Angewandte
International Edition Chemie

Nanosensors

DOI: 10.1002/anie.201203387

Selecting Fruits with Carbon Nanotube Sensors**

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carbon nanotubes · gas detection ·
molecular recognition · sensors

The development of chemical sensors has long been motivated by the need for portable, low-cost, and real-time detection methods that can be applied where traditional laboratory-based instrumental analysis techniques are not practical.[1] The increased public awareness of the health implications of chemical exposure and more strict government regulations necessitate more frequent analysis of trace amounts of chemicals in both working and living environments. Additionally, the development of modern healthcare and clinical practice has reached the point where many patients desire portable analytical tools for self-diagnosis and self-assessment. Overall, the revolutionary development of sensing technologies could dramatically impact various branches of industry and change the way people practice medicine.

Whereas the basic principles of chemical sensors were established in the last century,[2] the past decade has witnessed additional progress in sensors as a result of the emergence of nanotechnology. Among the different types of nanomaterials that have been explored for this application, carbon nanotubes (CNTs) and particularly single-walled carbon nanotubes (SWNTs) represent an ideal platform for chemical sensing.[3] Their lattice of conjugated sp^2-hybridized carbon atoms enables highly efficient electron transport (near ballistic) along the axis of SWNTs, and as they are composed entirely of surface atoms, their electrical conductivity is highly dependent on the surrounding environment. The high length-to-diameter aspect ratio of these nanotubes creates an ideal sensing architecture that effectively transduces any changes in the chemical environment into electrical signals. The ultrasensitivity of SWNT-based devices, coupled together with their low power consumption, opens up several promising and exciting areas of applications for SWNT sensors.

Numerous studies have been conducted on SWNT-based sensors mostly to improve their sensitivity and selectivity to a wide range of specific chemical analytes.[3–5] By far, chemical modification of SWNTs with different functional groups suitable for molecular recognition was generally employed to achieve this task, including decoration with metal nanostructures[4a] and different sidewall-functionalization schemes using small organic functional groups[4b,c] and macromolecules.[4d–i] Although ultrahigh sensitivities to a large number of analytes have been reported,[3] chemical selectivity has been demonstrated in only rare cases where specific affinities such as Au–S interactions were employed.[4a,5] The fundamental challenge behind the selectivity problem of SWNT-based sensors lies in the limited toolbox of molecular recognition interactions to detect specific analytes, especially molecules that are nonpolar and chemically inert, and have weak adsorption energies.

In an article in *Angewandte Chemie*, Timothy Swager and co-workers[6] describe the clever design of a novel ethylene sensor, which included the noncovalent functionalization of SWNT network with a copper(I) complex (Figure 1a). Ethylene is the smallest plant hormone that initiates the ripening of fruit and influences other growth processes,[7a] and it is also a typical example of an analyte with low chemical activity and molecular polarity. For this reason, the development of a SWNT-based ethylene sensor has not been successful despite the interest of the horticultural industry in monitoring the concentration of ethylene to prevent overripening.

Swager and co-workers now describe how to achieve this aim by learning from nature. It has been previously established that the ethylene hormone regulates the ripening process through its strong binding to a receptor ETR1 (from *Arabidopsis*), and Cu^I was identified as a critical cofactor for the receptor proteins.[7b] Inspired by such efficient Cu^I–ethylene recognition in nature, the researchers synthesized the Cu^I complex **1** with a fluorinated tris(pyrazolyl) borate ligand (Figure 1a). Complex **1** selectively binds ethylene molecules with high affinity and forms the more stable Cu^I–ethylene complex **2**. This Cu^I complex and its coordination chemistry with ethylene was previously studied by the same group, and this work led to the successful development of a fluorescence sensor capable of detecting ethylene gas at concentrations of 1000 ppm.[8] To achieve the higher ethylene sensitivity required for the specific application of monitoring fruit ripening (1 ppm level), SWNTs were employed. The Cu^I complex **1** was mixed with SWNTs using ultrasonication, and the resulting Cu^I–SWNT complexes were incorporated into a sensor device by drop-casting the suspension onto a substrate with prefabricated gold electrodes (Figure 1a). Upon exposure to ethylene gas, the strong binding between **1** and

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[**] We acknowledge the National Energy Technology Laboratory (NETL) for financial support (under URS contract DE-FE0004000).

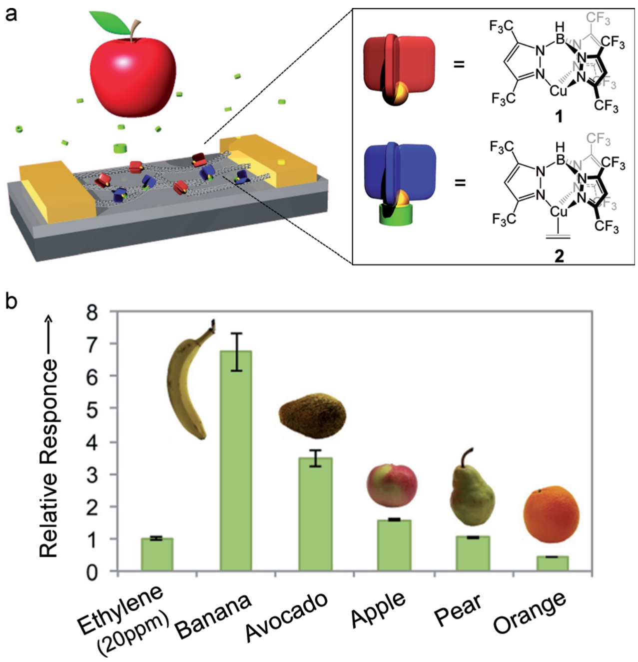

Figure 1. a) Schematic description of an ethylene sensor fabricated from a mixture of single-walled carbon nanotubes (SWNTs) and copper complex **1**. Upon exposure to ethylene gas, **1** binds to an ethylene molecule and forms the Cu–ethylene complex **2**, which leads to a change in the resistance of the SWNT network. b) Relative electrical response of **1**–SWNT devices to ethylene gas produced by 100 g of different fruits.[6]

ethylene molecules interrupts the interactions between **1** and SWNTs that originally existed in the network and therefore affects the conductivity of the SWNTs. Ultrahigh ethylene sensitivity was achieved using this sensor platform, and the detection of ethylene gas at concentrations lower than 1 ppm (0.5 ppm) was demonstrated.

The sub-ppm detection limit of the Cu^{I}–SWNTs sensor makes it possible to monitor the ethylene emission from fruits and follow their ripening process. With the sensor device fabricated in the Swager lab, ethylene emissions from a variety of common fruits (e.g. banana, apple, orange) were tested (Figure 1b). Moreover, the release of ethylene gas from stored fruit samples was monitored over several weeks, and the researchers were able to determine when the fruits had reached ripeness simply by finding the peak of the ethylene emission.

By developing this novel ethylene-recognition strategy, the researchers have effectively addressed two major challenges facing SWNT sensors: 1) the limited sensitivity of SWNTs towards nonpolar and chemically inert chemicals; and more importantly, 2) selective detection of the specific analytes in complex and dynamic chemical environments. Addressing these challenges has become critical for many other real-world sensor applications including the detection of explosive chemicals in public areas[4e] and disease markers in exhaled breath.[4c,d,5a] Additionally, the employment of nature-inspired molecular recognition strategies should serve as a motivation for the future development of SWNT-based sensors. Once the challenges have been met and the toolbox of molecular recognition strategies has been extended, portable and low-cost SWNT-based chemiresistive sensors may achieve significant commercial success through applications in industry, agriculture, and medicine. Moreover, this sensor technology offers an exciting opportunity for the development of chemical sensing arrays,[4a,9] in which multiple sensors based on the same SWNT platform but with distinct molecular recognition functionalities can be employed to detect different analytes in complex and dynamic environments. The ultimate objective would be an artificial olfactory system (also referred as an "electronic nose") that not only mimics the biological olfactory system but also goes beyond its limits.

Received: May 2, 2012
Published online: June 18, 2012

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