



# Improving sensitivity of electrochemical sensors with convective transport in free-standing, carbon nanotube structures



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## ARTICLE INFO

### Article history:

Received 27 October 2016

Received in revised form 2 February 2017

Accepted 3 February 2017

Available online 12 February 2017

### Keywords:

Electrochemical  
Amperometric sensing  
Carbon nanotube  
Platinum  
Microfluidics  
Convection

## ABSTRACT

High-aspect-ratio, porous membrane of vertically-aligned carbon nanotubes (CNTs) were developed through a templated microfabrication approach for electrochemical sensing. Nanostructured platinum (Pt) catalyst was deposited onto the CNTs with a facile, electroless deposition method, resulting in a Pt-nanowire-coated, CNT sensor (PN-CNT). Convective mass transfer enhancement was shown to improve PN-CNT sensor performance in the non-enzymatic, amperometric sensing of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). In particular, convective enhancement was achieved through the use of high surface area to fluid volume structures and concentration boundary layer confinement in a channel. Stir speed and sensor orientation especially influenced the measured current in stirred environments for sensors with through-channel diameters of 16 μm. Through-flow sensing produced drastically higher signals than stirred sensing with over 90% of the H<sub>2</sub>O<sub>2</sub> being oxidized as it passed through the PN-CNT sensor, even for low concentrations in the range of 50 nM to 500 μM. This effective utilization of the analyte in detection demonstrates the utility of exploiting convection in electrochemical sensing. For through-flow at 100 μL s<sup>-1</sup>, a sensitivity of 24,300 μA mM<sup>-1</sup> cm<sup>-2</sup> was achieved based on the frontal projected area (871 μA mM<sup>-1</sup> cm<sup>-2</sup> based on the nominal microchannel surface area), with a 0.03 μM limit of detection and a linear sensing range of 0.03–500 μM.

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## 1. Introduction

Transport in chemical reactions can play a critical role in introducing reactants to or removing products from the surface where the reaction takes place. In fact, mass transport is cited as having a major influence on the performance of many chemical technologies, including chemical reactors [1–3], lithium-oxygen batteries [4], and fuel cells [5]. In sensor applications where the target analyte may occur in low concentrations, transport of the analyte to the reacting surface can be the primary limitation of the sensor approach (i.e. “transport-limited” sensors). With the prominent reduction in feature sizes and corresponding reduction in sensing surface area available with microelectromechanical systems, some sensor platforms can suffer from a significant limitation in mass transfer rates to the sensing surface (e.g. micro-cantilevers). In cases where the analyte concentration is low, transport must be efficient to capitalize on the sparsely available target. Increasing the flow rate, increasing the surface area, and/or limiting growth

of the concentration boundary layer are techniques that can be exploited to increase the convective transport of the analyte. This work demonstrates an effective platform to increase convective transport with applications in chemical sensing.

Enhancement of the analyte introduction rate can be achieved by increasing the flow rate of the analyte in solution. As the motion of the analyte is increased, the probability of analyte reaching a reacting surface increases and results in an overall increase in introduction rate. A good example of increased analyte flow is the rotating disk electrode, where the introduction rate of analyte to the surface increases as the rotation rate increases [6]. Several recent studies have also investigated catalytic structures which move through the analyte solution [7–12], thereby increasing the *apparent* analyte flow and enhancing the chemical introduction rate. Although this approach is straightforward, the impact of convection is often overlooked or its effect disregarded when stir speeds or flow rates are not provided with electrochemical or amperometric sensing results.

Enhancement of the analyte introduction rate can also be achieved for diffusive or convective environments by increasing the exposed catalytic surface area. High surface area microstructures promote intimate contact between the analyte and the cat-

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alytic surfaces while minimizing the structure's spatial footprint. Microstructures such as three-dimensional graphene [13–15], magnesium oxide [16–18], and zeolites [19–21], all possess considerably large surface area to fluid volume ratios and can be appropriately functionalized for specific chemical reactions. In particular, high-aspect-ratio microstructures (pillars, channels, etc.) allow for large exposure of surface area to chemical volume and facilitate enhanced mass transport, much in the same way fin arrays are used to enhance heat transfer [22,23]. The utility of enhanced surface area structures in the literature has been shown to outperform similar planar geometries [24,25].

While external flow *past* microstructures can provide enhanced mass transport, internal flow *through* high-aspect-ratio microstructures allows for a third transport enhancement method: boundary layer confinement. For flow in a confined geometry such as a channel, concentration boundary layer growth is limited once the boundary layers have merged, resulting in a maximum transport distance of half the channel diameter. These short transport lengths result in high mass transport coefficients, especially as the channel diameter is reduced. The concept of flow-through electrodes originates in the 1970s [26–28], with application to hydrogen peroxide sensing beginning in the 1990s [29,30]. However, with recent developments in microfabrication and materials science, the ability to sense target analyte has greatly increased, yet many sensors have not taken advantage of flowing analyte through the sensor. For example, carbon nanotubes (CNTs) have been widely used in electrochemical sensing because of their unique structural, mechanical, and electronic properties [31]. CNTs on supporting membranes have been used as flow-through electrodes for electrochemical filtering [32], but only recently have membrane-supported CNT flow-through electrodes been used for electrochemical sensing [33]. The present work describes a free-standing CNT sensor with an array of micron-scale channels (2000–32,000 channels per mm<sup>2</sup>), a structure we previously used for the decomposition of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) at high concentrations for underwater vehicle propulsion [34]. Such a multi-channel CNT structure presents a departure from previous work as it is the first time CNTs have been arrayed in controlled patterns with flow through micron channels developed within the CNT membrane itself. Thus, this work presents the first steps in developing a more controlled CNT membrane for flow-through electrochemical microfluidic sensing devices (EMSDs) applications where the CNT membrane itself acts *both* as the highly catalytic working electrode and as the structure used to induce tunable microfluidic transport. These multi-channel CNT structures could also be fitted and placed within various sized flow channels including conventional microfluidic channels.

The importance of microfluidic transport in the context of electrochemical sensing/biosensing has shown to be tremendous promising in achieving efficient catalysis and low detection limits [35]. Such microfluidic sensing devices produce fast analysis times with extremely low sample and reagent volumes which are well-suited for point-of-service detection that circumvents the costs associated with conventional laboratory analysis (e.g., shipping/handling costs, highly trained technicians to operate polymerase chain reaction (PCR) or perform enzyme-linked immunosorbent assays (ELISAs)) [36,37]. Furthermore, EMSDs overcome challenges with optical-based sensing modalities where solution turbidity, optical path length, and power requirements can significantly hinder sensing results. However, there still exists a need to increase the sensitivity of EMSDs, and microfluidic sensors in general, as high sensitivity is required to detect target analytes in low concentrations or low volumes [38].

Herein, we increase the efficiency of electrochemical sensors that utilize convective flow environments by developing a high-aspect ratio, free-standing membrane (~250 μm height) of vertically aligned carbon nanotubes (CNTs) that form an array of

aligned, parallel microchannels (of 4 μm diameter with 32,479 channels per mm<sup>2</sup> or of 16 μm diameter with 2030 channels per mm<sup>2</sup>). The overall sensor dimensions can be scaled up to accommodate macroscale flow cells or any specific EMSD dimension where the fluid flow can be forced through a series of sensing microchannels. Subsequently, this CNT architecture capitalizes on all three mass transport enhancement methods to improve electrochemical sensing: high flow rate, large electroactive surface area, and concentration boundary layer confinement. The sensor architecture is realized through CNT-templated microfabrication, where CNTs are used as a scaffold to create a microporous membrane and achieve high-surface area to fluid volume structures that are electrically conductive. The structure is coated with urchin-like platinum nanowires (PN), developed through an electroless Pt deposition technique we have previously developed for use on CNTs, cellulose, and silicon oxide [34,39,40], to increase the CNT structures electrocatalytic capability during subsequent non-enzymatic, amperometric sensing of H<sub>2</sub>O<sub>2</sub>. Experiments reveal that stir speed and sensor orientation can greatly affect the current response of the PN-coated CNT (PN-CNT) sensors. Through-flow sensing (i.e., flow through the sensor architecture as would be experienced if the PN-CNT membranes spanned across the flow path of an EMSD) is shown to produce drastically higher signals at lower local fluid velocities than achieved with the traditional method of stirring. Further, we demonstrate near complete detection (>90%) of H<sub>2</sub>O<sub>2</sub> at concentrations down to 50 nM through exploitation of the sensor geometry and convective enhancement. Therefore, the CNT sensing platform utilized here offers an efficient method for chemical sensing/biosensing and shows promise for incorporation into the flow field of EMSD and larger macroscale flow cells as portrayed in this work.

## 2. Materials and methods

### 2.1. CNT sensing platform

Fabrication of the CNT sensing platform followed the methods outlined by Marr et al. [34]. An aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) film approximately 50 nm thick was deposited on a silicon (Si) wafer using a Denton e-beam evaporator. A 7 nm layer of iron (Fe) was thermally evaporated onto patterned photoresist to achieve two different CNT sensor pore geometries (4 μm and 16 μm diameter microchannels). The wafer was agitated in *N*-Methyl-2-pyrrolidone (NMP) for at least 10 min to remove the patterned photoresist in a lift-off process, resulting in a hexagonally packed arrangement of Fe free regions. The layers of construction for the CNT architecture are illustrated in Fig. 1A.

Diced Fe-patterned wafers were placed in a Lindberg/Blue M Tube Furnace for CNT growth in flowing hydrogen (230 sccm) and ethylene (250 sccm) at 750 °C for 6 min. After 6 min of growth, the multi-walled CNTs achieved a height of about 250 μm with diameters on the order of 20 nm (see Fig. 1B), but require somewhat delicate handling. To create a stronger, agglomerated structure, the CNTs were coated (infiltrated) with amorphous carbon in the furnace by flowing hydrogen (158 sccm) and ethylene (250 sccm) at 900 °C for 10 min (see Fig. 1C). This infiltration/coating process with amorphous carbon results in the attachment of neighboring CNTs and enables a mechanically robust yet porous array of microchannels (see Fig. 1D). The hydrogen gas during carbon infiltration allows the CNT microstructure to self-release from the Si substrate, creating a stand-alone microstructure comprised of carbon-coated, CNT walls (see Fig. 1E).

Although the CNT membranes self-released from the wafers, the side closest to the Si substrate was covered by a thin carbon layer during infiltration. To remove this layer, an oxygen (O<sub>2</sub>) plasma etch

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