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MnO₂ nanorods grown NGNF nanocomposites for the application of highly sensitive and selective electrochemical detection of hydrogen peroxide

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ABSTRACT

The tetragonal α -phase structured manganese dioxide nanorods were densely grown over the nitrogen Q3 doped graphite nanofibers (NGNF/MnO₂) via a facile and one-pot hydrothermal technique. The amperometric results depicted that NGNF/MnO₂ composite exhibited a high sensitivity of 1096 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ and a wide linear range from 0.1 to 11 mM with the lower detection limit of 1.25 μM toward the non-enzymatic hydrogen peroxide (H₂O₂) detection, owing to the synergistic effects of NGNF and MnO₂. In the prospect of excellent selectivity, real sample analysis and other striking advantages, the developed non-enzymatic sensors hold promising potential for the tight monitoring of H₂O₂ in the food and clinical diagnosis fields.

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Introduction

Enlarging a quantitative analysis of hydrogen peroxide (H₂O₂) in biological systems is of more significance in food science, pharmaceuticals, environment, agriculture and biomedicine fields, owing to its extensive applications as catalyst, fuel substrate, food manufacturing agents, strong oxidant, reactive oxygen species, pesticides, signaling molecule in the regulation of a variety of biological processes such as vascular renovation, stimulation of immune cell, rapid wound detection in animals, etc. [1]. It has also been obtained as a byproduct from the number of biological reactions catalyzed by the oxidative enzymes such as glucose oxidase, cholesterol oxidase, lactate oxidase, and urate oxidase [2,3]. However, the high exposure of H₂O₂ leads to cytotoxic effects including cytokines, damage of deoxyribo nucleic acid (DNA),

defective cell growth, cancer, propagation of cells, metastasis, angiogenesis and apoptosis resistance, whereas the lower level exposure of H₂O₂ induces apoptosis [4]. Hence, it is highly appropriate to develop the efficient H₂O₂ quantification systems with high sensitivity and selectivity. On the basis of above, numerous analytical strategies including fluorimetry [5], titrimetry [6], spectrometry [7], chromatography [8], fluorescence [9], chemiluminescence [10], spectrophotometry [11], surface plasmon resonance [12], colorimetric [13] and electrochemical methods [14] have been developed to efficiently detect the analyte H₂O₂, in which the electrochemical technique has grabbed keen attention. The constructive characteristics of electrochemical sensors including fast response, easier fabrication, possible miniaturization, reliability, portability, high sensitivity and selectivity have wide opened its commercial market [15]. Apart from the advantages of prompt sensitivity and selectivity, enzyme based sensors exhibited several limitations, such as lower electron mobility, high cost, lack of long-term stability, complexity of enzyme immobilization process, critical operation conditions, denaturation of enzymes and dependency on pH and temperature [16]. Hence, non-enzymatic electrochemical H₂O₂ sensors have

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elucidated ardent interest in the quantification of H_2O_2 due to its high sensitivity, fast response and long-term stability. However, the existing non-enzymatic sensors exhibit a large overpotential, resulting the poor electrochemical performances toward H_2O_2 detection. Therefore, it is highly essential to develop the new catalytic systems to lower the overpotential for the efficient electrochemical detection of an analyte. Recently, the modification of electrode materials by using one-dimensional (1D) inorganic nanomaterials has received significant attention, owing to its good electrocatalytic properties, high surface-to-volume ratio, high stability and wide availability [17]. Hence, various nanomaterials including gold [18], cuprous oxide [19], silica [20], Pt [21], and silver doped manganese oxhydroxide [22] have been developed for the H_2O_2 detection. Among the aforesaid metal and metal oxide nanostructures, MnO_2 nanostructures have received immense interest in H_2O_2 sensor applications, owing to its low cost, high energy density, environmental benign characteristics, high abundance, large surface area, number of active sites, elevated catalytic activity, etc. [23]. Although MnO_2 exists in three major forms such as α , β and δ , α - MnO_2 exhibited high catalytic activities, owing to the double chains of edge-sharing MnO_6 octahedra, which are linked at corners to form the 1D (2×2) and (1×1) tunnels that extend in a direction parallel to the *c*-axis of the tetragonal unit cell [23]. Thiagarajan et al. electrochemically deposited the MnO_2 nanoparticles on indium coated tin oxide (ITO) and evaluated its electrocatalytic activities toward the H_2O_2 reduction. The developed sensor exhibited the sensitivity and detection limit of $7.51 \mu\text{A mM}^{-1}$ and 0.02 mM , respectively, toward the electrochemical quantification of H_2O_2 [24]. McAuley et al. compared the non-enzymatic H_2O_2 electrochemical sensor performances of MnO_2 nanorods with the MnO_2 microparticles and concluded that MnO_2 nanorods exhibited the superior electrochemical performances over the MnO_2 microparticles with the lower detection limit of $2.9 \mu\text{M}$ [25]. MnO_2 nanorods exhibited the superior catalytic activities over the spherical counter parts, owing to its large tunnel structure, number of structural defects and large surface area, which may be beneficial for the adsorption of an analyte and followed by its electrochemical reduction [25,26]. Irrespective of phases and morphologies, MnO_2 usually exhibits the limitations such as poor electrical conductivity, mechanical instability, lower surface area, agglomeration in aqueous medium, etc., leading to the inferior electrochemical performances as reported elsewhere. Hence, it is highly essential to anchor the MnO_2 nanorods over the active carbon support to effectively tackle the aforesaid limitations, in which the role of graphite nanofibers (GNF) is highly important.

GNF consists of sp^2 hybridized carbon atoms, forming a hexagonal network with a large π bond and exhibits a high degree of graphitic structure and distinctive fibrous morphology [27]. It exhibits the elevated electrical conductivity and surface area due to the graphitic structure and nanofibrous morphologies. The electrocatalytic activity of GNFs could be further increased by doping nitrogen through electrostatic π - π interaction, which may facilitate the surface area, chemical active sites and electron mobility properties [28]. In general, N functionalization improves the hydrophilicity and wettability of host carbon matrix. The electron donating behavior of N in N doped GNFs (NGNF) may yield the chemically active localized areas with a higher electron density. In addition, the charge distribution and spin density of neighboring carbon atoms in NGNFs could also be influenced, which may enhance the electrocatalytic activity of N functionalized carbon matrix. The existence of N species on GNF surface could provide surface nucleation sites, which may facilitate the homogeneous dispersion of catalytic metal nanoparticles, resulting the strong interaction with carbonaceous support and catalytic materials. If the catalytically active MnO_2 nanorods could be

hybridized with NGNF, the individual limitations of aforesaid materials could be effectively tackled and influential catalytic properties toward H_2O_2 electroreduction could be achieved. Hence, this research effort is aimed to develop the α - MnO_2 nanorods grown NGNFs and identify the influences of active carbon support and MnO_2 nanostructures toward the efficient electrochemical detection of H_2O_2 .

Experimental details

Materials

GNFs were purchased from Carbon Nanomaterial Technology Co. Ltd., potassium permanganate (KMnO_4 , LR, $\geq 99\%$), sulfuric acid (H_2SO_4 , AR, $\geq 98\%$), potassium ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$, ACS reagent, $\geq 99\%$), Nafion (5 wt%, contains 15–20% H_2O), N,N-dimethyl formamide (DMF, AR, $\geq 99.5\%$), sodium hydroxide (NaOH, pellet, AR, $\geq 98.5\%$), urea (U, AR, $\geq 99\%$), uric acid (UA, HPLC, $\geq 99\%$), ascorbic acid (AA, AR, $\geq 99.5\%$), dopamine (DA, AR, $\geq 99\%$), acetaminophen (AP, AR, $\geq 99\%$), sodium chloride (NaCl, AR, $\geq 99.5\%$) and hydrogen peroxide (H_2O_2 , AR, $\geq 30\%$ (w/v)) were obtained from Sigma-Aldrich and used without further purification.

Synthesis of NGNF/ α - MnO_2 nanostructures

The derived GNFs were doped with nitrogen as per the procedure described elsewhere [29]. Appropriate amount of KMnO_4 was mixed with NGNFs under mortar and pestle conditions and dispersed in de-ionized water. To the NGNF/ KMnO_4 dispersion, 250 ml H_2SO_4 was added and hydrothermally treated at 80°C for 1 h. Finally, the prepared sample was washed with de-ionized water and dried under vacuum conditions.

For the comparison, bare MnO_2 nanorods were prepared by using the same procedure without the utilization of NGNFs.

Fabrication of modified glassy carbon electrode (GCE)

The GCE surface was polished according to the procedure described elsewhere [30]. $6 \mu\text{l}$ of as-synthesized nanostructure in DMF (0.5 mg ml^{-1}) dispersion was dropped on the surface of polished GCE and dried at room temperature. In order to attach the electrocatalysts, $6 \mu\text{l}$ Nafion solution was dropped on the surface of catalyst modified GCE and dried under normal atmospheric conditions.

Characterizations

The surface morphological properties of synthesized nanostructures were characterized by using S-4700, HITACHI field emission scanning electron microscopy (SEM) and JEOL JEM-2010 transmission electron microscope (TEM) coupled with an EDAX analyzer. The crystal phases and crystallinity of prepared nanostructures were examined with the Rigaku - X-ray powder diffractometer (XRD). The structural characterizations of as-synthesized nanostructures were investigated by Shimadzu FT-IR spectroscopy in the range of 4000 – 400 cm^{-1} .

Electrochemical characterizations

The electrochemical measurements were employed with a CHI-650E electrochemical work station under a conventional three electrodes configuration, which consists of GCE, Ag/AgCl (saturated 1 M KCl) and Pt wire as a working, reference and counter electrode, respectively. The electrochemical behavior of studied electrodes were investigated by using 0.1 M KCl in 5 mM

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