



Metal ion mediated imprinting for electrochemical enantioselective sensing of L-histidine at trace level

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ABSTRACT

Enantioselective trace level sensing of L-histidine (limit of detection, 1.980 ng mL^{-1} , $S/N = 3$) was feasible with the use of a typical, reproducible, and rugged complex imprinted polymer-based pencil graphite electrode, in aqueous samples. In the present instance, the Cu^{2+} ion-mediated imprinting of L-histidine in an molecularly imprinted polymer motif actually helped upbring electrocatalytic activity to respond an enhanced differential pulse anodic stripping voltammetric oxidation peak of L-histidine, without any cross-reactivity and false-positive, in real samples. The proposed sensor could be considered suitable for the practical applications in biomarking histidinemia, a disease associated with L-histidine metabolic disorders, in clinical settings.

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1. Introduction

Complex imprinted polymers (CIPs) based on "metal-ion mediated imprinting" approach have received due attention, owing to their water-compatibility and wide applicability in catalysis (Erdem et al., 2010), separation (Lee and Hong, 2000), recognition (Qin et al., 2009), and sensors (Gultekin et al., 2009; Sergeyeva et al., 2010). Recently, a novel CIP coated solid-phase micro extraction (SPME) fiber was developed for the effective recognition of 2,2'-bipyridine in water (Huang et al., 2011) with pre-ponderant adsorption capacity and selectivity, with little interference from the protic solvent, in comparison to molecularly imprinted polymer (MIP)- and non-imprinted polymer (NIP)-coated SPME fibers. However, despite very promising approach for MIP synthesis, appli-

cations of CIPs for enantio-selective recognition are still limited (Matsui et al., 1996).

In this study we have decided to use a "complex template" constructed with Cu (II) ion and L-histidine (L-his) or D-histidine (D-his), since many pharmaceutical systems show biological activities when they are in the form of metal complexes. Of the two isomers (D- and L-forms) of histidine, only L-his is bioactive that can be converted to histamine, which is a neurotransmitter in the brain and throughout the nervous system, and can help storing glucose in liver (Wade and Tucker, 1998). Other isomer, D-his, is not bioactive. The chiral recognition and quantitative assay of L-his isomer are associated with the diagnosis of L-his metabolism disorders, particularly 'histidinemia' at elevated levels (Rao et al., 1993; Zhang et al., 2010) in physiological fluids [normal level: $0.31\text{--}26.35 \mu\text{g mL}^{-1}$; elevated level: $29.5 \mu\text{g mL}^{-1}$ (Walters et al., 1980)]. Therefore, selective and sensitive detection of L-his is essentially required in clinical settings. Several methods, based on capillary electrophoresis (Heravi et al., 2005), colorimetry (Lata et al., 2005), fluorimetry (Li et al., 2004), and chromatography (Ruta et al., 2007), were used for the analysis of histidine. However, these are not always as simple and accurate as electroanalysis. Due to the electrochemical inactivity of L-his in water and its easy adsorption on the surface of electrode which results in electrode fouling, a very little attention has been paid to the electrochemical studies of histidine and its metabolites, in water. For instance, iron (II) porphyrin bearing 2,6-di-tert-butylphenol pendants deposited on gold electrode (Kurzatkowska et al., 2009) and molecularly imprinted sol-gel functionalized indium tin oxide electrode (Zhang et al., 2010) have

Abbreviations: CIPs, complex imprinted polymers; SPME, solid-phase micro extraction; MIP, molecularly imprinted polymer; NIP, non-imprinted polymer; L-his, L-histidine; D-his, D-histidine; HMDE, hanging mercury drop electrode; PGE, pencil graphite electrode; MWCNTs, multiwalled carbon nanotubes; TDW, demineralized triple distilled water; DMSO, dimethyl sulphoxide; EGDMA, ethylene glycol dimethylacrylate; CPTMS, 3-chloropropyltrimethoxysilane; EDTA, ethylene diamine tetraacetic acid disodium salt; DPASV, differential pulse anodic stripping voltammetry; CV, cyclic voltammetry; SEM, scanning electron microscope; AFM, atomic force microscopy; AEDP, 2-acryl amidoethyl dihydrogen phosphate; IIP, ion imprinted polymer; his-IP, his-imprinted polymer; LOD, limit of detection; RSD, relative standard deviation.

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recently been reported for highly sensitive determination of L-his. However, with above sensing probes, the non-specific contributions from the sample matrices and co-existing interferences could not be fully mitigated. Insofar as metal ion mediated imprinting of histidine is concerned, a seminal work on the synthesis and rebinding properties of $[\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{z-histidine})]$ imprinted polymer has been reported; without emphasizing, however, the quantitative estimation of histidine (Chaitidou et al., 2009). A new zwitterionic L-his imprinted polymer, based on poly (ethylene-diamine tetraacetic acid-co-cholranil), was also reported for the modification of a hanging mercury drop electrode (HMDE) (Prasad et al., 2009); but this involved environmental risk. We report, for the first time, a modified L-his selective pencil graphite electrode (PGE), a mercury-free solid sensor, through metal ion mediated imprinting technology. In this work the complexation of Cu (II) ion with monomer and template constituted a typical coordination system, which could behave like an 'organic-metal' inculcating electronic effects in terms of redox activation (Murata et al., 2007).

For the CIP-modified sensor fabrication, the firm integration of recognition element with the transducer is warranted. This could easily be obtained by applying a "surface grafting-from" approach, where an iniferter (initiator-transfer agent-terminator) was grafted onto a solid substrate (ormosil-modified PGE) in order to grow a polymer film of controlled thickness through photo initiated free-radical polymerization. In principle, grafted iniferters do not initiate polymer chains in solution (the radicals liberated into the solution are unable to initiate polymerization) and thereby have a good tolerance against any non-specific adsorption, with a range of functional groups. The synthetic methodology could involve a sol-gel process that is one of the fastest emerging fields of nanostructured material preparation with inherent flexibility and low density, enabling thin film to be readily fabricated under mild polymerization condition. Furthermore, the multiwalled carbon nanotubes (MWCNTs) incorporation in entire coating could help enhancing the sensitivity of the electrochemical detection. To improve water-compatibility the monomer used was a typical acryl phosphate that could effectively bind Cu (II) ion in both in vivo/in vitro conditions. In this study, we originally prepared Cu (II) mediated MIP for L-his in water-containing system and found that Cu (II) bridged L-his and monomer to form a complex of one L-his, one Cu (II), and three phosphate monomers. The fabricated CIP-modified water-compatible sensor is able to discriminate L- and D-his enantiomers in complex aqueous, biological, and pharmaceutical solutions owing to the enantioselectivity of imprinted sites. The electrochemical detection of L-his is feasible on account of inherent catalyzing action of Cu (II) ion in the MIP-film, which turned electro-conductive after complexation during rebinding. Here Cu (II) ion being an activated electron-acceptor at +0.1 V might inject positive holes in L-his (protein residue) as p-type semiconductor, and conductivity thus may be enhanced many fold in the presence of water (Beales et al., 1978).

2. Experimental

2.1. Reagents

Demineralized triple distilled water (TDW) (conducting range $0.06\text{--}0.07 \times 10^{-6} \text{ S cm}^{-1}$) was used throughout the experiment. D- and L-his, sodium N,N'-diethyldithiocarbamate, and acrylic acid, were purchased from Loba chemie (Mumbai, India). Solvents, dimethyl sulphoxide (DMSO) and ethanol, were purchased from Spectrochem Pvt. Ltd. (Mumbai, India). Ethylene glycol dimethylacrylate (EGDMA), 3-chloropropyltrimethoxysilane (CPTMS), MWCNTs (internal diameter 2–6 nm, outer diameter 10–15 nm, length 0.2–10 μm , and purity >90%), 2-aminoethylidihydrogen

phosphate, and all interferences, were obtained from Aldrich (Steinheim, Germany) and Fluka (Steinheim, Germany). Copper sulphate, zinc sulphate, nickel sulphate, and ethylene diamine tetraacetic acid disodium salt (EDTA), were purchased from E-Merck Ltd. (Mumbai, India). Borate buffer solution (pH 8.0, ionic strength 0.1 M), was used as a supporting electrolyte. The pH values of solutions were adjusted by addition of a few drops of either 0.1 M HCl or 0.1 M NaOH. Standard stock solution of L-his ($500.0 \mu\text{g mL}^{-1}$) was prepared daily using TDW. All working solutions were prepared by diluting stock solution with TDW. The pharmaceutical sample analyzed was L-histidine hydrochloride (astymin[®]) which is purchased from Tablets India Ltd. (Chennai, India). Human blood serum was obtained from the Institute of Medical Science, Banaras Hindu University (Varanasi, India) and kept in a refrigerator at $\sim 4^\circ\text{C}$, before use.

Pencil rods (2B), 0.5 mm in diameter and 5 cm in length, were purchased from Hi Par, Camlin Ltd. (Mumbai, India). All chemicals were of analytical grade and used without further purification.

2.2. Apparatus

Differential pulse anodic stripping voltammetry (DPASV), chronocoulometry, and cyclic voltammetry (CV), were performed using a three electrode cell assembly consisted of a CIP-modified PGE, a platinum wire, and an Ag/AgCl (3.0 M KCl) as working, counter, and reference electrodes, respectively. Voltammetric measurements were carried out with a polarographic analyzer/stripping voltammeter [model 264 A, EG & G Princeton Applied Research (PAR), USA] in conjunction with an electrode assembly [PAR model 303 A] and a X-Y chart recorder (PAR model, RE 0089). Chronocoulometry measurements were performed with an electrochemical analyzer (CH instruments, USA, model 1200 A). FT-IR (KBr) and ^1H NMR spectra of coated layers (scraped out from the electrode surface) were recorded on Varian FT/IR (USA) and JEOL AL 300 FT/NMR (Japan) spectrometers, respectively. Morphological images of bare and modified electrode surfaces were recorded using scanning electron microscope (SEM), JEOL, JSM, Netherland, model 840A. Exeter Analytical Inc., model CE-400 Elemental analyzer, Mexico, was used for elemental analysis. Atomic force microscopy (AFM) experiments were performed using a dimension 3100 scanning electron microscopy (Veeco Instruments Inc., USA) in the tapping mode. UV-vis analysis was performed on Varian Cary 100 Bio UV-visible spectrophotometer (USA).

2.3. Electrode preparation

A pencil rod (2B, 0.5 mm) was first pretreated by dipping in 6 M HNO_3 for 15 min, washing with water, and subsequently smoothed the surface by soft cotton. This was inserted into a Teflon tube, where the tip of the pencil rod at one end was gently rubbed with an emery paper (No. 400) to level the pencil surface along the tube orifice. Electrical contact was obtained by soldering a metallic wire to the exposed reverse side of the pencil rod.

2.4. Grafting of photoactive iniferter layer onto the PGE

The electrode surface was modified, as depicted in Scheme 1, in two steps. First of all, the exposed tip of PGE surface was spin coated with 12.0 μL sol-gel slurry in 'syneresis' stage (1.0 mL CPTMS, 1.0 mL ethanol, 0.5 mL TDW, and 50.0 μL of 0.1 M HCl), containing 20.0 mg MWCNTs, at 2600 rpm for 45 s and left to dry at room temperature. The sol-gel so produced effectively blocked any passage in between the rod along its edge and Teflon tube to avoid leakage. In next step, 10.0 μL of sodium N,N-diethyldithiocarbamate

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