Picking Flowers with Carbon Nanotube Sensors

Ethylene is responsible for spoiling a significant portion of the 1.3 billion tons of agriculture products every year, according to the UN Food and Agriculture Organization. Ethylene is a gaseous plant hormone that triggers the ripening and blooming of fruits and flowers. Even a single bad apple that excessively produces ethylene can spoil an entire basket of apples during transportation and storage. However, this type of spoilage can be prevented if the exposure to ethylene is limited by selectively removing fruits and vegetables that excessively produce ethylene or by adding a thin protective coating around them. Imagine all the food waste that can be prevented and healthier food options that can be provided to the general public through cheaper food prices! In this work, Swager and co-workers fabricated an ethylene sensor by combining the semiconducting carbon nanotube (sc-SWCNT) as a transducer and a Pd(II) complex that selectively oxidizes alkenes over other volatile organic compounds. The ethylene sensor was shown to be able to monitor the ethylene production of red carnations and purple lisianthus flowers in real time.\(^1\)

A good chemical sensor has several important metrics including sensitivity, selectivity, limit of detection, and recoverability. Swager and co-workers were able to fabricate an ethylene sensor that scored high on all these attributes. The sensitivity is defined as the ratio between the output signal and the concentration of the analyte being measured. The electrical conductivity of semiconducting single-walled carbon nanotubes is very sensitive to charge changes in their environment because nanotubes are made up of all surface carbon atoms. When the nanotubes are incorporated into a two-terminal resistor, the changes in the charges around the nanotubes or their interface with metal can be measured as

Figure 1. (a) When ethylene is converted to acetaldehyde, the Pd(II) is reduced to Pd(0). The electron withdrawing effect of Pd(II) on the carbon nanotube is neutralized, and the measured current through the nanotube is decreased. (b) (left) The sensor response is measured as the negative of the relative change in conductance, which is proportional to current, increases as ethylene is introduced to the sensor at the 1 min mark. Once the sensor is purged with air at the 2 min mark, the Pd(0) is oxidized back to Pd(II). (right) The response of the sensor to ethylene is directly proportional to the concentration of ethylene, enabling a linear calibration of the ethylene sensor. Sensor data is reproduced with permission from ref 1. Copyright 2020 American Chemical Society.

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conductance or resistance. This property of nanotubes gives the nanotube-based sensors high sensitivity and exceptional lower limit of detection, which can be as low as a single enzyme molecule. However, without any specific receptor, the nanotube sensors are not selective toward any specific compound and sensitive to all charge changes happening on the nanotube surface. They are especially insensitive to a nonpolar molecule like ethylene.

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To detect ethylene, Swager and co-workers used a relatively novel strategy of combining an organometallic catalyst with SWCNT transducers. This combined strategy is currently at the beginning phase of exploration. Specifically, PdCl₂(PhCN)₂ and a nitrite cocatalyst were used to catalyze the Wacker oxidation which converts an alkene to an aldehyde or a ketone. During the reaction, Pd(II) cycles to Pd(0) that has an electron doping effect on the nanotubes, resulting in a large sensor response to alkenes (Figure 1). A previous design of a nanotube-based ethylene sensor used Cu(I) complexes. When ethylene molecules are coordinated to the charged Cu(I) centers, the doping effect of Cu(I) on the nanotubes is partially decreased. Further effective strategy by Swager and co-workers involved changing the oxidation state of the Pd center of the complex. As a result, sensitivity and calculated limit of detection were improved by a whole order of magnitude.

An additional benefit to using a reaction specific catalyst is the improved selectivity. The Pd(II) complex used in this work has high preference for oxidizing alkenes. Compared to other volatile organic compounds such as acetone and tetrahydrofuran, alkenes produced an up to 2 orders of magnitude greater sensing response. Selectivity over acetonitrile was still an impressive 1 order of magnitude. The last metric to consider is recoverability, which refers to how quickly and to what level the sensor signal recovers once the analyte is removed. The catalytic reaction required gaseous oxygen, which is readily available in the atmospheric air.

Using transition metal catalysts to increase the sensitivity and selectivity toward a target analyte has been demonstrated previously for detecting hydrogen by decorating carbon nanotubes with palladium nanoparticles. This continued trend of harnessing known catalytic reactions by using organometallic compounds is an exciting strategy to broaden the selective detection of analytes. It would be interesting to investigate how this organometallic catalysis reaction of ethylene could be transduced to other carbon nanotube sensors. Beyond chemiresistors, semiconducting SWCNTs can also be configured into three terminal field-effect transistors (FETs). FET devices can provide rich information about the sensor mechanism and have found many applications in chemical sensing. Another way to measure the changes in the electronic properties of semiconducting carbon nanotubes is by probing their band gap fluorescence. The (6,5) SWCNT used in this work has a well-defined emission peak in near-infrared region at 975 nm when excited with 567 nm visible light. This emission wavelength is highly sensitive to any charge perturbation in the nanotube’s local environment and shifts in both wavelength and intensity when the charge environment changes. This property also enables nanotubes to be used as an optical sensor.

As the carbon nanotube sensing technology matures, it is exciting to see new sensors showing improved selectivity and sensitivity using novel ideas and showing viability in real-world applications. The real-time monitoring of ethylene production in flowers shows the potential application of nanotube sensors. As catalytic chemical reactions continue to be combined with nanotubes as selective sensors, one can imagine an array of carbon nanotube sensors with different organometallic catalysts capable of detecting different classes of analytes. Another exciting application of carbon nanotube sensors, as demonstrated by Swager and co-workers, is the electrical monitoring of organometallic catalysts conjugated to the carbon nanotube walls. They effectively demonstrated how carbon nanotube sensors can become a unique tool in organometallic chemistry alongside traditional analytical instruments, such as nuclear magnetic resonance, Fourier-transform infrared spectroscopy, and mass spectrometry.

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Author Information
Corresponding Author
Alexander Star — Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States; orcid.org/0000-0001-7863-5987; Email: astar@pitt.edu

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