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Surface analysis and electrochemistry of a robust carbon-nanofiber-based electrode platform H_2O_2 sensor

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ABSTRACT

A vertically aligned carbon nanofiber-based (VACNF) electrode platform was developed for an enzymeless hydrogen peroxide sensor. Vertical nanofibers have heights on the order of 2–3 μm, and diameters that vary from 50 to 100 nm as seen by atomic force microscopy. The VACNF was grown as individual, vertically, and freestanding structures using plasma-enhanced chemical vapor deposition. The electrochemical sensor, for the hydrogen peroxide measurement in solution, showed stability and reproducibility in five consecutive calibration curves with different hydrogen peroxide concentrations over a period of 3 days. The detection limit was 66 μM. The sensitivity for hydrogen peroxide electrochemical detection was 0.0906 mA cm^{-2} mM^{-1}, respectively. The sensor was also used for the measurement of hydrogen peroxide as the by-product of the reaction of cholesterol with cholesterol oxidase as a biosensor application. The sensor exhibits linear behavior in the range of 50 μM–1 mM in cholesterol concentrations. The surface analysis and electrochemistry characterization is presented.

1. Introduction

A robust, stable, reliable, reusable and accurate sensor for the determination of hydrogen peroxide (H_2O_2) is of interest in many fields such as food and environmental monitoring, quality control and particularly in biosensing since H_2O_2 is a by-product of reactions catalyzed by a large number of oxidase enzymes such as glucose oxidase, cholesterol oxidase, lactose oxidase, etc. [1–3]. Different techniques have been employed for the determination of H_2O_2 such as titration [4], spectrophotometry [5], and chemiluminescence [5,6]. Among them, electrochemical methods have attracted considerable interest due to their high sensitivity, fast response, low-cost and convenient operation [7]. Different carbon base material have bee used for hydrogen peroxide electrochemical determination such as carbon nanotubes [8,9], grapheme [10], diamond [11–13], mesoporous carbon[14] and carbon nanofibers [15–17]. Most of carbon-based materials for hydrogen peroxide measurements need the addition of an inorganic metal and metal oxide for surface stability, signal enhancement and robustness. The most common inorganic metals employed are Pt [18–20], Ag [21,22], Au [9,23,24]. However, the introduction of a metal catalyst adds for more complicated material synthesis.

Therefore we developed an efficient and robust H_2O_2 sensor based on a vertically aligned carbon nanofiber (VACNF) electrode (Scheme 1-A). Where H_2O_2 is in solution and oxidized to produce $2H^+ + O_2$, and 2e- that are measured at the electrode surface. Vertical nanofibers have heights on the order of 2–3 μm, and diameters that vary from 50 to 100 nm. The carbon nanofibers can be grown as individual, vertical, freestanding structures using plasma-enhanced chemical vapor deposition (PECVD) [25–28]. The main characteristic that distinguishes CNFs from nanotubes is the stacking of graphene sheets of varying shapes, producing more edge sites on the outer wall, which facilitates electron transfer of electroactive analytes to the surface. Moreover, the whole surface can be activated with nitric acid or electrochemical oxidation to produce a range of oxygen-containing groups without the degradation of the structural integrity of their backbone, thus allowing their modification through interactions or reactions with other molecules [28–33]. Applications for CNFs have focused on catalyst support, gas storage systems, probe tips, etc. and also as sensors [15,33–37]. The ability to grow CNFs in a controllable manner on 100–200 mm silicon wafers – both patterned and unpatterned – allows the construction of nanoelectrode arrays for biosensing applications [13–15]. Here, we report on the stability of an enzymeless carbon nanofiber electrode toward the electro-oxidation of hydrogen per-

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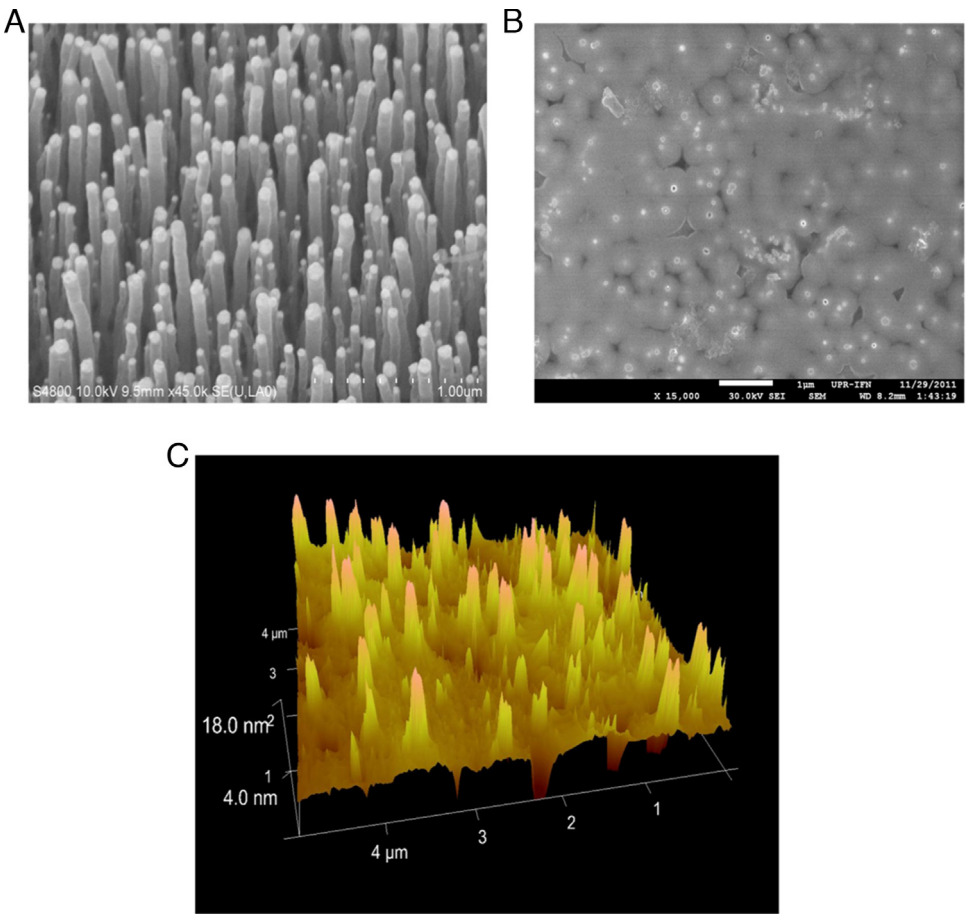
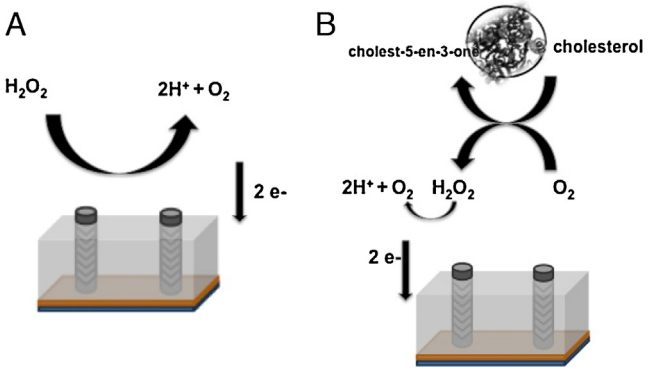


Fig. 1. SEM images of (A) as-grown, vertically-aligned, carbon nanofiber array and (B) CNF electrode after chemical-mechanical polishing and electrochemical treatment (magnification ×15,000) and (C) three dimensional AFM image of the electrode surface.

oxide, as well as its operation as a biosensor, specifically a biosensor for the determination of cholesterol with cholesterol oxidase as the bioreceptor element in solution and H_2O_2 as the by-product measured at the electrode surface. Cholesterol oxidase (ChOx), that is industrially important for applications in bioconversions, is used for clinical determination of cholesterol and also for other applications such as the determination of cholesterol in food samples[38]. The well-known principle of an enzyme-based cholesterol sensor is typically based on the reaction between cholesterol and the cholesterol oxidase (ChOx) enzyme. Free cholesterol is oxidized by cholesterol oxidase to produce 4-cholestene-3-one and hydrogen peroxide (H_2O_2), and the H_2O_2 produced can be used for indirect quantification of cholesterol (Scheme 1-B) [39].



Scheme 1. (A) Representation of the electrooxidation of hydrogen peroxide at the CNF-surface and (B) representation of the cholesterol determination, in the presence of cholesterol oxidase in solution and measuring hydrogen peroxide as the electroactive by product.

2. Materials and methods

2.1. Sensor fabrication and reagents

VACNFs were grown by PECVD on a silicon wafer using a 200 nm thick layer of chromium and 20 nm nickel as the catalyst [40]. A dc-biased plasma reactor (Aixtron, Cambrige, UK) was used to grow the CNFs with 125 sccm acetylene and 144 sccm of ammonia as feedstock at 6.3 mbar, 700 deg. C and 180 W power. The individual CNFs were isolated by intercalating the gaps between the CNFs with SiO_2 using chemical vapor deposition and a tetraethoxysilane precursor. The oxide encapsulated each nanofiber, and subsequent mechanical polishing allowed exposure of the CNF tips [41–43]. This process has been previously used on 100–150 mm wafers to fabricate sensor arrays for the detection of cardiac biomarkers and ricin biothreats [13–16,23–27] and details regarding the process, uniformity of CNF growth, electrode array fabrication and reliability of electrodes can be found in these reports.

All solutions were prepared using water that was distilled water pumped through a nanopure system (Barnstead). Cholesterol, Triton X-100, NaH_2PO_4, Na_2HPO_4, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$ were purchased from Sigma-Aldrich; ChOx from VWR; H_2SO_4, HNO_3 and NaOH from Fisher (USA). For chemical-mechanical polishing (CMP), alumina particles of different sizes were used.