanalytical chemistry, flow injection analysis coupled electrochemical detection (FIA-ECD) is referred as an advanced amperometric technique which offers direct, selective, sensitive- and low volume (~20 μL) detection [25,29]. So far, a copper based modified electrode was **reported for** the selective detection of CA without interference of HQ and RE, wherein, occurrence of selective complexation reaction between copper and 1,2-dihydroxy benzene isomers, which produce a current signal at narrow potential, −0.05 V vs Ag/AgCl, was further tuned [25]. Unfortunately, in the above mentioned technique, fixing the right copper complexation potential for the formation of five membered Cu(II)-*ortho*-quinolate intermediate is highly difficult task. In the present study, palladium nanoparticles stabilized chitosan polymeric composite modified ITO electrode was prepared by simple potential cycling in pH 7 PBS (ITO/CHIT@Pd_{nano}), which showed elegant and selective detection of CA. Note that Pd-chitosan based chemically modified electrode has been used as a base material for biosensor development [30,31] and small molecule electrochemical oxidation [32]. The amino functional group in the chitosan favors immobilization of the Pd species through a weak complexation bonding as in Scheme 1. A homemade FIA was further developed using ITO/CHIT@Pd_{nano} ECD and demonstrated the selective detection of 1,2-dihydroxy benzene and its derivatives in wine and tea real sample analysis with good recovery values.

2. Experimental

2.1. Reagents and materials

ITO (resistivity = 30–60 Ω/sq), Chitosan flacks, CH_3COOH **(99.98%)**, isomers of dihydroxy benzenes (CA, HQ, RE) of analytical grade were all purchased from Sigma-Aldrich, USA and used as received without any further purification. Palladium atomic absorption standard (AAS) solution (1000 mg/L) was purchased from SRL, India. Aqueous solutions were prepared using deionized water and alkaline potassium permanganate distilled water and pH 7 phosphate buffer solution (PBS) of ionic strength = 0.1 M was used as a supporting electrolyte in this study.

2.2. Electrochemical measurements

Electrochemical measurements were carried out using a CHI model 440 B electro-chemical work station, USA with 10 mL working volume. The three electrode system consisting of ITO, which is covered with transparent insulating tape, leaving a working area of 3 mm diameter or glassy carbon electrode (GCE, BASi) or carbon screen printed electrode (SPE, Zensor R&D) and it's chemically modified form as a working electrode, Ag/AgCl with 3 M KCl as a reference electrode and platinum wire as a counter electrode. Hydrodynamic amperometric measurements were performed using a CHI 760D electrochemical workstation (Austin, TX, USA) [29]. The FIA operating system consisting of Hitachi L-2130 pump delivery, a Rehodyne model 7125 sample injection valve (20 μL looping system) interconnecting Teflon-tube (BAS, USA). The microfludic device made up of two ITO glass plates, i.e., working electrode, interfaced with 3 mm gasket having inlet and outletstainless steel (SS) tubing as counter electrode and a long Ag wire placed symmetrically as pseudo reference electrode were clamped by binding clips was served as leakage proof FIA-ECD in this work. A JASCO 4100 Spectrophotometer for Fourier transform infrared spectroscopy (FTIR), FEI TECNAI 20 (Netherland) instrument for Transmission electron microscopy (TEM) and Hitachi S-4800 (Japan) for Field Emission Scanning Electron Microscope (FESEM) were used.

2.3. Preparation of the chemically modified electrode

In a typical preparation of ITO/CHIT@Pd_{nano} modified electrode, the surface of the ITO was cleaned by performing electrochemical cyclic voltammetry (CV) for 10 number of cycles (n) in a potential window −0.2 to 1.0 V vs Ag/AgCl at a scan rate (ν) of 50 mV s^{-1} in pH 7 PBS (i.e., 6 min). Next, 5 μL of a mixture containing palladium (II)-chitosan solution, wherein, 50 μL of palladium (II) AAS standard solution (1000 ppm) mixed with 500 μL of 0.5% chitosan solution, was drop casted on the cleaned ITO electrode and kept it for drying in room temperature for about 5 ± 1 min. Then, it was subjected to CV experiment (n = 10) in a potential window −0.8 to 1 V vs Ag/AgCl at ν = 50 mV s^{-1} in pH 7 PBS (i.e., 12 min) (Fig. S1). Such a procedure resulted to uniform formation of thin layer of palladium nanoparticles immobilized chitosan modified ITO electrode. Overall, only 25 ± 2 min time is required to complete the preparation of ITO/CHIT@Pd_{nano} modified electrode (Scheme 1A–C). In a similar manner, other chemically modified electrodes such as GCE/CHIT@Pd_{nano} and SPE/CHIT@Pd_{nano} were also prepared (Fig. S1). Wine and tea real samples purchased from local shops in Vellore were subjected to FIA. Prior to the analysis, accurately weighed tea dust was boiled with distilled water at 80 ± 3 °C in an oil bath and kept for 30 min stirring [3]. A clear extract filtered and diluted with 0.1 M pH 7 PBSwas subjected to FIA. Similarly, wine sample was suitably diluted with pH 7 PBS and then injected to FIA-ECD directly.

3. Result and discussion

Fig. 1 displayed the CV responses on CHIT@Pd_{nano} modified electrode prepared on different underlying substrates like GCE, SPE and ITO, with 1 mM of CA or HQ or RE in pH 7 PBS at a scan rate