

Protocol for Preparing a Chemiresistive Sensor Based on Functionalized CNTs

Contributed by Shao-Xiong Luo, Maggie He and Timothy M. Swager
Department of Chemistry
Massachusetts Institute of Technology

Background

The Swager group has recently reported a carbon nanotube-based chemiresistive sensor for the detection of carbon monoxide.¹ These methods are general and are being extended for environmental sensors relevant to Superfund research. In this specific sensor (Figure 1), pyridyl-functionalized SWCNT was employed as the matrix and iron porphyrin was used as the selector that could selectively bind carbon monoxide. Activated by an applied gate voltage, our sensor was capable of detecting carbon monoxide at 80 ppm, well within the OSHA limit of 200 ppm during a 5 minute period.

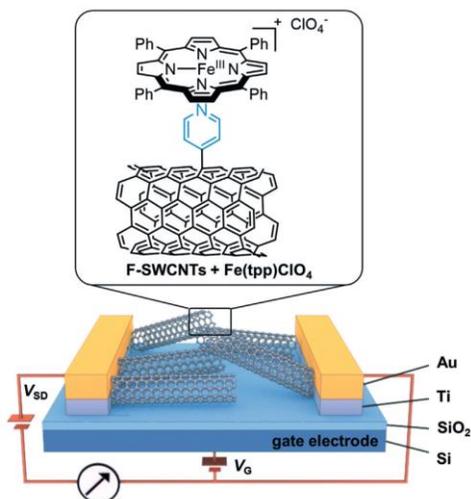


Figure 1. Schematic of a field-effect transistor(FET) substrate with Au source-drain electrodes and Ti adhesion layer deposited on SiO₂ dielectric layer and Si gate electrode. Chemical structures of pyridyl-functionalized single-walled carbon nanotubes(F-SWCNTs) and iron porphyrin(Fe(tp_p)ClO₄), depicting the coordination chemistry of the pyridyl group to the iron center of the porphyrin.

CNT Functionalization

Pyridyl-functionalized SWCNTs were fabricated according to a previous report from Superfund researcher, Dr. Maggie He.² The reaction is illustrated in Figure 2.

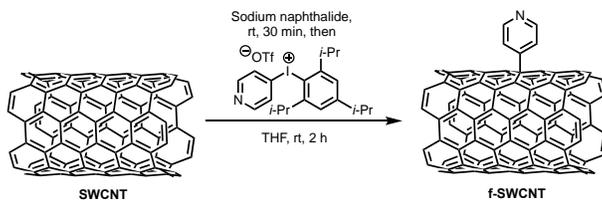


Figure 2. Reaction of pyridyl-iodonium salt with pristine SWCNTs.

Preparation of Sodium Naphthalide Solution

The preparation of sodium naphthalide in tetrahydrofuran (THF) was carried out inside a glovebox under a nitrogen atmosphere. A 40 mL vial was charged with a Pyrex-glass-coated stir bar, naphthalene (80 mg, 0.62 mmol), and THF (20 mL). A piece of freshly cut sodium (~80 mg) was added to the naphthalene solution and then cut into small pieces with a spatula. The naphthalene solution immediately turned green, indicating the formation of sodium naphthalide. The reaction was stirred at room temperature overnight, yielding a deep green solution that contained excess unreacted and insoluble sodium metal.

Synthesis of Pyridyl-Iodonium Salt

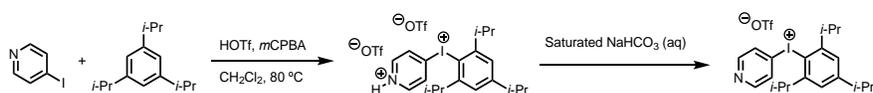


Figure 3. Synthesis of pyridyl-iodonium salt.

Triflic acid (4 equiv) was added slowly to a solution of iodopyridine (1.0 equiv) in CH_2Cl_2 (0.24 M) at 0 °C over 5 min in a seal tube. After 15 min of stirring, *m*-CPBA (1.50 equiv) and 1,3,5-triisopropylbenzene (1.10 equiv) was added sequentially at room temperature. The reaction mixture was heated to 60 °C for 1 h 45 min. After cooling to room temperature, the reaction mixture was directly loaded over a column packed with silica gel in 100% CH_2Cl_2 . Purification by column chromatography (100% CH_2Cl_2 to elute unreacted starting materials and nonpolar impurities then CH_2Cl_2 :MeOH 20:1 to elute the product) afforded a brown solid. The brown solid was dissolved in minimum CH_2Cl_2 and Et_2O was added until a gel was formed. The gel was collected by filtration and dry under vacuum to obtain a white solid as the iodonium bistriflate product. The conversion to iodonium monotriflate product was obtained by extraction with CH_2Cl_2 :saturated aqueous NaHCO_3 3:1 (100 mL/g). The organic layer was dried over MgSO_4 and concentrated under reduced pressure to afford product as a white solid.

Procedure for CNT Functionalization with Pyridyl-Iodonium Salt

Prior to functionalization, CNTs were dried under vacuum at room temperature overnight. In a glovebox, a 40 mL vial was charged with a Pyrex glass coated stir bar, CNTs (10 mg, 0.83 mmol C), and THF (20 mL). A deep green solution of sodium naphthalide (2.7 mL, 0.083 mmol) was transferred to the CNT suspension via a graduated glass pipet. The vial was capped, sealed tightly with electrical tape, removed from the glovebox, and sonicated in an ultrasonic bath for 30 min. The greenish color disappeared upon sonication indicating transfer of electrons from the naphthalide to the CNTs. After sonication, the vial was transferred to the glovebox and a solution of iodonium salt (0.083 mmol) in THF (2 mL) was added. The reaction was stirred at room temperature for 2 h.

Purification of functionalized CNT

The reaction was removed from the glovebox and filtered through a 0.6 μm polypropylene membrane. The collected CNT product was washed by dispersing the material in EtOH:H₂O 10:1 (100 mL), sonicated for 30 min, and filtered through a 0.6 μm polypropylene membrane. This washing step was performed a total of four times. The resulting CNT product was dried in a vacuum oven at 70 °C for 24 h.

Fabrication of CO Sensor

Sensors were prepared on field-effect transistor-based substrates with a bottom gate, bottom contact configuration. Heavily p++ doped silicon wafers were used as the common gate with 300 nm of SiO_2 grown on top acting as the dielectric layer. The source and drain electrodes (10 nm Ti and 100 nm Au) were photolithographically patterned on the SiO_2 surfaces with a channel length and width of $L = 200 \mu\text{m}$ and

W = 3 mm, respectively. The patterned substrates were cleaned by bath sonication in DI water, acetone, IPA, (Brenson 3510 bath sonicator, 5 min) and dried under an N₂ flow.

In a typical device, the sensors were prepared by two-step deposition of F-SWCNTs via drop-casting and infusion of Fe(tp)ClO₄. Functionalized SWCNTs were suspended in *o*-DCB at the concentration of 0.25 mg mL⁻¹ and drop-casted onto the patterned substrates between the source/drain channels using a micropipette. Each substrate contained four identical channels. The solvent was removed in vacuo. The drop-casting was repeated until the resistance across the electrodes reached a resistance of 1-10 kΩ as measured by a multimeter. Subsequently, the substrates with F-SWCNTs were then submerged in a solution of Fe(tp)ClO₄ in CH₂Cl₂ at the concentration of 1 mg mL⁻¹ for 1 min and dried under N₂ flow.

References

1. Savagatrup, S.; Schroeder, V.; He, X.; Lin, S.; He, M.; Yassine, O.; Salama, K. N.; Zhang, X. X.; Swager, T. M. Bio-Inspired Carbon Monoxide Sensors with Voltage-Activated Sensitivity. *Angew. Chem., Int. Ed.* **2017**, *56*, 14066–14070.
2. He, M. G.; Swager, T. M. Covalent Functionalization of Carbon Nanomaterials with Iodonium Salts. *Chem. Mater.* **2016**, *28*, 8542–8549.