Trace Ethylene Sensing via Wacker Oxidation

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Experimental

General

(6,5) single-walled carbon nanotubes (SWCNTs) [lot #: MKBZ1159V; (6,5) chirality, ≥ 93% carbon as SWCNT; 0.7 - 0.9 nm diameter by fluorescence], PdCl$_2$(PhCN)$_2$, CuCl$_2$, and $^4$Bu$_4$N(NO$_2$)$_4$ were purchased from Sigma-Aldrich and used as received. All other palladium sources were purchased from Strem Co. and used as received. (7,6) SWCNTs [lot #: MKCJ6188; (7,6) chirality, ≥ 90% carbon basis; 0.83 nm average diameter], double-walled carbon nanotubes (lot #: MKBH3079V), few-walled carbon nanotubes (lot #: MKCD5241), and multi-walled carbon nanotubes (lot #: MKBB2306) were purchased from Sigma-Aldrich and used as received. Ultra-purified (UPT) SWCNTs (lot #: UPT-1210-133) were purchased from Nano-C and used as received. RN120 SWCNTs (batch # RNB738-120) and Pure Wave Graphene (batch # GRN32-075) were purchased from Nanointegris and used as received. For the ZnO nanofibers, poly(vinylpyrrolidone) (PVP, $M_w = 1.3$ MDa), tetraethyl orthosilicate (TEOS), zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) and poly(styrene sulfonate) (PSS, $M_w = 75,000$ g·mol$^{-1}$) solution 30% w/v in H$_2$O were purchased from Sigma-Aldrich. Conc. HNO$_3$ and EtOH and were purchased from Synth, Brazil. These reagents were analytical grade and used without further purification. Purple lisianthus flowers were purchased freshly cut from Kendall Flower Shop (Boston, MA, USA). Red carnations were purchased from GlobalRose via Amazon.com, Inc. (ASIN: B00M8TP04M). Nutrient packages (FloraLife) were provided with the carnations and used as received. Gas chromatography-mass spectrometry (GC-MS) was performed on a nominal mass Agilent 5977B mass spectrometer detector attached to a 7890B gas chromatograph using a 30 m, 0.25 mm, 0.25 μm J&W HP-5ms Ultra Inert column with autosampler. Samples were ionized using electron impact with measured m/z from 10 to 300 and a temperature gradient from 45 to...
300 °C with a ramp rate of 20 °C/min. Data was acquired using ChemStation acquisition software, while data was analyzed using ChemStation/MassHunter data analysis software with access to the National Institute of Standards and Technology (NIST) mass spectra library. NMR was performed on a Bruker Avance III DRX 400 MHz instrument and shift-referenced to the residual solvent resonance. A gas cylinder containing 1% ethylene in nitrogen was purchased from Airgas (Airgas, Dorchester, MA) and equipped with a gas flow regulator to control the output pressure to ~15 psi. Mass flow controllers (MFCs) were purchased from Alicat Scientific, with carrier gas flow rates (air or nitrogen) controlled using an MC-10SLPM-D/5M and ethylene flow rates controlled using an MC-10SCCM-D/5M. Flow rates were remotely controlled by connecting the MFCs to the sensing laptop via a 6’ USB-MD8-232 double-ended 8-pin mini-DIN to USB serial cable (Alicat Scientific) and using Flow Vision SC software (Alicat Scientific; available free of charge online) to change flow rates using a script. Resistance was measured using an Agilent Keysight 34970A potentiostat equipped with a 34901A 20-channel multiplexer (2/4-wire) module. The potentiostat was connected to the sensing laptop using an Agilent 82357B GPIB-USB Interface High-Speed USB 2.0 serial cable and controlled using BenchLink Data Logger 3 (available free of charge online). The scan rate was set to 1 scan/second. Raman spectra were collected using a Horiba Jobin-Yvon LabRam (Model HR 800) Raman confocal microscope with a 633 nm laser (1.4 μm spot size). Laser intensity was set to 10% for the 532 and 633 nm excitation wavelength. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-Alpha+ X-ray photoelectron spectrometer. Thermogravimetric analysis (TGA) was performed on a TA Discovery TGA system. Experiments were carried out under a nitrogen atmosphere with a gas flow rate of 25 mL/min. Samples were heated at a rate of 10 °C/min to 800 °C.
GC-MS Solvent Screening Experiment

A glass vial equipped with a magnetic stir bar was charged with [PdCl$_2$(PhCN)$_2$] (6.8 mg, 17.6 µmol), CuCl$_2$·2H$_2$O (3 mg, 17.6 µmol), $^6$Bu$_4$N[NO$_2$] (2.5 mg, 8.8 µmol), and solvent [benzyl alcohol, 1-decanol, ethylene glycol, 2-phenyl-2-propanol, tetrahydromyrcenol, toluene, benzyl cyanide, or acetophenone] (860 µL). 1-Decene (1.2 mL) was mixed with the internal standard anisole (900 µL), and then 140 µL of this solution was added to each reaction mixture. The reaction mixtures were stirred for 16 h at RT and then filtered through a silica plug (~1 cm in a glass pipette). The reaction mixtures were diluted to an analyte concentration of 1 ppm in HPLC-grade CH$_2$Cl$_2$ and subjected to GC-MS analysis (see Table S1). Analytical standards of anisole, 1-decene, 2-decanone, and decanal were injected separately to confirm the retention times (4.330, 4.773, 5.740, and 5.796 min, respectively) and mass spectra. All mass spectra were cross-referenced with the NIST mass spectrum library.

$^{1}H$ NMR Ethylene Oxidation Experiment

A J. Young NMR tube was charged with [PdCl$_2$(PhCN)$_2$] (32.2 mg, 84 µmol), $^6$Bu$_4$N[NO$_2$] (18.2 mg, 63 µmol), benzyl alcohol (600 µL), and MeOH-d4 (100 µL). The NMR tube was put under vacuum, backfilled with ethylene gas, and immediately sealed. The resulting reaction mixture was analyzed using $^{1}H$ NMR. For comparison, the same reaction mixture containing PdCl$_2$(PhCN)$_2$ and $^6$Bu$_4$N[NO$_2$] was prepared and treated with a drop of acetaldehyde from the tip of a glass pipette. The resulting mixture was also analyzed using $^{1}H$ NMR. $^{1}H$ NMR data are shown in Figure S4 and COSY NMR data are shown in Figure S5.
Discussion of $^1$H NMR in Ethylene Oxidation Experiment

We observed the appearance of two doublets at 1.25 and 1.34 ppm in the reaction mixture upon ethylene exposure (Figure S4). A 2D COSY NMR experiment revealed that these doublets are adjacent to proton signals at 4.46 and 4.70 ppm, respectively (Figure S5). These signals arise from acetics of acetaldehyde, which are formed from the condensation of acetaldehyde with the alcoholic solvents. The $^1$H and COSY NMR spectra are identical to a reaction mixture sample spiked with commercially purchased acetaldehyde, confirming that acetaldehyde was formed under the sensing conditions we used. We did not observe free acetaldehyde under these conditions.

Device Preparation

Glass slides (VWR microscope slides) were bath sonicated in acetone for 15 min and then dried with a stream of nitrogen. Using an aluminum mask, chromium (15 nm) followed by gold (50 nm) was deposited using a Thermal Evaporator (Angstrom Engineering), leaving a 1 mm gap between gold electrodes. Each glass slide had three devices, and each device had four channels. The devices were separated by scoring the glass with a diamond-tipped pen and then pulling the glass pieces apart. For pristine (6,5) SWCNTs: A stock solution of (6,5) SWCNTs (5 mg) was prepared in o-dichlorobenzene (DCB) (20 mL) by bath sonication at RT for 1 h, and then the stock solution was diluted 5-fold with fresh DCB and bath sonicated for another 30 min. 1 µL of the diluted (6,5) SWCNT dispersion was drop-casted in between the gold electrodes and dried at RT under house vacuum in a desiccator or vacuum oven. This drop-casting procedure was repeated until the resistance measured 1 – 3 kΩ using a handheld multimeter (Fluke 114 True RMS Multimeter).
**Ethylene Sensing Measurements**

For a given reaction condition, 1 µL of the reaction mixture was added on top of the drop-casted SWCNTs and the device was enclosed in a homemade Teflon gas flow chamber. The carrier gas (air) was held constant at 1 L/min (except for sensitivity studies, where the flow rate was held constant at 2 L/min to obtain lower concentrations of ethylene), while the ethylene MFC was adjusted accordingly to control the concentration of ethylene (0.5 – 10 mL/min). The resistance of the device was measured over time (1 scan/sec), with typical parameters including 10 min equilibration time (for the baseline resistance to stabilize) followed by 1 min exposure to ethylene in air and then 5 min of recovery (air only). All presented data are given as the numeral average ($N \geq 6$) accompanied by the standard deviation.

**Theoretical Limit of Detection (LOD) Calculation**

The limit of detection was calculated following literature procedures.$^1$ We first calculated the root-mean-square noise (rms) deviation in conductance of the baseline prior to analyte exposure. We took 60 consecutive data points prior to exposure to ethylene, plotted the data, and fitted to a fifth-order polynomial using Microsoft Excel. We then calculated $V_{x^2}$ using Eq. S1. In this equation, $y_i$ is the measured conductance value and $y$ is the corresponding value from the fifth-order polynomial fit. We then use Eq. S2 to calculate $\text{rms}_{\text{noise}}$ of the sensors, where $N$ is the number of data points used for curve fitting ($N = 60$). In Eq. S3, the slope of the linear regression fit for the sensor response vs concentration plot (shown in Figure 5b) is used to yield the theoretical LOD of the sensors.
\[ V_x^2 = \sum (y_i - \bar{y})^2 \quad \text{Eq. S1} \]
\[ \text{rms}_{\text{noise}} = \sqrt{\frac{V_x^2}{N}} \quad \text{Eq. S2} \]
\[ \text{LOD} = \frac{3(\text{rms}_{\text{noise}})}{\text{slope}} \quad \text{Eq. S3} \]

**Gas Sensing Measurements (Interferents)**

Device setup was identical to above, except that a gas generator (FlexStream, Kin-Tek) is used to produce gas vapours from liquid sources. A trace amount of analyte is emitted from a permeation tube diluted in air, which is further diluted with more air to adjust the concentration (in ppm) of analyte. Solvents and alkenes were calibrated by placing 2 – 3 mL of the liquid in the oven flow and measuring the mass loss after a known length of time at a constant temperature (usually 40 °C).

**Flower Studies**

**General.** Flowers were stored in a ventilated office at 22 °C (~23% relative humidity). To measure the response to flower volatiles, a homemade enclosure was prepared and is depicted in Figure S16. A large Ziploc bag was cut in the bottom corners of the bag, such that the holes were smaller in diameter than 1 mL syringes. 1 mL syringes with the plunger and handle removed were placed in the incisions and then taped at the incision. Tubing was placed over the syringe barrel/tape and hose clamps were used to keep the apparatus together. Prior to exposure to flower volatiles, a blank injection with the empty, inflated Ziploc bag was tested to ensure no baseline change due to extraneous factors.

**Measurement.** Prior to each measurement, the flowers were weighed. If the flowers were treated with water, a paper towel was used to dry the immersed portion of the flower prior to mass measurement. Devices \((N \geq 6)\) were prepared using 4-pyridyl functionalized (6,5) SWCNTs and 1
µL per channel of a benzyl alcohol solution containing 120 mM [PdCl₂(PhCN)₂] and 90 mM "Bu₄N[NO₂]. Devices were equilibrated under air at a flow rate of 200 mL/min and then exposed to flower volatiles for 1 min in air (200 mL/min). The device response was normalized to 100 g of flowers relative to 500 ppb of ethylene in air. The response to flower volatiles was measured every several hours.

**Red Carnations.** For each condition, 25 – 50 stems were cut until the flower was at a height of 10 – 12 cm. The mass of the flower populations ranged from ~175 – 450 g. The carnations were treated with (i) nothing, (ii) water, or (iii) the nutrient packet dissolved in water. Plant nutrition packets (FloraLife) that came with the purchased flowers were dissolved in tap water (1 packet/L) and then distributed into plastic water cooler cups (~75 mL per cup). For condition (ii), ~75 mL of tap water-only was also used per cup. Each cup held at most three stems.

**Purple Lisianthus.** Stems were cut to a height of 10 – 15 cm. Each stem had 2 – 10 flower heads. A total of 52 stems with 256 flower heads (27 already opened or partially opened) were prepared with an initial mass of 293.2 g. Plant nutrition packets (FloraLife) were dissolved in tap water (1 packet/L) and then distributed into plastic water cooler cups (~75 mL per cup). Each cup held at most four stems.

**Solvent Screening for Sensing Devices**

A glass vial was charged with 120 mM [PdCl₂(PhCN)₂], 120 mM CuCl₂, and 60 mM "Bu₄N[NO₂] in solvent [benzyl alcohol, 1-decanol, ethylene glycol, 2-phenyl-2-propanol, PEG₄₀₀, tetrahydromyrcenol, or toluene] (300 µL). The reaction mixture was aliquoted onto the (6,5) SWCNTs (1 µL per device) and then resistance vs time was recorded.
**Stoichiometry Optimization (With CuCl$_2$) for Devices**

The initial conditions for the stoichiometry optimization experiment were 120 mM [PdCl$_2$(PhCN)$_2$], 120 mM CuCl$_2$, and 60 mM $^\text{Bu}_4$N[NO$_2$] in benzyl alcohol. To test the effect of reagent concentration on sensing response, two of the ingredients were held at the initial condition concentrations, while the concentration of the third ingredient was varied from 0 – 240 mM. To minimize weighing error, stock solutions of each reagent were prepared in benzyl alcohol and mixed in various ratios to produce the test condition (see Table S2). For the CuCl$_2$ stock solution, gentle heating with a heat gun to homogenize the solution was required prior to aliquoting it. After combining the ingredients, each reaction mixture was bath sonicated for 5 min prior to testing the sensing response.

**Conductive Nano-Carbon and Palladium Source Screening**

**Conductive Nano-Carbon Screening.** The reaction mixture used in this experiment contained 120 mM [PdCl$_2$(PhCN)$_2$] and 90 mM $^\text{Bu}_4$N[NO$_2$] in benzyl alcohol. 1 µL of the carbon electrode material (dispersed in DCB) was drop-casted in between the gold electrodes and dried at RT under house vacuum. This drop-casting procedure was repeated until the resistance measured 1 – 3 kΩ using a handheld multimeter (Fluke 114 True RMS Multimeter). The reaction mixture was aliquoted onto the carbon electrode material (1 µL per device) and then resistance vs time was recorded.

**Palladium Source Screening.** The reaction mixture used in this experiment contained 120 mM palladium source and 90 mM $^\text{Bu}_4$N[NO$_2$] in benzyl alcohol. The mixture was sonicated for several min until homogenous and then used directly to prepare devices containing pristine (6,5) SWCNTs. Resistance vs time was recorded.
**Raman G-Band Experiment**

Pristine or 4-pyridyl functionalized (6,5) SWCNTs were drop-casted and dried in between gold electrodes until black residue (i.e., the carbon nanotubes) was visible by eye. These SWCNT thin films were treated with (i) nothing, (ii) 1 µL of [PdCl$_2$(PhCN)$_2$/CuCl$_2$/nBu$_4$N[NO$_2$] (120 mM/120 mM/60 mM), or (iii) 1 µL of [PdCl$_2$(PhCN)$_2$/nBu$_4$N[NO$_2$] (120 mM/90 mM). Samples (including the SWCNT-only samples) were exposed to 1-heptene in nitrogen at a flow rate of 3 L/min (using the gas generator) until solvent was evaporated. Raman analysis was performed using a 532 nm laser (10% intensity, 5 accumulations, and 3 sec integration time). For each sample, three different spots were examined and then the spectra were averaged.

**SiO$_2$/ZnO Nanofiber Fabrication**

Zn(NO$_3$)$_2$·6H$_2$O (4.8% w/w) and PVP (9.5% w/w) were dissolved in DMF and stirred for 6 h at RT. Separately, TEOS (12.5% w/w) was dissolved in HNO$_3$/EtOH (100:1 TEOS:HNO$_3$ molar ratio) and stirred for 2 h at RT. The TEOS solution was added to the Zn/PVP solution (Si$^{2+}$/Zn$^{2+}$ molar ratio of 3.5:1) and stirred for 6 h RT. Electrospinning was performed on this solution by placing in a glass syringe and then applying voltage (12 kV) with a flow rate of 0.3 mL·h$^{-1}$ at a working distance of 6 cm. Nanofiber fabrication was followed by annealing at 60 °C for 6 h and calcination at 500 °C for 4 h. Field-emission gun scanning electron microscopy (FEG-SEM) and high-resolution transmission electron microscopy (HR-TEM) were performed with a JEOL-JSM 6701F and FEI Tecnai G2F20 microscope, respectively. The SiO$_2$/ZnO nanofibers were suspended in PSS aqueous solution (50 µg·mL$^{-1}$ of PSS) for a final concentration of 10 mg·mL$^{-1}$ of nanofiber and then 1 µL of the suspension was drop-casted onto the gold electrodes for gas sensing.
Synthesis of Covalently Functionalized (6,5) SWCNTs

4-pyridyl functionalized SWCNTs were prepared according to literature procedures, and the same procedure was adapted for the preparation of phenyl functionalized SWCNTs. In a glovebox, a 40 mL glass vial was charged with a Teflon-coated stir bar, (6,5)-SWCNTs (5 mg, 0.42 mmol C), and THF (20 mL). Appropriate amount of freshly prepared solution of sodium naphthalide (0.021, 0.042, or 0.083 mmol) was transferred to the SWCNT suspension. The vial was capped, sealed tightly with electrical tape, removed from the glovebox, and sonicated in an ultrasonic bath for 30 min. The greenish colour disappeared upon sonication, indicating transfer of electrons from the naphthalide to the SWCNTs. After sonication, the vial was transferred to the glovebox and a solution of phenyl(2,4,6-triisopropylphenyl)iodonium triflate (0.021, 0.042 or 0.083 mmol) in THF (2 mL) was added. The reaction was stirred at RT for 3 h. The reaction was removed from the glovebox and filtered through a 0.2 µm nylon membrane. The collected SWCNT product was re-dispersed in 10:1 EtOH:H₂O (100 mL), sonicated for 30 min, and filtered through a 0.2 µm nylon membrane. This washing step was performed a total of four times. The resulting phenyl-functionalized (6,5) SWCNT product was dried in a vacuum oven at 60 °C for 24 h.

Covalently Functionalized (6,5) SWCNT Screening

The reaction mixture used in this experiment contained 120 mM [PdCl₂(PhCN)₂] and 90 mM “Bu₄N[NO₂] in benzyl alcohol. 1 µL of the covalently functionalized (6,5) SWCNTs in EtOH was drop-casted in between the gold electrodes and dried at RT under house vacuum. This drop-casting procedure was repeated until the resistance measured 0.1 – 0.3 MΩ using a handheld multimeter (Fluke 114 True RMS Multimeter). The reaction mixture was aliquoted onto the SWCNTs (1 µL per device) and then resistance vs time was recorded.
Table S1. Reaction solvent screening via GC-MS for the conversion of 1-decene using 4 mol % [PdCl$_2$(PhCN)$_2$], 4 mol % CuCl$_2$·2H$_2$O, and 2 mol % n$^\text{Bu}_4$N(NO$_2$) under ambient conditions with anisole as an internal standard.

| Solvent           | 4-Decene$^a$ | 2-Decanone$^{a,b}$ |
|-------------------|--------------|--------------------|
| Benzyl Alcohol    | 55%          | 21%                |
| 1-decanol         | 41%          | 37%                |
| Ethylene glycol   | 0%           | 0%                 |
| 2-phenyl-2-propanol | 0%      | 0%                 |
| Tetrahydromyrcenol | 0%         | 28%                |
| Toluene           | 0%           | 0%                 |
| Benzyl Cyanide    | 0%           | 0%                 |
| Acetophenone      | 0%           | 0%                 |

$^a$Products were identified by comparing the mass spectra obtained to the NIST mass spectra library. Conversion was determined by comparison to an anisole internal standard. No evidence of decanal was observed in any of the reaction mixtures.
Figure S1. (a) Pictorial demonstration of device fabrication. (i) 15 nm of chromium and 50 nm of gold are deposited onto glass using a thermal evaporator, (ii) SWCNTs are drop-casted in between the gold electrode gap, (iii) and then the reaction mixture is deposited on top of the SWCNTs. Photographs of (b) actual gold electrodes on glass before and after deposition of SWCNTs and the reaction mixture, and (c) the device inserted into a blue edge connector on a breadboard. (d) Photographs of the homemade Teflon enclosure inserted onto the edge connector. Cork rings are used to keep the device upright. Tubing for the carrier gas and the electrical wires connecting the breadboard to the potentiostat are omitted for clarity.
Figure S2. Solvent vs sensor response (–ΔG/G₀). (a) Devices containing 120 mM [PdCl₂(PhCN)₂], 120 mM CuCl₂, and 60 mM "Bu₄N[NO₂] in solvent (benzyl alcohol, 1-decanol, ethylene glycol, 2-phenyl-2-propanol, PEG₄₀₀, or tetrahydromyrcenol) were exposed to 50 ppm of ethylene in air for 1 min (N ≥ 3). (b) Plot of –ΔG/G₀ vs oxidation yield (refer to Table S1).

Table S2. Stock solutions of [PdCl₂(PhCN)₂] (480 mM), CuCl₂ (480 mM), and "Bu₄N[NO₂] (240 mM) in benzyl alcohol were mixed in various ratios to produce the test conditions in Figure S3

| Condition                      | [PdCl₂(PhCN)₂] | CuCl₂ | "Bu₄N[NO₂] | Benzyl Alcohol |
|--------------------------------|----------------|-------|------------|---------------|
| Initial Conditions             | 20 µL          | 20 µL | 20 µL      | 20 µL         |
| Pd Optimization (240 mM)       | 40 µL          | 20 µL | 20 µL      | 0 µL          |
| Pd Optimization (60 mM)        | 10 µL          | 20 µL | 20 µL      | 30 µL         |
| Pd Optimization (0 mM)         | 0 µL           | 20 µL | 20 µL      | 40 µL         |
| Cu Optimization (240 mM)       | 20 µL          | 40 µL | 20 µL      | 0 µL          |
| Cu Optimization (60 mM)        | 20 µL          | 10 µL | 20 µL      | 30 µL         |
| Cu Optimization (0 mM)         | 20 µL          | 0 µL  | 20 µL      | 40 µL         |
| Nitrite Optimization (240 mM)  | 20 µL          | 20 µL | 40 µL      | 0 µL          |
| Nitrite Optimization (60 mM)   | 20 µL          | 20 µL | 10 µL      | 30 µL         |
| Nitrite Optimization (0 mM)    | 20 µL          | 20 µL | 0 µL       | 40 µL         |
Figure S3. Optimization of the [PdCl\(_2\)(PhCN)\(_2\)]:CuCl\(_2\):\(^{n}\)Bu\(_4\)N[NO\(_2\)] stoichiometry using benzyl alcohol as solvent. When optimizing a given reagent, the other two ingredients were held at constant concentration. Sensing response upon exposure to 50 ppm of ethylene in air for 1 min with varying concentrations of (a) [PdCl\(_2\)(PhCN)\(_2\)], (b) \(^{n}\)Bu\(_4\)N[NO\(_2\)], and (c) CuCl\(_2\) (N ≥ 3).

Figure S4. Investigation of ethylene oxidation under the sensing conditions with [PdCl\(_2\)(PhCN)\(_2\)], \(^{n}\)Bu\(_4\)N[NO\(_2\)], and benzyl alcohol in the reaction mixture. \(^1\)H NMR spectra of the reaction mixture (RM) prior to ethylene exposure (blue trace), post-exposure to ethylene gas (red trace), and spiked with commercially purchased acetaldehyde (purple trace). The inset shows an expansion in the 1 to 1.6 ppm range. The aldehyde peak at 9.75 ppm corresponds to benzaldehyde already present in the commercially purchased benzyl alcohol from the shelf.
Figure S5. Investigation of ethylene oxidation under sensing conditions with [PdCl$_2$(PhCN)$_2$], "Bu$_4$N[NO$_2$], and benzyl alcohol. 2D COSY NMR spectra of (a) the reaction mixture post-exposure to ethylene gas and (b) the reaction mixture spiked with commercially purchased acetaldehyde.
Figure S6. Optimization of $^{n}$Bu$_4$N[NO$_2$] concentration using benzyl alcohol as the solvent. [PdCl$_2$(PhCN)$_2$] was held constant at 120 mM. Samples were exposed to 50 ppm of ethylene in air for 1 min ($N \geq 8$). (a) Sensing curves and (b) response vs $^{n}$Bu$_4$N[NO$_2$] concentration.

Figure S7. Optimization of the (a) transducer material (using [PdCl$_2$(PhCN)$_2$]) and (b) Pd source using benzyl alcohol as the solvent. 120 mM Pd(II) and 90 mM $^{n}$Bu$_4$N[NO$_2$] were used for each experiment. Devices were exposed to 50 ppm of ethylene in air for 1 min ($N \geq 6$). dppe = ethylenedibis(diphenylphosphine); dppf = 1,1′-bis(diphenylphosphinoo)ferrocene; (NHC)$_2$Pd$_2$Cl$_4$ = dichloro(di-μ-chloro)bis[1,3-bis(2,6-di-i-propylphenyl)imidazol-2-ylidene]dipalladium(II); XPhos Pd G2 = chloro(2-dicyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenyl)2-(2′-amino-1,1′-biphenyl)palladium(II).
**Figure S8.** Characterization of SiO$_2$/ZnO nanofibers. (a) FEG-SEM reveals smooth nanofibers with a mean diameter of 160 ± 60 nm and no observable bead defects. (b) HR-TEM reveals that the nanofibers are composed of crystalline nanoparticles with interplanar distances of 2.45 Å, corresponding to the d-spacing of the (101) plane in hexagonal ZnO.

**Figure S9.** Response upon multiple 1 min exposures to 50 ppm ethylene in air using SiO$_2$/ZnO nanofibers as an n-type semiconductor ($N \geq 6$). The reaction mixture contains 120 mM [PdCl$_2$(PhCN)$_2$] and 90 mM $^+$Bu$_4$N[NO$_2$] in benzyl alcohol.
**Figure S10.** Raman spectra collected at 633 nm of (a) 4-pyridyl and (b) phenyl functionalized (6,5) SWCNTs. Spectra were normalized to the G-band at ~1590 cm$^{-1}$.

**Figure S11.** (a-c) Survey XPS spectra of (6,5) SWCNTs covalently functionalized 4-pyridyl groups.

**Figure S12.** TGA data showing mass loss upon heating under a nitrogen atmosphere of phenyl-functionalized (6,5) SWCNTs.
Figure S13. Investigation of the n-doping effect upon exposure of 4-pyridyl functionalized (6,5) SWCNTs to Pd(0) generated in situ (Pd = [PdCl$_2$(PhCN)$_2$] and nitrite = $^6$Bu$_4$N[NO$_2$]). Raman spectra were collected using 532 nm excitation wavelength with spectra intensity normalized to the G-band.

Figure S14. Sensitivity using pristine (6,5) SWCNTs. In each condition, the reaction mixture contains 120 mM [PdCl$_2$(PhCN)$_2$] and 90 mM $^6$Bu$_4$N[NO$_2$] in benzyl alcohol. Devices were exposed to ethylene in air for 1 min ($N \geq 6$).
**Figure S15.** Sensitivity vs relative humidity (R.H.) normalized to the response at 2% R.H. for comparison of 4-pyridyl functionalized and pristine (6,5) SWCNTs. Devices were exposed to 50 ppm ethylene in air for 1 min ($N \geq 6$).

**Figure S16.** Comprehensive stability study of (a) 4-pyridyl (covalently) functionalized and (b) pristine (6,5) SWCNTs. In each condition, the reaction mixture contains 120 mM [PdCl$_2$(PhCN)$_2$] and 90 mM $n$Bu$_4$N[NO$_2$] in benzyl alcohol. Devices were exposed to 50 ppm ethylene in air for 1 min ($N \geq 6$).
Figure S17. Selectivity using pristine (6,5) SWCNTs. In each condition, the reaction mixture contains 120 mM [PdCl$_2$(PhCN)$_2$] and 90 mM Bu$_4$N[NO$_2$] in benzyl alcohol. Devices were exposed to analyte in air for 1 min ($N \geq 6$). Selectivity (a) in the presence of various interferents and (b) in the presence of various alkenes. In (a), the y-axis for VOCs is expanded by 8X.

Figure S18. Schematic for the sensing experiment setup to analyze flower volatiles. Mass flow controllers (MFCs) are used to control the overall flow rate to 200 mL/min.

Figure S19. Representative photographs of (a) lisianthus flowers and (b) carnations as received.
Figure S20. Representative photographs of the populations for (a) lisianthus flowers and (b) carnations after one week of growth in nutrient water.

References
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