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Timothy M. Swager

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14. ABSTRACT
This program was directed at generating functionalized surfaces and assemblies for electronic and sensory function. New functional systems and assembly methods were developed based on carbon nanotubes and mechanical abrasion, respectively. These schemes allow for distributed as well as on site manufacturing.

15. SUBJECT TERMS
Sensors, Surface Chemistry, Transparent Oxides, Nanomaterials

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Timothy Swager
UU	UU	UU	UU		19b. TELEPHONE NUMBER 617-253-4423

Report Title

Final Report: Precision Assembly of Systems on Surfaces (PASS)

ABSTRACT

This program was directed at generating functionalized surfaces and assemblies for electronic and sensory function. New functional systems and assembly methods were developed based on carbon nanotubes and mechanical abrasion, respectively. These schemes allow for distributed as well as on site manufacturing.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
02/05/2015	4.00	Katherine A. Mirica, Joseph J. Walish, Timothy M. Swager, Kelvin M. Frazier. Fully-drawn carbon-based chemical sensors on organic and inorganic surfaces, Lab Chip, (08 2014): 0. doi: 10.1039/C4LC00864B
TOTAL:	**1**	

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received		Paper
TOTAL:		

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Single-walled Carbon Nanotube-Metalloporphyrin Chemiresistive Gas Sensor Arrays for Volatile Organic Compounds

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received		Paper
02/05/2015	5.00	Sophie F. Liu, Lionel C. H. Moh, Timothy M. Swager. Single-?walledCarbonNanotube-?MetalloporphyrinChemiresistiveGasSensorArraysforVolatileOrganicCompoundsds, Chemistry of Materials (01 2015)
09/03/2014	2.00	Kelvin Frazier, Katherine Mirica, Joseph Walish, Timothy Swager. Drawing Sensors on Chips: Deposition of Carbon-Based Materials on Diverse Surfaces by Mechanical Abrasion, Lab on a Chip (07 2014)
TOTAL:	**2**	

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Methods And Devices For Deposition Of Materials On Patterned Substrates

Patents Awarded

Awards

Humboldt Senior Research Award
Council for Chemical Research-Diversity Award
Fellow of the American Chemical Society

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Sophie Liu	0.20	
Kelvin Frazier	0.50	
FTE Equivalent:	**0.70**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Sibo Lin	0.90
Bora Yoon	0.10
FTE Equivalent:	**1.00**
Total Number:	**2**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Timothy M. Swager	0.15	Yes
FTE Equivalent:	**0.15**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Vera Schröder	1.00	Chemistry
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 1.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 1.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 1.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 1.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
Brian Pretti	0.10
FTE Equivalent:	**0.10**
Total Number:	**1**

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

It is likely that the patent filed will be licensed to C2Sense LLC.

PRECISION ASSEMBLY OF SYSTEMS ON SURFACES (PASS)

PI: Timothy M. Swager
Massachusetts Institute of Technology

Final Report: DARPA, Defense Science Office (DSO)
Contract #: W911NF-14-1-0087

Summary:

This program was directed at generating functionalized surfaces and assemblies for electronic and sensory function. Efforts were made to create functionalized carbon nanotube devices with high fidelity as chemical sensors and we selected extended π-electronic structures based upon porphyrins. The modularity of this system with regard to the metal ions incorporated provides facile access to a wide range of sensing behaviors as demonstrated with a sensor array. In terms of creating new fabrication methods, we have demonstrated that complete sensor chips can be produced by a simple mechanic abrasion (effectively drawing) method and that these sensors have performance comparable with devices using metallic gold electrodes. The power of this latter approach is that sensors can be produced on demand with nothing more than a substrate and solid materials that can be deposited by physically drawing the circuit. An additional direction was explored with the approval of DARPA, wherein we explored routes to low temperature processing of forms of transparent oxide conductors. In this effort we targeted fluorinated tin oxide (FTO) and were seeking methods to create composite structures at low temperature (>150° C) for compatibility with plastic with increased ductility. In this latter effort we were less successful and find that we were unable to achieve materials with sufficiently high conductivity at the target temperatures.

Publications:

1. Frazier, K. M., Mirica, K. A.; Walish, J. J.; Swager, T. M. "Drawing Sensors on Chips: Deposition of Carbon-Based Materials on Diverse Surfaces by Mechanical Abrasion" *Lab on a Chip* **2014**, *14*, 4059 – 4066.
2. Liu, S. F.; Moh, L. C. H.; Swager, T. M. "Single-Walled Carbon Nanotube-Metalloporphyrin Chemiresistive Gas Sensor Arrays for Volatile Organic Compounds" Submitted and Under Review

Patent:

1. Swager, T. M., Frazier, K. M., Mirica, K. A.; Walish, J. J. "Methods And Devices For Deposition Of Materials On Patterned Substrates" (8/20/2014) U. S. Provisional Application No.: 62/039787

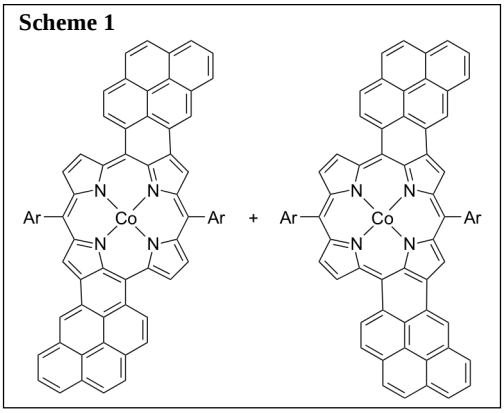
Technical Report:

Functionalization of Carbon Nanotubes: Chemiresistors represent a powerful class of chemical sensors that have the critical attributes that they can be readily integrated into any electrical system, can be miniaturized, are readily multiplexed, and take nearly zero-power to operate. One of the greatest limitations to these sensors is a lack of selectivity, which is the electronic equivalent of noise. Interference from large varying background signals, such as humidity, can compromise the sensor signal to a point wherein there is no useful data. To address this challenge we have focused on new ways to integrate molecular constructs into carbon nanotube compositions that produce enhanced selectivity to certain molecules or classes of molecules. The goal is simply to increase the signal to noise level in chemical sensors. To this end we have been interested in developing new superior ways to functionalize carbon nanotube materials.

Many of our olfactory receptors have transition metal complexes, which explains our acute sensitivity to molecules that bind to metals. With this bio-inspired basis we have been interested to investigate the ability of assemblies of metal complexes with carbon nanotubes to differentiate chemical space. It is assumed that any molecular recognition of reactivity-based selectivity in our sensors will not be perfect and indeed, this is also the case with olfaction. However, by suitably differentiating between different types of reactivities we can generate higher degrees of orthogonality and create robust sensor arrays where others have failed. To realize the full diversity of the first row transition metal sensors we have targeted metal porphyrin complexes. These materials have extended π-electron systems that make them ideal candidates to bind through non-covalent mechanisms to the surfaces of carbon nanotubes.

To promote strong interactions we initially focused on a porphyrin system containing fused pyrene systems that had been recently reported.[1] Although the synthetic procedures were reproducible and we were able to make the regioisomeric Co^{+2} complexes of these molecules (Scheme 1), we found that the tendency to self-associate precluded their ability to form strong complexes with carbon nanotubes. As a result, we found that functionalization of single walled carbon nanotubes (SWCNTs) with these molecules has minimal effects on their response to specific chemicals of interest.

Scheme 1



To properly evaluate the ability to utilize porphyrins to create selectively modified surfaces for chemical sensing we have conducted a study wherein the first row transition metal series of complexes (Figure 1) based on tetraphenyl-porphyrin (tpp) were prepared and used to functionalize the SWCNTs. Previous studies on porphyrins in chemical sensing note that despite their promise for this application, a drawback that limits their usage is that they are relatively unselective.[2] However, earlier studies with sensors fabricated from porphyrin-CNT composites measured chemiresistive responses of only 2-3 metal centers to only 4-5

different analytes. We have now completed a more comprehensive study on the chemiresistive responses. As summarized here we find the responses of metalloporphyrin-SWCNT-based sensors to vapors of various volatile organic compounds (VOCs) were strong and were subjected to statistical analyses that enabled the successful classification of representative VOCs into five different categories (aliphatic hydrocarbons, alcohols, ketones, aromatic hydrocarbons, and amines) with 98% accuracy. With the exception of amines, which are capable of strong charge transfer interactions, the basis of classification appears to correlate with the differences in the solubility properties of the porphyrin compounds in the various VOCs as solvents. This feature suggests that solvent vapors modulate the strength of interactions between the porphyrins and the nanotubes. These results further demonstrate the potential for porphyrin-functionalized SWCNT-based electronic noses for applications in inexpensive, portable chemical sensors for the identification of VOCs.

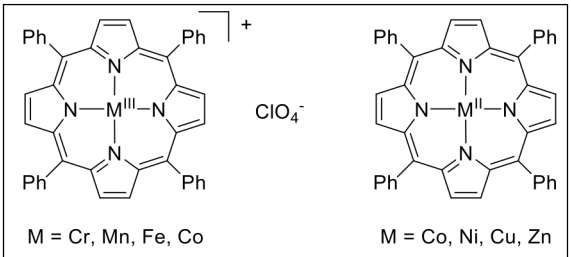


Figure 1. Chemical structures of metalloporphyrin complexes employed in the chemiresistive sensor array. Axial H_2O ligands have been omitted for clarity.

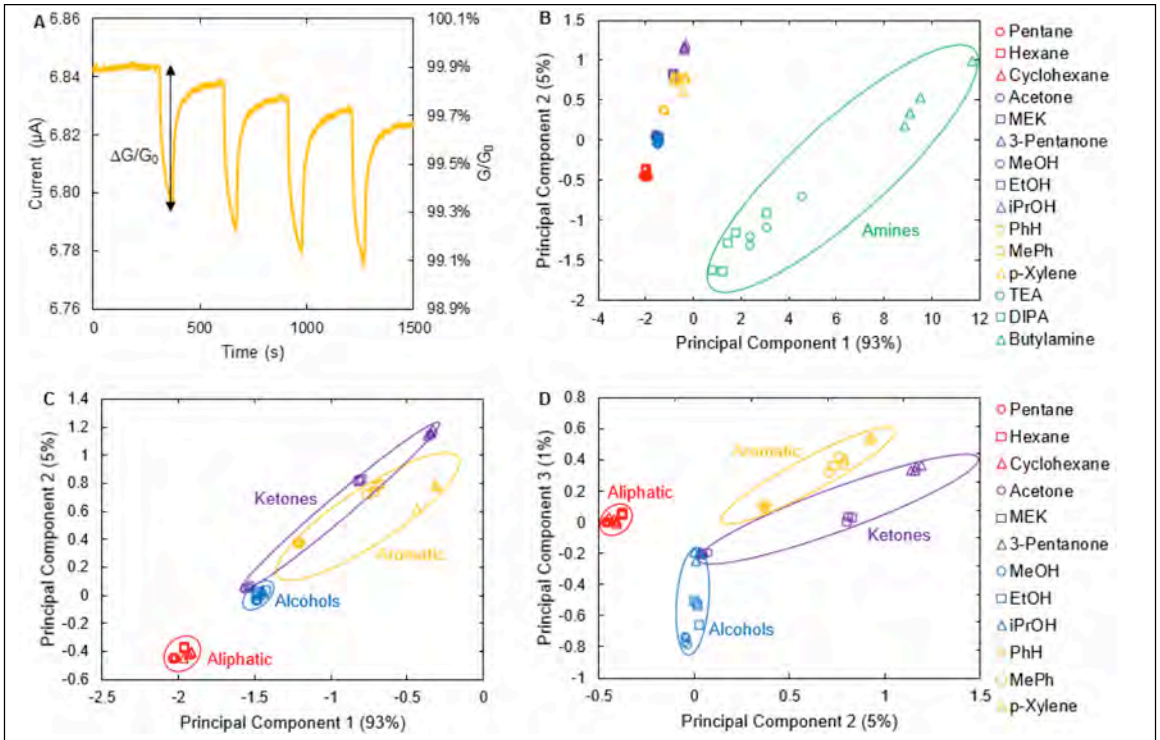


Figure 2. Principal component analysis of chemiresistive sensor array's responses to VOCs. (A) Sample current trace of SWCNT-$[Fe(tpp)(H_2O)_2]ClO_4$ composite with 0.100 V potential applied during four 60 s exposures of 1000 ppm toluene in N_2 gas. (B) PC 2 plotted against PC 1 for an array of 10 different SWCNT-based chemiresistors to 15 VOCs (3-4 trials each). (C) PC 2 plotted against PC 1 with amines excluded from the plot. (D) PC 3 plotted against PC 2 with amines excluded from the plot.

The data in Figure 2 reveals that the porphyrin functionalization with a diversity of transition metals has the ability to create differentiation of different classes of organic compounds. It is very clear that amines stand out as analytes that produce the largest response. As a result, under other funding we are pursuing applications of this method for the detection of biogenic amines that are indicators of meat spoilage.

Novel Sensor Deposition: The ability to create on demand chemical sensors with minimal infrastructure offers a useful capability in support of covert and/or battlefield applications. In this context we have endeavored to develop a rapid, scalable, portable, and cost-effective approach for the fabrication of fully-drawn chemical sensing arrays on a variety of different substrates (e.g., paper, plastic, and undoped float zones silicon wafer). This approach is entirely solvent-free, requires only small amounts of sensory materials, and is capable of producing highly-sensitive chemical sensors. We demonstrate this approach in the context of sensing and differentiating a variety of vapors at ppm concentrations. Our demonstration employs solid composites of single-walled carbon nanotubes (SWCNTs) and small molecules as the sensing material and graphite as electrodes. We utilize a previously established method to generate sensing materials, or PENCILs (**P**rocess **E**nhanced **N**ano**C**arbon for **I**ntegrated **L**ogic), by the mechanical

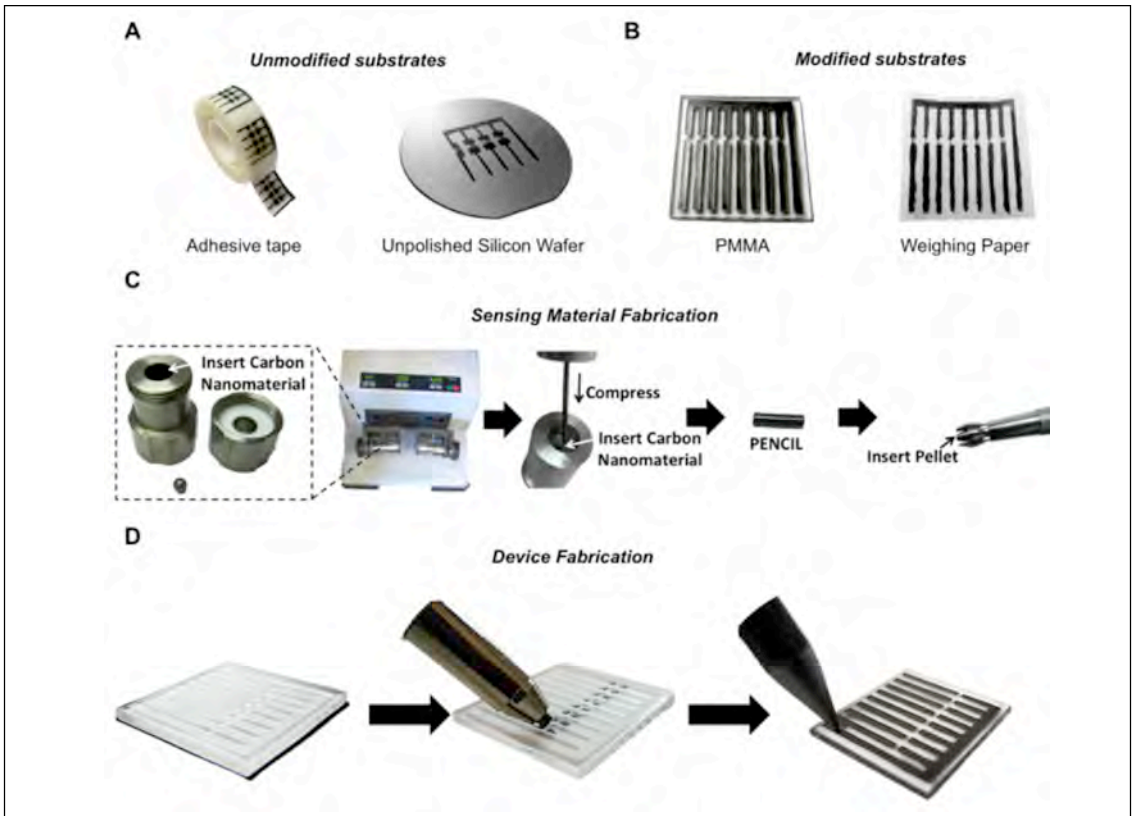


Figure 3. Fabrication of chemiresistive chemical sensors by drawing. Sensing materials (SWCNT-based) and graphite as electrodes were both deposited by mechanical abrasion to yield fully-drawn, chemiresistive gas-sensors on various A) unmodified substrates such as adhesive tape and unpolished silicon wafer, and B) laser-etched substrates such as PMMA and weighing paper. C) Fabrication of the sensing material consists of mechanically mixing and compressing SWCNT composites into a pellet. D) Three-step fabrication of fully drawn chemiresistive sensors on PMMA: laser-etch PMMA, deposit SWCNTs by abrasion (sensing material), and deposit graphite by abrasion (electrodes).

mixing of SWCNTs with commercially available small molecules (solid or liquid). We then utilize DRAFT (**D**eposition of **R**esistors with **A**brasion **F**abrication **T**echnique) to deposit these materials on a variety of substrates. Sequential deposition by mechanical abrasion of sensing materials and commercial graphite pencils on various etched and non-etched substrates yields precisely fabricated fully-drawn chemiresistive sensing arrays (Figure 3).

The performance of the arrays were benchmarked against those created using conventional metal based electrodes. We found that in all cases that the fully drawn sensors were able to match the performance of those on similar substrates with metal (Au) electrodes. The fully drawn method may actually be superior in the fact that the fabrication involves a larger interpenetrating boundary layer between the materials. This gives a higher degree of interfacial contact between the materials and can give rise to more stable contacts, in particular in the case of corrosive chemicals that can damage a metal electrode and give a boundary layer. The reproducibility of this method is also high and we were able to fabricate sensor arrays using functionalized carbon nanotubes that had the necessary stability and stability.

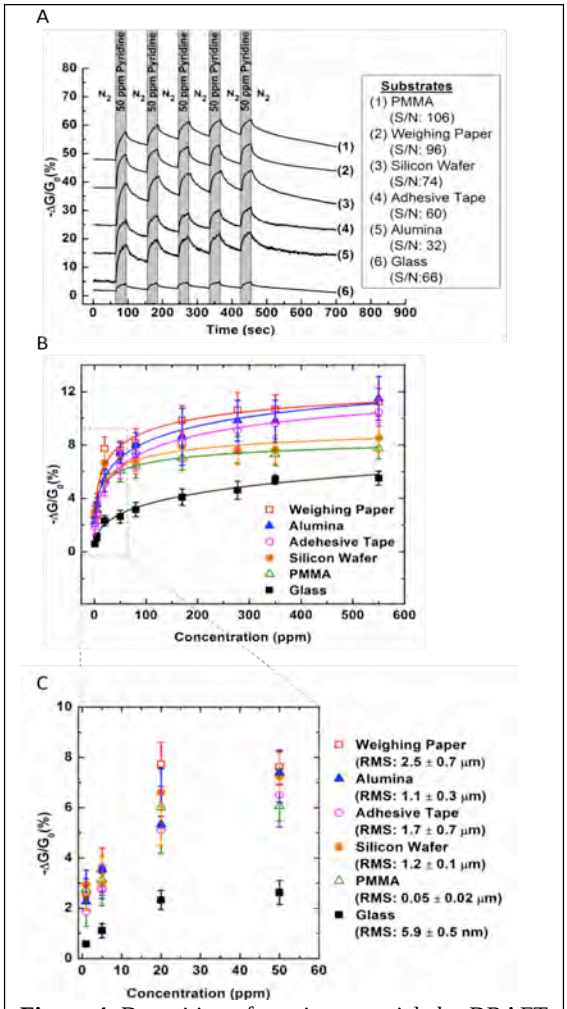


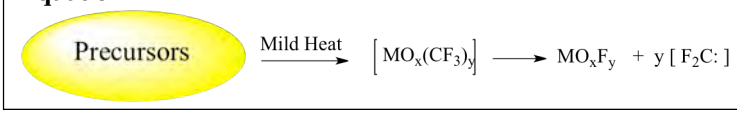
Figure 4. Deposition of sensing materials by DRAFT on six different substrates. SWCNT:TEC (1:2 wt. ratio) was deposited on top of and between gold electrodes (1 mm gap) on six different substrates (PMMA, weighing paper, silicon wafer, glass, adhesive tape, and alumina) by mechanical abrasion. A) Expansion of the scope of the abrasion method substrates. The normalized conductance over time of each device upon 5 consecutive exposures to 50 ppm pyridine for 30 s, with 60 s recovery time. B-C) The average normalized conductance response (first exposure exempt) of at least 6 devices upon 5 consecutive exposures to various concentrations of pyridine for 30 s, with 60 s recovery time.

Novel Routes to Transparent Oxide Conductors: Transparent oxides are used in almost all liquid crystal and organic light emitting diode displays. There is further interest in transparent semiconductors to produce new generations of transparent electronics. The majority of the conductive materials are made from indium tin oxide or fluorinated tin oxide. The latter involves the substitution of a F^- for an O^{-2} and leads to n-type conductors. Both of these transparent oxide materials have limitations in that they are produced by high temperature processes that are incompatible with deposition on plastic substrates. Additionally, the metal oxide structure is one that is brittle and cracks can be generated with low degrees of strain

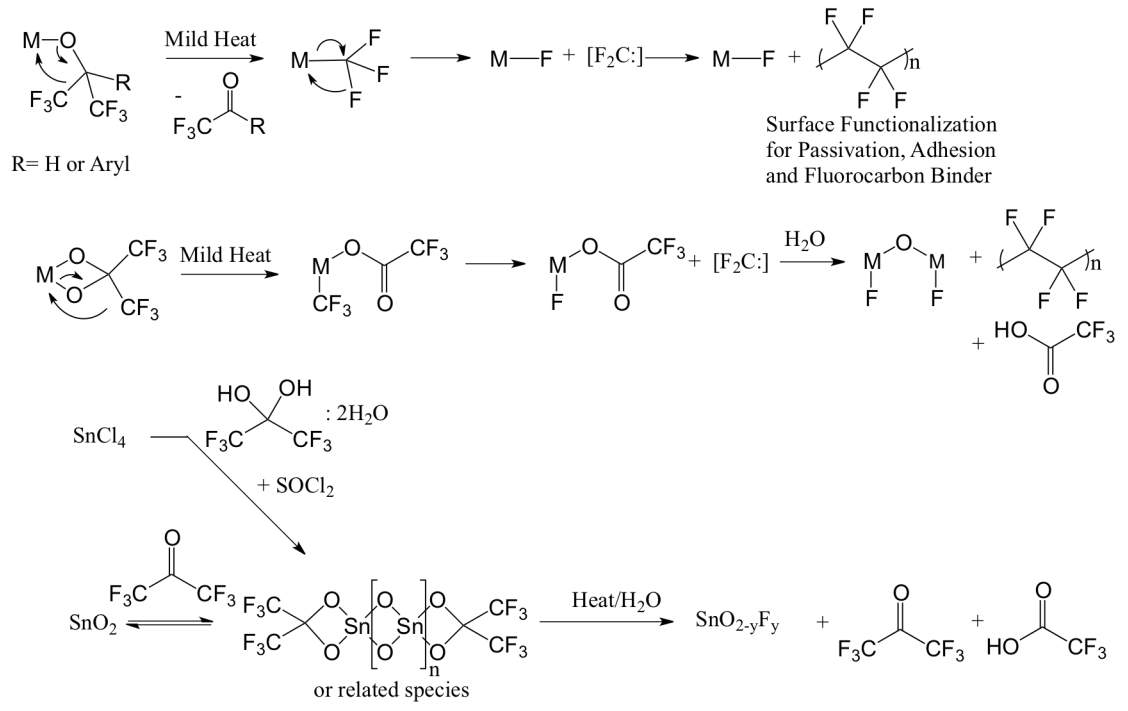
caused by thermal processes or by bending of a flexible substrate. As a result, at the onset of this program we sought to create materials that could be synthesized by low temperature processes and retain some organic functionality that could give rise to better mechanical compliance without causing cracks.

Our initial focus was to make use of the reaction in Equation 1 wherein we expected based on chemistry wherein M = K or Na, that the compound would break down to give the necessary metal fluoride (MF) and a reactive difluorocarbene that could oligomerize or react with the metals to soften the lattice in composite structure. The different related embodiments of this type of reactivity are shown in the reactions shown in Scheme 1.

Equation 1



Scheme 1

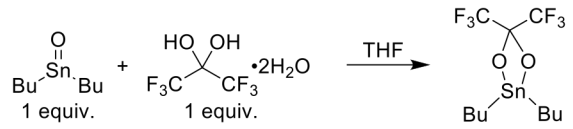


Although precursor compounds with M = Sn^{+4} were made, it was found that the more electron withdrawing nature of this metal relative to K^+ and Na^+ stabilized the starting material and decomposition required higher temperatures (> 150°C) to occur. We were encouraged, however, by the fact that at these high temperatures (400°C) transparent films were formed with low surface resistivity ($\rho_s \approx 35$ Ω/sq).

To get to lower decomposition temperatures we investigated other organo-tin precursors (Equation 2) that decompose at less than 200°C. The butyl groups gave considerable carbon residue as determined by the dark color and we hence, endeavored to synthesize

the dimethyl analog, which was expected to decompose more cleanly. However, these experiments were not successful at giving highly conductive films. We also experimented with a number of liquid/gel precursors having Sn nitrates. However, we were never able to achieve a low resistivity transparent coating at temperatures that are compatible with plastic substrates.

Equation 2



THF-insoluble solid

air-stable, soluble solid

Ongoing Impact of DARPA Funding

This program has successfully resulted in identifying novel carbon nanotube porphyrin compositions for the creation of highly sensitive sensors for amines. A recently demonstrated application has been for the detection of biogenic amines generated by spoiling meat. Our fully drawn sensors and ability to fabricate materials on many substrates has assisted us in ongoing experiments directed at the fusion of complex materials sets to create sensors networks that have rectifying junctions (diodes) and we are examining the potential of these materials to create new generations of sensors. We are further looking into the applications of fully drawn sensors, wherein a composite of an alkoxy silane and carbon nanotubes is created for the conjugation with biological molecules. Hence, this seedling has been very successful in creating enduring new methods for the creation of functional surfaces.

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[1] Zhong, Q.; Diev, V. V.; Roberts, S. T.; Antunez, P. D.; Brutchey, R. L.; Bradforth, S. E.; Thompson, M. E. "Fused Porphyrin Single-Walled Carbon Nanotube Hybrids: Efficient Formation and Photophysical Characterization" *ACS Nano* **2013,** *7*, 3466–3475.

[2] Penza, M.; Alvisi, M.; Rossi, R.; Serra, E.; Paolesse, R.; D'Amico, A.; Di Natale, C. *Nanotechnology* **2011**, *22*, 125502.