Carbon Nanotube/Green Tea Composite for the Electronic Detection of Hydrogen Peroxide

Yanan Chen, Yang Doo Lee, Harindra Vedala, Brett L. Allen, and Alexander Star[*]

[*] Department of Chemistry, University of Pittsburgh and the National Energy Technology Laboratory, Pittsburgh, PA 15260, USA, astar@pitt.edu

ABSTRACT

Single-walled carbon nanotubes (SWNTs) and their composites are ideal candidates for chemical and biological sensing application, due to their unique electronic, chemical and physical properties. Green tea, or more specifically its main antioxidant component, epigallocatechin gallate (EGCG), has been found to disperse SWNTs in water and form SWNT/green tea (SWNT/EGCG) composite. With the presence of EGCG, this SWNT composite should have strong antioxidant properties and thus respond to reactive oxygen species (ROS). Here we report the fabrication and characterization of a SWNT/Green Tea (SWNT/EGCG) sensing system for the detection of H_2O_2 in solution phase. By liquid-gating field-effect (FET) transistor measurements and conductance measurements, it was observed that the conductance of SWNT/EGCG composite thin film increased with increase in H_2O_2 concentrations. These findings suggest that SWNT/Green Tea composite has a great potential for developing simple resistivity-based nanoscale sensors for the electronic detection of ROS.

Keywords: single-walled carbon nanotubes, antioxidant, resistivity sensors, ROS, hydrogen peroxide

1 INTRODUCTION

The determination of hydrogen peroxide is very important, because it is a by-product of many biological processes and an essential mediator in food, pharmaceutical, clinical, industrial and environmental analysis.[1] There have been many demonstrated examples of hydrogen peroxide sensors using various techniques, including spectrometry,[2] chemiluminescence[3] and electrochemistry[4]. However, carbon nonamaterial-based resistivity sensors for hydrogen peroxide have not been fully explored. Here we report a carbon nanotube/green tea (EGCG) composite-based resistivity sensor for the detection of hydrogen peroxide.

Single-walled carbon nanotubes (SWNTs) have been of increasing importance in a variety of areas including materials and life sciences.[5-7] Because of their size (approximately 1-3 nm in diameter, 1 µm long) and unique physical and electronic properties, SWNTs are an ideal material to interface with biological systems. Made solely from the leaves of *Camellia sinensis*, green tea has been extensively studied for its antioxidant abilities.[8] Specifically, antioxidant properties can be derived from the presence of catechins. Catechins are a group of water-soluble polyphenols, consisting of epicatechin (EC), epicatechin gallate (ECG), epigallocatechin (EGC), and epigallocatechin gallate (EGCG). Such compounds possess biological activity exhibiting not only antioxidant behavior, but antitumor and anticancer effects as well. Among antioxidants present in green tea, EGCG is the most abundant and has the strongest activity.[9] This compound reacts readily with reactive oxygen species (ROS) such as superoxide (O_2^-), hydroxyl radicals (·OH), and hydrogen peroxide (H_2O_2).[10] It has been reported that green tea or EGCG can disperse nanotubes in aqueous solutions and for SWNT/green tea (EGCG) composite. [11]

2 RESULTS

2.1 Device Fabrication

We obtained the SWNT/EGCG composite (Figure 1a) by sonicating approximately 1 mg of SWNTs in 20 mL of 0.3 mg/mL green tea (or 4×10^{-4} M EGCG) at room temperature (Sonicator: Branson 5510) for 1 hr. The solution was then centrifuged (Fisher Scientific centrific model 228) at 3400 RPM for 15 minutes. The supernatant was then filtered and washed with deionized water subsequently to remove any unbound green tea (EGCG). The resulting material was then dispersed in water to obtain SWNT/green tea (SWNT/EGCG) suspension (resulting concentration 0.05 mg/mL). This composite material was characterized by ultraviolet-visible-near-infrared (UV-Vis-NIR) absorption spectroscopy Fourier transform infrared (FTIR) spectroscopy, transmission electron microscopy (TEM), and atomic force microscopy (AFM) in thin films.[12] Spectroscopic measurements were taken of a spray-cast film on a quartz slide using UV-Vis-NIR spectroscopy. The resulting spectrum is a superposition of SWNTs and EGCG spectra (Figure 1b), in a good agreement with previous solution studies.[11]

Metal interdigitated devices (Au/Ti, 100 nm/30 nm) with interelectrode spacing of 10 µm were patterned on a Si/SiO_2 substrate using conventional photolithography. One chip (2mm×2mm) containing four identical devices was then set into a 40-pin ceramic dual in-line package (CERDIP) and wire-bonded using Au wire. Devices were subsequently isolated from the rest of the package by epoxying the inner cavity. Fabrication of bare SWNTs conductance measurement was made by sonicating approximately 1 mg

NSTI-Nanotech 2011, www.nsti.org, ISBN 978-1-4398-7138-6 Vol. 3, 2011

of SWNTs in 20 mL DMF and drop-casting 40 µL of the dispersion directly on the Si chip in the package device mentioned above. The fabrication of SWNT/EGCG composite devices was carried out by drop-casting 40 µL SWNT/EGCG suspension on a chip and allowing to dry in ambient (Figure 1c). [12]

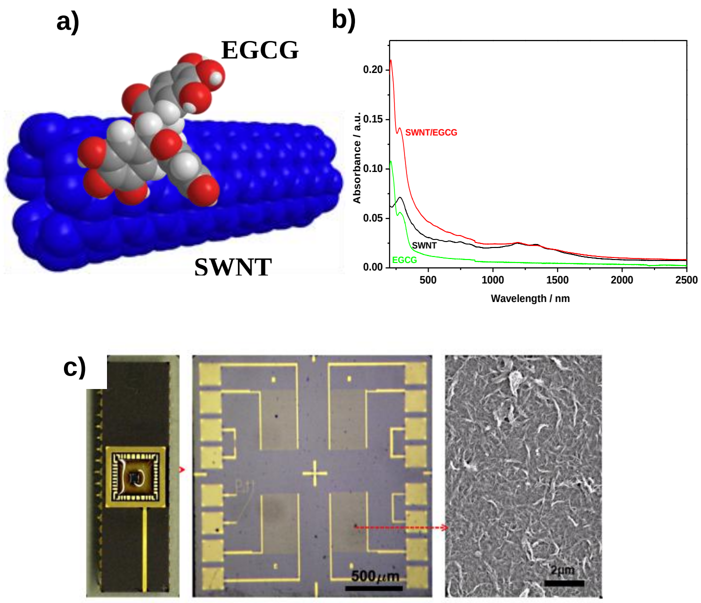

Figure 1 (a) Schemativ illustration of SWNTs and epigallocatechin gallate (EGCG). (b) UV-Vis-NIR absorption spectra of SWNT (black), EGCG (green), and SWNT/EGCG (red) as thin films on quartz. Inset displays a photograph of transparent SWNT/EGCG conductive film on a quartz slide. (c) Optical images (scale bar: 500 µm) and scanning electron microscope (SEM) image (scale bar: 2 µm) of the SWNT/EGCG film deposited on CERDIP package with Si chip containing four interdigitated Au electrodes (interelectrode spacing of 10 µm).

2.2 Hydrogen Peroxide Sensitivity Test

To understand the interaction between SWNTs and EGCG and the response of this composite to hydrogen peroxide, we studied the effect of H_2O_2 concentrations on SWNT/green tea composite conductance in a liquid gate FET configuration. It has been demonstrated in earlier reports that an electrolyte-gated FET configuration can be effectively used for understanding the interaction of various molecules (charged ions or biomolecules) with SWNTs.[13] Figure 2a shows a schematic illustration of the FET device. Figure 2b shows the I_d vs V_{lg} for SWNT/green tea composite device measured at different concentrations of H_2O_2. A gradual shift in the threshold voltage for each curve was observed with the increasing concentrations of H_2O_2 from 10^{-4} M to 10^{-2} M (Figure 2b inset). This shift towards positive gate voltages indicates a p-doping of the FET device which can be attributed to the negative charge donated into the channel from the H_2O_2 molecule.

The proposed mechanism for the conductance response to H_2O_2 is derived from the antioxidant properties of EGCG, which has been the subject of much debate.[14] Catechins are oxidized by radicals and thus lose electrons (Figure 3d), which segues into the response for SWNT/EGCG devices. Presumably interactions between EGCG and SWNTs are such that some electron density is transferred between the species. As EGCG is oxidized and loses electrons, it may be that this causes subsequent withdrawal of electron density from the nanotube network resulting in an increase in the majority charge carrier, holes, and increasing conductance. [12]

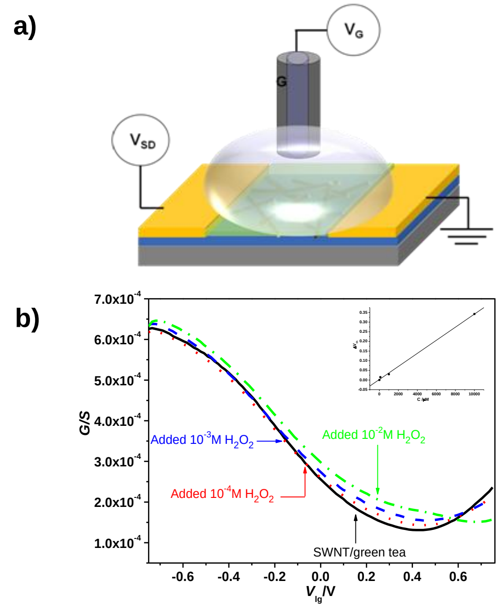

Figure 2 (a) Schematic illustration of the liquid-gate FET testing device setup. (b) Current versus liquid gate potential curves of SWNT/green tea composite device acquired before (black solid) and after adding 10^{-4} M (red dot), 10^{-3} M (blue dash) and 10^{-2} M (green dot dash) H_2O_2.

In order to examine the chemical sensitivity of the composite to varying concentrations of H_2O_2, SWNT/EGCG composite devices were fabricated by drop-casting SWNT/EGCG on Si chips with four interdigitated Au electrodes (Figure 1c). Conductance measurements on composite devices were carried out on a custom test-board using Zephyr software. Using a Keithley 2602 dual-source meter and Keithley 708A switching mainframe, all devices were monitored on a single chip at a given time.

To overcome effects of relative humidity, we performed liquid measurements. We have already made mention that EGCG is a strong antioxidant and, as such, should have a specific response for ROS such as H_2O_2, as opposed to response of the thin films to water. In liquid measurements, the composite should be fully hydrated, and thus, the conductance change will be only due to the result of ROS in the solution. We examined SWNT/EGCG composite devices for changes in conductance in real time. Devices were initially exposed to four additions of 10 µL deionized water to create a stable hydrated layer within SWNT/EGCG composites. As can be seen from Figure 3a, the initial exposure to 10 μL of water elicited the same conductance decrease as witnessed in the relative humidity experiments. After four additions of deionized water, any subsequent response should be solely due to the concentrations of H_2O_2. An addition of 10^{-4} M H_2O_2 (10 μL) resulted in a slight increase in the conductance of the device. Then the higher concentrations of H_2O_2 (10^{-3} M and 10^{-2} M) were added subsequently and the responses increased accordingly. As a control experiment, bare nanotube device were tested for the same concentrations of H_2O_2, as well as the initial additions of deionized water. As can be seen from Figure 3b, after additions of deionized water, the bare SWNT device cannot reach a stable baseline as effectively as the SWNT/EGCG composite, which may be due to the hydrophobicity of bare nanotubes, and the device has no obvious response to the subsequent additions of H_2O_2.

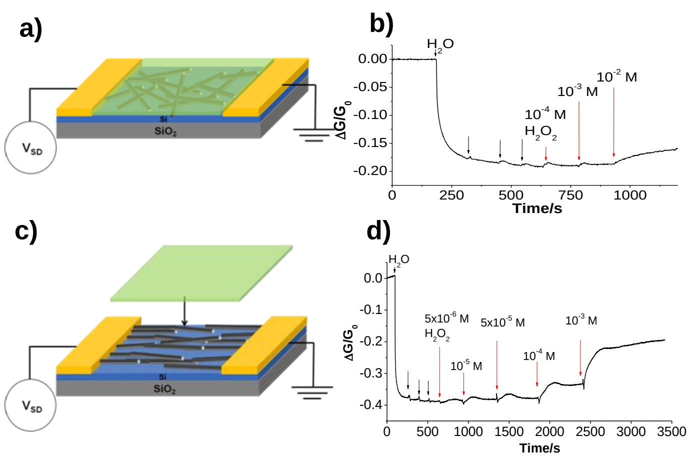

Figure 3 (a) schematic device architecture of SWNT/EGCG pre-mixed composite, (b) relative conductance versus time response to varying concentrations of H_2O_2 of SWNT/EGCG pre-mixed composite, (c) schematic device architecture of SWNT/EGCG layer-by-layer composite, (d) Relative conductance versus time response to varying concentrations of H_2O_2 of SWNT/EGCG layer-by-layer composite

2.3 Device Architecture Optimization

To improve the H_2O_2 response, we explored layer-by-layer architecture to fabricate the SWNT/EGCG device (Figure 3c). We first deposited SWNTs (DMF suspension) onto the electrodes using a dielectrophoresis (DEP) method.[15] After washing with DMF and drying at 180 °C, the chips were incubated with EGCG solution (in water, 4.4×10^{-4} M) for two hours to deposit EGCG on the surface of SWNTs and then washed with deionized water and dried in ambient. This device architecture demonstrated improved response to H_2O_2 (Figure 3d). H_2O_2 concentration as low as 5×10^{-6} M was detected with signal to noise ratio of 8. The improvement in the sensor performance can be attributed to dielectrophoretic assembly of nanotube between the metal electrodes and layer-by-layer deposition of EGCG on bare SWNTs. DEP aids in alignment of the nanotubes between the electrodes and results in increased field-effect mobility as compared to devices fabricated by drop casting[39]. Layer-by-layer deposition of EGCG results in direct contact of nanotubes with metal electrodes, thereby reducing the contact resistance.

3 CONCLUSIONS

In conclusion, we fabricated SWNT/green tea and SWNT/EGCG composites-based resistivity sensor and detected hydrogen peroxide in solution. Because of EGCG's antioxidant properties and hydrophilic nature, this composite exhibits sensitivity to hydrogen peroxide in aqueous solution. We propose that these responses are the result of the oxidation of EGCG and electron transfer between EGCG and SWNTs. The H_2O_2 response was further improved by changes in the device architecture. Such solid-state electrical measurements indicate that SWNTs functionalized with common-or-garden green tea have great potential for electronic detection of ROS.

4 ACKNOWLEDGEMENTS

The project described was supported by NIEHS R01ES019304. Y. D. L. acknowledges support of the Korea Research Foundation Grant (KRF-2007-357-D00051) funded by the Korean Government (MOEHRD). We thank the Department of Materials Science and Engineering at the University of Pittsburgh for access to the SEM and TEM instrumentation.

REFERENCES

[1] Y. Xiao, H.-X. Ju, and H.-Y. Chen, Hydrogen peroxide sensor based on horseradish peroxidase-labeled Au colloids immobilized on gold electrode surface by cysteamine monolayer, Analytica Chimica Acta 391, 73-82, 1999.

[2] C. Matsubara, N. Kawamoto and K. Takamura. Oxo[5, 10, 15, 20-tetra(4-pyridyl)porphyrinato]titanium(IV): an ultra-high sensitivity spectrophotometric reagent for hydrogen peroxide, Analyst 117**,** 1781, 1992.

[3] K. Nakashima, K. Maki, S. Kawaguchi, S. Akiyama, Y. Tsukamoto and I. Kazuhiro. Peroxyoxalate chemiluminescence assay of hydrogen peroxide and glucose using 2, 4, 6, 8-tetrathiomorpholinopyrimido [5, 4-*d*]-pyrimidine as a fluorescent component, Anal. Sci. 7, 709, 1991.

[4] J. Tang, B. Wang, Z. Wu, X. Han, S. Dong and E. Wang. Lipid membrane immobilized horseradish peroxidase biosensor for amperometric determination of hydrogen peroxide, Biosens. Bioelectron. 18, 867, 2003.

[5] A. Star, E. Tu, J. Niemann, J.-C. P. Gabriel, C. S. Joiner, and C. Valcke. Label-free detection of DNA hybridization using carbon nanotube network field-effect transistors. Proc. Natl. Acad. Sci. USA, 103, 921-926, 2006.

[6] D. R. Kauffman, C. M. Shade, H. Uh, S. Petoud, and A. Star. Decorated carbon nanotubes with unique oxygen sensitivity. Nature Chem. 1, 500-506, 2009.
[7] B. L. Allen, P. D. Kichambare, and A. Star. Carbon nanotube field-effect-transistor-based biosensors. Adv. Mater. 19, 1439-1451, 2007.
[8] S. G. Khan, S. K. Katiyar, R. Agarwal and H. Mukhtar, Enhancement of Antioxidant and Phase II Enzymes by Oral Feeding of Green Tea Polyphenols in Drinking Water to SKH-1 Hairless Mice: Possible Role in Cancer Chemoprevention. Cancer Res. 52, 4050-4052, 1992.
[9] Weisburger, J. H. in Handbook of Anitoxidants; Cardenas, E., Packer L., Eds.; Marcel Dekker Inc.: New York, 469-486, 1996.
[10] H. Sies, Oxidative Stress: Oxidants and Antioxidants, Exp. Physiol. 82, 291-295, 1997.
[11] G. Nakamura, K. Narimatsu, Y. Niidome and N. Nakashima, Green Tea Solution Individually Solubilizes Single-walled Carbon Nanotubes. Chem. Lett. 9, 1140-1141, 2007.
[12] Y. Chen, Y. D. Lee, H. Vedala, B. L. Allen, and A. Star. Exploring the chemical sensitivity of a carbon nanotube/green tea composite. ACS Nano, 4, 6854–6862, 2010.
[13] S. Rosenblatt, Y. Yaish, J. Park, J. Gore, V. Sazonova and P. L. McEuen, High Performance Electrolyte Gated Carbon Nanotube Transistors, Nano Lett. 2, 869-872, 2002.
[14] K. Kondo, M. Kurihara, N. Miyata, T. Suzuki and M. Toyoda, Mechanistic Studies of Catechins as Antioxidants against Radical Oxidation. Arch. Biochem. Biophys, 362, 79-86, 1999.
[15] Z. B. Zhang, X. J. Liu, E. E. Campbell and S. L. Zhang, Alternating current dielectrophoresis of carbon nanotubes, J. Appl. Phys. 98, 056103, 2005.