ScienceDirect

Ceramics International

Available online 17 November 2024

In Press, Corrected Proof What's this?

Electrochemical detection of p-nitrophenol using glassy carbon electrode modified using high-entropy oxide nanoparticles

Mariappan Anandkumar [a], P.K. Kannan [b], R.S. Morozov [a], O.V. Zaitseva [a], Shanmugavel Sudarsan [a], E.A. Trofimov [a]

Show more

Share Cite

https://doi.org/10.1016/j.ceramint.2024.11.254

Get rights and content

Highlights

- A high-entropy oxide nanoparticle based electrochemical sensor is proposed.
- The modified electrode detects nitrophenol at sub-micromolar concentrations.
- Modified electrode effectively employed in tap water samples to monitor p-nitrophenol.
- Minimal interference by other ions during p-nitrophenol sensing is observed.

Abstract

The electrochemical detection of p-nitrophenol (PNP) has gained significant attention due to its potential application in environmental monitoring and food safety. In this study, a novel electrochemical sensor based on a $(CeGdHfPrZr)O_2$ (HEO) nanoparticle-modified glassy carbon electrode (GCE) has been developed for the detection of PNP. Hydrothermal synthesis was employed to

prepare a single-phase HEO nanoparticle. Various characterization techniques were employed to investigate the prepared HEO nanoparticles. The GCE was modified with HEO nanoparticles to enhance its electrocatalytic activity for the detection of PNP. As a result, the oxidation peak current of PNP was greatly enhanced compared to unmodified GCE, indicating an improved electrode reaction kinetics. The sensor showed high sensitivity ($0.1517\,\mu A\,\mu M^{-1}\,cm^{-2}$) and selectivity towards PNP, with a detection limit as low as $0.321\,\mu M$. The developed electrochemical sensor exhibited excellent reproducibility and selectivity towards PNP over other interfering species. The reusability and stability of the sensor were also investigated. The modified GCE exhibited good long-term stability and could be reused for at least 50 cycles without significant loss of sensitivity.

Introduction

Chemical fertilizers, pesticides, and wastewater originating from agricultural and industrial sources have triggered severe water pollution, which can adversely affect human health, aquatic ecosystems, and the economy. As a raw material for the organic synthesis industry, nitrophenols, especially p-nitrophenol and o-nitrophenol are important since they can be used to manufacture rubber, dyes, petroleum, pesticides, and oil derivatives [1,2]. Typically, the permissible level of PNP in water should not exceed $0.43\,\mu M$ (60 ppb). However, any concentration beyond this level may be hazardous and damaging to human health [3,4]. Thus, it is essential to monitor and manage the concentration of PNP in drinking water. In order to protect the environment and ensure public safety, it is essential to develop an environmental monitoring system that is fast, sensitive, and with a better low limit of detection (LOD). In general, PNP can be determined by different techniques, such as UV–vis spectroscopy, capillary electrophoresis, liquid chromatography, chemiluminescence, and flow injection methods [2, [5], [6], [7]]. Nevertheless, there are many drawbacks associated with these technologies, including the high costs of detection, the use of large instruments and the time it takes. These drawbacks have made them difficult to achieve rapid detection of PNP.

On the other hand, electroanalytical techniques using glassy carbon (GC) as electrodes, offer a wide variety of advantages, including ease of sample preparation, convenience in using techniques and equipment, and obtaining rapid results. In addition to their cost-effectiveness, simplicity of operation, portable, they allow real-time testing to take place on-site. On the other side, the challenges associated with electrochemical detection using conventional glassy carbon electrodes notably substantial overpotential, low selectivity, low sensitivity, and poor reproducibility [[7], [8], [9]]. As a result, different approaches have been taken to modify the electrode surface to overcome these shortcomings. There has been significant improvement in the electrochemical response signal of GCE when an active material is added to the electrode surface [1,10,11].

Several nanomaterials combined with GCE and reduced graphene oxide have been reported to enhance the electrochemical sensing of analytes [[11], [12], [13], [14], [15], [16], [17]]. Nanomaterials possess high surface to volume ratio, high reactivity, structural stability and therefore, can be used to enhance the sensor performance by increasing (i) the contact area (between active site and electrolyte), (ii) the number of active sites, and (iii) the current density of the catalyst. In this way, the microenvironment of modified electrode will be improved in terms of increased electrical conductivity and catalytic activity promoting better sensitivity.

Recently, high-entropy materials (HEM) have gained significant attention due to its unique properties and applications. HEMs are designed by combining five or more principal elements together in