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Disposable cerium oxide/graphene nanosheets based sensor for monitoring acebutolol in environmental samples and bio-fluids

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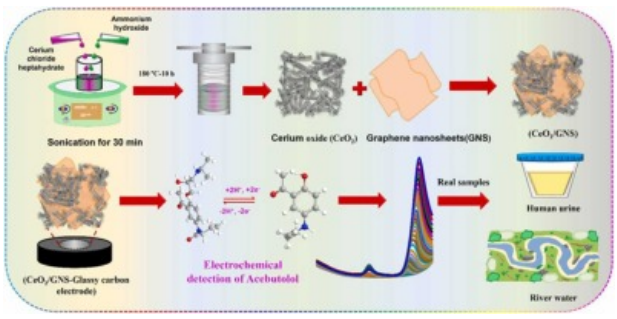
Abstract

The production and utilization of medicines strives to be an essential factor in the modern world in treatment, diagnosis and prevention. On the other hand, the medical discharge and the unmetabolized drugs all turns out into environmental polluting agents. The demand for detecting and solving these issues are essential. Herein, we report an electrochemical sensor for quantifying β-adrenoreceptor blocker acebutolol (ACT) in environmental and biological samples. Cerium oxide (CeO_2) was implied with graphene nanosheets (GNS) as highly conducting material for electrochemically detecting ACT. The structural and morphological studies were studied and electrochemical analysis were also performed to efficiently study oxidation mechanism of ACT at CeO_2/GNS interface. Electrochemical impedance spectroscopy (EIS) proved the higher conducting behavior of CeO_2/GNS. Moreover, CeO_2/GNS/SPCE holds higher surface area with more edge sites facilitating the electro-oxidation of ACT. The linear range of detecting ACT was in the range of 0.039μM to 486.6μM. The limit of detection was found to be 0.007μM with the sensitivity about $27.3\mu A\mu^{M-1}cm^{-2}$. The real samples like river water and urine samples were utilized for real time detection of ACT. Thus, the fabricated electrode with more efficiency and higher conducting property will enhance the real time sensing of ACT in environmental and biological samples.

Graphical Abstract

Synthesis of CeO_2/GNS and electro-oxidation of ACT.



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Introduction

Global environmental crisis streams out one of the major growing drawbacks related to pollutants that terrify routine life of human and wildlife [1]. There are several environmental pollutants like waste sewage from dye industries, pharmaceutical manufacturers, and includes plenty of daily usage products [2]. Pharmaceutics accompanies huge impact since it cannot be violated as it is required in the form of vaccines, in treating severe diseases to mild pains as painkillers as antibiotics and many [3]. Even though pharmaceutics is mandatory, their large quantity of sewage causes environmental pollution which is capable to penetrate the biological life forms [1]. β-adreno receptors are one among them which is prescribed for cardiovascular diseases. The drug intakes have the chance of being exposed as unmetabolized products through urine and excreted [4]. Acebutolol (ACT) is one of the β-adrenoreceptor blocker which is implied to treat disease like ventricular arrhythmia and hypertension [5]. One among the eminent β-blockers ACT notably has higher influence over human and environment [6]. The residues of ACT and the effluents from waste water treatment stand as a huge hindrance in reducing environmental pollution [7]. The higher intake of ACT is able to cause several side effects and one among them is drug induced lupus erythematosus which occurs due to cutaneous eruptions with the antinuclear antibodies produced in plasma [8], [9]. Significant insights are being reported and explored for ACT detection with several modern techniques [10]. Some of the techniques are high performance liquid chromatography (HPLC), fluorescence detection, photodiode array UV detection, thin layer chromatography, spectrofluorimetric assay, gas chromatography with mass spectroscopy and electrochemical cell coupled several spectroscopies are also reported [11], [12], [13], [14]. The oxidation/reduction reactions which is related to the toxicity aspects can be well understood and studied with electrochemical cell. The electrochemical detection of ACT was studied. To utilize this technique, the working electrode should be fabricated with highly conducting material.

Metal oxides are termed to be more eminent in all fields of application due to their cost effectiveness, higher theoretical capacity, environmentally friendly nature, easily available, higher chance of being applicable to varied implications etc [15], [16]. The poor electronic conductivity has reduced its usage but modulating their structure with highly conducting materials can destroy the disadvantage of metal oxides [17]. Carbon derived materials have the capacity to form homogenous matrix enriching the electron transport at metal oxide surface [18], [19]. In order to detect ACT, cerium oxide (CeO_2) was chosen to be entrapped with graphene nanosheets (GNS) to successfully activate the oxidation. Cerium oxide a kind of metal oxide has the ability to absorb OH^- species from the working electrode matrix and further boosts the oxidation process of ACT.[20] CeO_2 one among the rare earth materials is combined with several carbon matrices, polymers, metal/metal oxides and so on with its low cost, chemical stability, surface to bulk ratio and redox behavior [21], [22]. GNS is a two-dimensional layered carbon structure holding enormous properties to enhance the reaction mechanism [23]. The highly flexible nature of GNS and the good electrical conductivity with wide surface area is gained attention [24]. When GNS is combined with CeO_2 the hybrid material is able to show excellent conducting performance, higher specific surface area and several unique properties. GNS reduces the agglomeration of nanoparticles which enables easier mobility of reactants at the surface of the hybrid composite [25]. In order to reduce the defects that occurs due to the π-π interactions between the single graphene sheets of GNS, incorporating a metal oxide or any other conducting medium will be more significant [26]. Reports have used metal oxides with varied composites either carbon based composites or other materials as for different applications. Mehmet Turemis et al., reported zinc oxide/polyaniline composite for determining acetic acid vapor [27], [28]. Fedorenko et al., employed the application of polydopamine functionalized zinc oxide for glucose biosensing [29]. Herein, the nanocomposite CeO_2/GNS with all significant properties will likely enhance the electro-oxidation of ACT in the present study. Reports over ACT detection has been focused over varied materials with different techniques. Bussy et al. reported the electrochemical oxidation of acebutolol by liquid chromatography and mass spectrometry [30]. Mariana Silva et al. constructed a electrochemical sensor for simultaneously detecting β-adrenoreceptors with amino functionalized mesoporous silica [31]. Zhang et al. utilized cerium oxide/graphene for sensing cholesterol [25]. Moreover, the construction of CeO_2/GNS/SPCE for ACT detection is the first report in the field of electrochemical sensors.

The developed disposable sensor based on CeO_2/GNS/SPCE is efficiently constructed for monitoring acebutolol environmentally in river water and in addition biological sample urine is also meant to be studied. These both samples remain as a major source of ACT discharge and is likely to be monitored. Moreover, CeO_2/GNS/SPCE was investigated for electrochemical performance to estimate the efficiency in detecting ACT. CeO_2/GNS nanostructures are recognized

for their presence analyzing the physico-chemical behaviors. The developed CeO_2/GNS composite with excellent features as faster kinetics process, environment friendly properties, high volume to mass ratio and other peculiar features will grab researchers' interest. Most probably the lower conductivity of CeO_2 will be hindered by GNS and will provide higher conductance with lower aggregation of nanoparticles.

Section snippets

Materials and characterization techniques

The materials and characterization techniques utilized are briefed in S1. Supporting information.…

Synthesis procedure of CeO_2

The synthesis procedure of CeO_2 was carried out via hydrothermal method. Initially, 0.1 M of cerium chloride heptahydrate was dispersed in 45 mL of distilled water under sonication for 30 min. The solution mixture was introduced with the addition of NH_4OH dropwise. The above mixture was transferred into autoclave and maintained at 180 °C for 10 h. Moreover, the final solution obtained was centrifuged for 15 min at 1600 rpm followed by washing with ethanol and distilled water many times. The…

Structural analysis

The structural representation of CeO_2, GNS and CeO_2/GNS was initially confirmed with XRD. The presence of CeO_2 was matched with the JCPDS card number 03–065–2975 with the space group *Fm*-3*m*. The cubic structure as obtained by CeO_2 has been found with the corresponding plane values as (111), (200), (220), (311), (222), (400), (331), (420), (422) with the theta values as 28.5º, 32.9º, 47.2º, 56.1º, 58.9º, 68.9º, 76.4º, 78.7º and 88.1º. All these planes confirm the formation of CeO_2 and no other…

Anti-resistance analysis of different modified electrodes

The resistance of the electrodes being modified with CeO_2, GNS and CeO_2/GNS was analyzed initially with electrochemical impedance spectroscopy (EIS). Fig. 4A gives the EIS spectra for bare SPCE (a), CeO_2/SPCE (b), GNS/SPCE (c) and CeO_2/GNS/SPCE (d) performed in the presence of 5 mM of Fe $(CN_6)^{3-/4-}$ and 0.1 M of KCl. The lower resistance results with higher conductance of the electrode and the results suggest that CeO_2/GNS/SPCE has obtained the lowest resistance than other electrodes. The…

Electrochemical analysis

The surface area of all the SPCE's modified with CeO_2, GNS and CeO_2/GNS were further investigated for effective active surface area analysis. Cyclic voltammetry (CV) was utilized for further recognition with different modified SPCE. Fig. 4B depicts the CV curves achieved in the presence of 5 mM Fe $[(CN)_6]^{3-/4-}$ with 0.1 M of KCl for bare SPCE (a), CeO_2/SPCE (b), GNS/SPCE (c) and CeO_2/GNS/SPCE (d) at 50 mV/s. The redox peaks depicted are observed with sharp anodic and cathodic peak current…

Conclusion

In summary, the novel construction of CeO_2/GNS/SPCE for acebutolol detection seems to be more significant in the electrochemical sensor. The prepared CeO_2/GNS offers tremendous unique features with large surface area, higher conducting surface, high speedy transfer of electrons at the CeO_2/GNS/SPCE surface and ACT interface. Moreover, CeO_2/GNS is cost effective with higher abundance which can be easily synthesized. The structural and electrochemical properties prove that the fabricated sensor…

CRediT authorship contribution statement

Subash Vetri Selvi: Conceptualization, Methodology, Experimental Investigation, Formal analysis, Data curation. **Nandini Nataraj:** Investigation, Validation, Writing – review & editing, Writing – original draft, Formal analysis. **Tse-Wei Chen**: Validation, Formal analysis. **Shen-Ming Chen:** Funding acquisition, Project administration, Resources, Supervision, Formal analysis. **Prakash Balu:** Formal analysis. **Xiaoheng Liu:** Validation, Resources, Formal analysis.…

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

Acknowledgments

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> ...CTR has also been used to treat periodic allergic rhinitis and recurrent hives. Electrochemical (EC) techniques have been in great demand in pharma-based industries, environmental science, agriculture, health care, food, and textile industries [5–14]. This demand for EC determination over other techniques can be due to inexpensive instrumentation with a quick and user-friendly interface....

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> ...The FT-IR graph of FO and FO/rGO was recorded to analyze the surface functional groups (Fig. 4). The strong bonding between Fe and O atoms is confirmed by peaks at 585 cm−1 and 632 cm−1 in the FT-IR spectrum of both pristine FO and FO/rGO (Selvi et al., 2022). The C–C bonding FT-IR peak is observed at 1633 cm−1....

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