



Novel Fe@Fe-O@Ag nanocomposite for efficient non-enzymatic sensing of hydrogen peroxide



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ABSTRACT

Here, we present a novel non-enzymatic electrochemical sensor based on a zerovalent iron-iron oxide-silver nanocomposite (Fe@Fe-O@Ag) which is suitable for highly sensitive detection of hydrogen peroxide. Silver nanoparticles were prepared by simple reduction of silver ions on the surface of nanoscale zerovalent iron (nZVI) owing to the strong reductant efficiency of nZVI. The morphology, chemical and phase composition of the Fe@Fe-O@Ag nanocomposite was monitored by TEM, SEM, X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX). The electrochemical properties of Fe@Fe-O@Ag modified glassy carbon electrodes were characterized by voltammetric techniques and electrochemical impedance spectroscopy (EIS). The experimental data indicated that Fe@Fe-O did not contribute significantly to hydrogen peroxide sensing. Thus, Fe@Fe-O just serves as a substrate for the deposition of silver nanoparticles, whereas H₂O₂ detection is principally effected by the silver nanoparticles. Electrodes modified with the Fe@Fe-O@Ag nanocomposite showed a stable and sensitive response towards hydrogen peroxide reduction, exhibiting a wide linear dependence over H₂O₂ concentrations from 5 μmol L⁻¹ to 1 mmol L⁻¹ with a sensitivity of 460.34 μA μM⁻¹ cm⁻² and detection limit of 5.19 × 10⁻⁹ mol L⁻¹. These results imply that the proposed Fe@Fe-O@Ag nanocomposite could be successfully used as a highly efficient and stable platform for hydrogen peroxide detection.

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1. Introduction

Hydrogen peroxide plays an important role in industrial, environmental, pharmaceutical and clinical research [1–4]. Moreover, it is involved in many basic biological processes, such as immune cell activation or apoptosis [5–7]. Further, its presence and/or absence may also be connected with neurodegenerative disorders, cancer or cardiovascular diseases [8,9]. Hydrogen peroxide is also used in many industrial and related applications, e.g., wastewater or air pollution treatment, organic contaminants degradation or in Fenton reactions as oxidizing and bleaching agent [10]. Therefore, it is important to find an appropriate way to detect it. Common methods for detection of H₂O₂ include techniques such as fluorimetry [11], chemiluminescence [12], spectrophotometry [13] and various electrochemical methods [14].

Compared to other methods available, electrochemical sensing offers a simple, fast and cost-effective approach for sensitive determination of H₂O₂. However, electrochemical sensing of H₂O₂ at bare solid electrodes is often hampered by slow electrode kinetics and high overpotentials, thus limiting the sensing performance [14]. For this reason, current research on H₂O₂ detection is mainly focused on electrode modifications. Most studies dealing with H₂O₂ detection have examined materials such as heme proteins [15], transition metals [16,17], metal oxides [18–21], carbon nanostructures (e.g., carbon nanotubes, graphene) [22–24] or redox polymers [25].

Recently, metal nanoparticles (NPs) have been demonstrated to be suitable for H₂O₂ detection in several studies [26,27]. It is very well known that metal NPs exhibit many unique properties, such as excellent chemical and electrical properties or large surface area, that are significantly different from their bulk materials [28]. So far, NPs have been used for hydrogen peroxide determination in various real samples related to different fields. For example, determination of glucose in biological samples such as serum, blood or urine, has been described in literature [29–31]. Other research works on detection of H₂O₂ in food [32], beverages [33],

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disinfectant samples [34] or in industrial processes [35] can be found as well.

It has been shown that among the various NPs, silver NPs exhibit good catalytic activity and stability towards H_2O_2 reduction, and thus have attracted much scientific interest [36,37]. So far, different morphologies, e.g., flower like silver microspheres [38], iron oxide–silver submicrospheres [39], nanoporous silver NPs [40], multiwalled carbon nanotubes decorated with silver NPs [41] and silicon wafers modified by silver film [42], have been described in the literature for enhanced electrochemical sensing of hydrogen peroxide (H_2O_2). Co-immobilization of silver NPs together with horseradish peroxidase [43] or hemoglobin [44,45] has also been reported.

Here, we describe a simple, fast and cost-effective approach for the detection of H_2O_2 based on a Fe@Fe-O@Ag nanocomposite prepared through the reduction of silver ions on the surface of nZVI. The electrochemical characteristics of glassy carbon electrodes (GCEs) modified by the Fe@Fe-O@Ag nanocomposite were studied by means of cyclic voltammetry, electrochemical impedance spectroscopy and square wave voltammetry. The electrochemical results revealed that Fe@Fe-O@Ag modified GCE exhibit a remarkable sensitivity and stability, and thus offer a promising system for hydrogen peroxide electrochemical sensing.

2. Experimental

2.1. Chemicals

Nanoscale zero-valent iron (nZVI) particles were obtained from NANOIRON, Ltd. (thermally synthesized from iron (III) precursor and commercially available as NANOFEAR 25N and stored under a nitrogen atmosphere). Hydrogen peroxide (30%, Fluka), silver nitrate (Sigma–Aldrich), potassium phosphate dibasic (Sigma–Aldrich), potassium phosphate monobasic (Penta), potassium chloride (Sigma–Aldrich), potassium hexacyanoferrate (III) (Sigma–Aldrich), hexacyanoferrate (II) (Sigma–Aldrich) were all of analytical grade and used without further purification. All solutions were prepared with deionized water ($18 \text{ M}\Omega \text{ cm}^{-1}$).

2.2. Preparation of Fe@Fe-O@Ag nanocomposite

The preparation of the Fe@Fe-O@Ag nanocomposite used in this work was based on the ability of nZVI to reduce Ag^+ ions from solution, promoting the deposition of Ag^0 onto the surface of oxidized nZVI [46]. The synthesis was performed according to previously published work [47]. Briefly, AgNO_3 was dissolved in deionized water and injected into vials covered with a septum and containing nZVI (which was stored under nitrogen atmosphere before the addition of AgNO_3). The reaction mixture was immediately sonicated, followed by shaking for

15 minutes. The reaction between nZVI and AgNO_3 was terminated by magnetic separation and subsequent washing with deionized water.

2.3. Characterization techniques

Transmission electron microscope (TEM) images were obtained using a JEOL JEM-2010 electron microscope operating at 160 kV with a point-to-point resolution of 1.9 Å. Scanning electron microscope (SEM) images were obtained with a Hitachi SU6600 FEG instrument operating at an accelerating voltage of 15 kV and working distance of 6.8 mm. Energy dispersive X-ray spectrometry (EDS) measurements were performed on a NORAN System 7 X-ray Microanalysis System (Thermo Scientific). For X-ray elemental mapping images, an accelerating voltage of 15 kV, working distance of 15 mm and lifetime of 4000 s were used.

The XRD pattern of magnetic bimetallic NPs was recorded on a PANalytical X'Pert PRO diffractometer (iron-filtered $\text{CoK}\alpha$ radiation: $\lambda = 0.178901 \text{ nm}$, 40 kV and 30 mA) in Bragg–Brentano geometry, which was equipped with an X'Celerator detector, programmable divergence and diffracted beam anti-scatter slits. A drop of magnetically pre-concentrated suspension was deposited on a zero-background Si slide, allowed to dry by evaporation at room temperature and then scanned in continuous mode (resolution of 0.017° 2 Theta, scan speed of 0.008° 2 Theta per second, 2 Theta range of $20\text{--}105^\circ$) under ambient conditions.

2.4. Electrochemical measurements

All electrochemical experiments were performed using a PGSTAT128N potentiostat (Metrohm Autolab B.V.) coupled with NOVA software. A conventional three electrode cell configuration was employed. Film modified GCEs were used as working electrodes, while a saturated Ag/AgCl electrode (2Theta, Czech Republic) and platinum wire served as reference and counter electrodes, respectively. Prior to electrochemical measurements, solutions were deoxygenated by purging with pure argon. Electrochemical impedance spectroscopy (EIS) measurements were performed in 0.1 mol L^{-1} KCl containing 5 mmol L^{-1} $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe, otherwise 0.1 mol L^{-1} phosphate buffer solution (pH = 7.0) was used as electrolyte. All experiments were carried out at room temperature.

2.5. Modification of electrodes

The GCEs (3 mm in diameter, 2Theta Czech Republic) were first polished on wet silicon carbide paper using 1 and $0.05 \mu\text{m}$ Al_2O_3 powders sequentially, and then washed with water followed by ethanol for a few minutes. The GCEs were afterwards modified with Fe@Fe-O@Ag nanocomposite by drop-coating: a $10 \mu\text{l}$ drop of

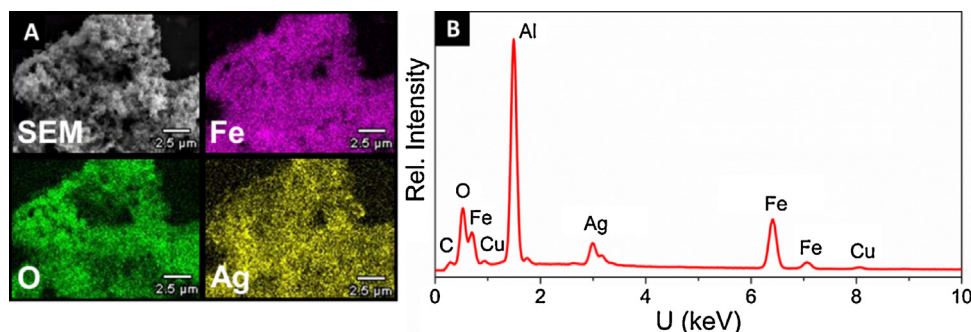


Fig. 1. (A) SEM image and X-ray elemental mapping with identification of iron (Fe), oxygen (O), and silver (Ag). (B) Energy dispersive X-ray spectrum with identification of elemental composition (Al and Cu originated from aluminum holder).

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