Synergistic activity of single crystalline bismuth sulfide and sulfur doped graphene towards the electrocatalysis of tryptophan

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A B S T R A C T

In the present study, a single step and template-free synthesis was proposed for the preparation of heterostructured single crystalline rod like bismuth sulfide/sulfur doped graphene (SGr- Bi₂S₃) nanocomposite. The structural properties and physical interactions of SGr- Bi₂S₃ were investigated by various physicochemical techniques which provide the knowledge about growth mechanism and orientation of reactive sites. These highly oriented edge reactive sites of SGr- Bi₂S₃ promoted the fascinating electrochemical performance towards the electrocatalysis of tryptophan (Trp). Trp is an essential biological compound it’s monitoring in human diet is quite important. Thereby, the SGr- Bi₂S₃ modified screen printed carbon electrode (SPCE) is applied to the determination of Trp. Trp is determined by differential pulse voltammetry (DPV) which revealed an acceptable sensitivity and lowest detection limit about 1.2 μA μM⁻¹ cm⁻² and 0.004 μM, respectively. These values are highly encouraged for the real time analysis of Trp in human blood (12–13 μg/mL). Moreover, it exhibited good selectivity over the range of interfering compounds (which present in blood co-exist with Trp). Therefore, this low-cost disposable SGr- Bi₂S₃/SPCE can applicable for the determination of Trp in biological samples.

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Minimizing the effects of oxygen interference on l-lactate sensors by a single amino acid mutation in *Aerococcus viridans* l-lactate oxidase

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**ARTICLE INFO**

Keywords:
- L-lactate oxidase
- L-lactate
- Oxygen
- Screen-printed carbon electrode
- Site-directed mutagenesis
- Biomedical engineering

**ABSTRACT**

l-lactate biosensors employing l-lactate oxidase (LOx) have been developed mainly to measure l-lactate concentration for clinical diagnostics, sports medicine, and the food industry. Some l-lactate biosensors employ artificial electron mediators, but these can negatively impact the detection of l-lactate by competing with the primary electron acceptor: molecular oxygen. In this paper, a strategic approach to engineering an AvLOx that minimizes the effects of oxygen interference on sensor strips was reported. First, we predicted an oxygen access pathway in *Aerococcus viridans* LOx (AvLOx) based on its crystal structure. This was subsequently blocked by a bulky amino acid substitution. The resulting Ala96Leu mutant showed a drastic reduction in oxidase activity using molecular oxygen as the electron acceptor and a small increase in dehydrogenase activity employing an artificial electron acceptor. Secondly, the Ala96Leu mutant was immobilized on a screen-printed carbon electrode using glutaraldehyde cross-linking method. Amperometric analysis was performed with potassium ferri-cyanide as an electron mediator under argon or atmospheric conditions. Under argon condition, the response current increased linearly from 0.05 to 0.5 mM l-lactate for both wild-type and Ala96Leu. However, under atmospheric conditions, the response of wild-type AvLOx electrode was suppressed by 9–12% due to oxygen interference. The Ala96Leu mutant maintained 56–69% of the response current at the same l-lactate level and minimized the relative bias error to ~10% from ~49% of wild-type. This study provided significant insight into the enzymatic reaction mechanism of AvLOx and presented a novel approach to minimize oxygen interference in sensor applications, which will enable accurate detection of l-lactate concentrations.

![Diagram](image)

**Fig. 1. The l-lactate oxidase (LOx) reaction scheme.** The reductive half-reaction is shown progressing from LOx/FMN_red to LOx/FMN_red via the LOx/FMN_red - l-lactate and the LOx/FMN_red - pyruvate complex. The oxidative half-reaction is a FMN reoxidizing reaction from LOx/FMN_red to LOx/FMN_red using molecular oxygen (O2) as the primary electron acceptor or an artificial electron mediator (Med).
Direct Measurement of a Biomarker’s Native Optimal Frequency with Physical Adsorption Based Immobilization

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ABSTRACT: The optimal frequency (OF) of a biomarker in electrochemical impedance spectroscopy (EIS) is the frequency at which the EIS response best reflects the binding of the biomarker to its molecular recognition element. Commonly, biosensors rely on complicated immobilization chemistry to attach biological molecules to the sensor surface, making the direct study of a biomarker’s native OF a challenge. Physical adsorption presents a simple immobilization strategy to study the native biomarker’s OF, but its utility is often discouraged due to a loss in biological activity. To directly study a biomarker’s native OF and investigate the potential of OF to overcome the limitations of physical adsorption, a combination of EIS and glutaraldehyde-mediated physical adsorption was explored. The experimental sensing platform was prepared by immobilizing either anti-lactoferrin (Lfn) IgG or anti-immunoglobulin E (IgE) onto screen printed carbon electrodes. After characterizing the native OFs of both biomarkers, investigation of the platform’s specificity, stability, and performance in complex medium was found to be sufficient. Finally, a paper-based tear sampling component was integrated to transform the testing platform into a prototypical point-of-care dry eye diagnostic. The investigation of native OFs revealed a correlation between the native OFs (57.44 and 371.1 Hz for Lfn and IgE, respectively) and the molecular weight of the antibody—antigen complex. Impedance responses at the native OFs have enabled detection limits of 0.05 mg/mL and 40 ng/mL for Lfn and IgE, respectively, covering the clinically relevant ranges. The native OFs were found to be robust across various testing mediums and conditions.

KEYWORDS: point-of-care, electrochemical impedance spectroscopy, optimal frequency, glutaraldehyde immobilization, tear sampling component, integrated sensor, dry eye

Scheme 1. Sensor Fabrication Schematics a

Steps 1–3 describe the fabrication process of SPCE-alpha prototype while 4 and 5 show the additional manufacturing steps required to assemble the SPCE-beta prototype.
"Design of novel WO₃/CB nanohybrids" An affordable and efficient electrochemical sensor for the detection of multifunctional flavonoid rutin

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The multifunctional properties of rutin have been utilized in the preparation of various pharmaceutical products. As a result, rutin is considered to be one of the most consumed flavonoid substances in pharmaceutical applications. Hence, researchers have been devoted to developing a simple, cheap and highly efficient electrochemical sensor for the detection of rutin. Nowadays, inorganic nanomaterials, especially metal oxides, with distinct structures and properties are being used for the development of various kinds of electrochemical sensors. The wide band gap values of WO₃ make it a potentially important sensing material. Therefore, we have synthesized novel CB/WO₃ nanohybrids using a single step hydrothermal technique and applied them for the electrochemical detection of rutin. In this work, we have chosen the inexpensive and superconductive CB for the synthesis of the nanohybrids, which is an alternative to other carbonaceous materials. The structural, morphological and compositional properties of the synthesized material were systematically characterized by various suitable spectrophotometric techniques. Moreover, the as-prepared electrode materials exhibited a good electrochemical performance towards the electro-oxidation of rutin. Fascinatingly, the lowest LOD of about 2 nM with appreciable linearity from 0.01 to 75.46 μM was obtained for the electrochemical determination of rutin. Furthermore, the practical feasibility of the proposed sensor was investigated using commercially available rutin-containing tablets.
Molecularly imprinted electrochemical sensor, formed on Ag screen-printed electrodes, for the enantioselective recognition of $D$ and $L$ phenylalanine

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ARTICLE INFO

Keywords:
Molecularly imprinted polymers
Phenylalanine
Enantiomer
Screen-printed-electrode

ABSTRACT

In this study, electrochemical sensors for the enantioselective recognition of $D$ and $L$ phenylalanine were prepared using a molecular imprinting technique in which the electro-polymerization of pyrrole was carried out by Chronopotentiometry (CP) with the target molecules being present on an Ag screen printed electrode’s (SPE) surface. The sensing performance was evaluated by multi-potential steps at 0 and 2 V (vs. Ag/AgCl) held for 1 s and 2 s, respectively, for 20 cycles (with the two enantiomers being present at the same concentration). The individual selectivity’s for $l$ and $d$-phenylalanine on their respective imprinted films were estimated to be $L/D = 23.480 \pm 2.844/1$ and $D/L = 19.134 \pm 1.870/1$ respectively, based on the current change between 0 and 2 V (vs. Ag/AgCl) with the two enantiomers being present at the same concentration (10 mM). Several parameters affecting recognition ability were investigated including: cross-selectivity of $d$ and $l$-phenylalanine imprinted film, phenylalanine concentration effects, interfering species, deactivation and the storage life of electrode. The phenylalanine imprinted films were also characterized by AC impedance, chronoamperometry, Fourier-transform infrared spectroscopy (FTIR), Scanning Electron Microscope(SEM), and Energy Dispersive X-Ray Spectroscopy (EDS). Finally, a recognition mechanism for the interaction of the polypyrrole film with its template under the influence of applied negative and positive potentials is proposed.

Fig. 12. Schematic diagram of (A) the electopolymerization of pyrrole to embed the template forming the $l$-phenylalanine imprinted film, by a driving force of positive potential (B) swelling the $l$-Phenylalanine imprinted film to remove the template by a negative potential in solvent and (C) the rebinding test of $l$-phenylalanine induced by a positive potential to measure the current change.