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Hybrid Semiconducting Polymer/ Carbon Nanotube Superstructures for Optical, Electro-optic, and Spintronic Applications

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14. ABSTRACT

This proposal targeted three specific objectives: (1) Engineering short wavelength infrared detection materials. We aimed to open and modulate the band gaps of m-SWNTs using chiral, ionic
semiconducting polymers that helically wrap the nanotube surface at constant morphology and rigorously fixed chirality. We have introduced novel “band gap by design” approaches, that enable
organic/nanomaterial hybrid compositions having unique detection capabilities of ~ 2-2.5 Î¼m, thereby providing selective detector and sensor elements that cannot be realized or replicated with established inorganic semiconductors. (2) Developing materials that enable active refractive index control. We exploit helically wrapped semiconducting polymer s-SWNT structures to realize new classes of processable materials that possess dramatically enhanced utility for all-optical signal processing, which enables information processing rates that are much faster than that currently realized using opto-electrical switching.

These novel compositions leverage the richness of accessible m- and s-SWNT electronic structures, the ability to further tune electronic signatures through the nature of the polymer that wraps the SWNT surface, the unique one-dimensional conjugation of these species, the fact that the ground and excited states of these species delocalize over spatial dimensions that are long with respect to every conjugated polymeric material examined to date, and distinctive opportunities to introduce mid-gap states in these compositions, to realize hybrid nanoscale compositions having extraordinary microscopic second-order hyperpolarizabilities (Î³ values) that provide for facile organization in a bulk material. (3) Elucidating spintronic materials. Leveraging rather on the spin than on the charge of an electron, organic spintronics has emerged as an appealing approach to process and carry information at high frequency and low voltage operation cost. We have developed a new class of surfactants that enable the isolation of enantioenriched SWNTs, and when helically wrapped by chiral semiconducting polymers can define novel spintronic materials through a combination
of their unique electronic structures and their potential to express the chirality induced spin selectivity (CISS) effect over long distances at ambient temperature due the combination of their intrinsic chirality, inherent low spin-orbit coupling, and ability to support ballistic charge transport.

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Publications:

Printable and recyclable carbon electronics using crystalline nanocellulose dielectrics, N. X. Williams, G. Bullard, N. Brooke, M. J. Therien, and A. D. Franklin, *Nat. Electron*. **2021**, *4*, 261–268. DOI: 10.1038/s41928-021-00574-0.

Abstract: Electronic waste can lead to the accumulation of environmentally and biologically toxic materials and is a growing global concern. Developments in transient electronics—in which devices are designed to disintegrate after use—have focused on increasing the biocompatibility, whereas efforts to develop methods to recapture and reuse materials have focused on conducting materials, while neglecting other electronic materials. We have reported all-carbon thin-film transistors made using crystalline nanocellulose as a dielectric, carbon nanotubes as a semiconductor, graphene as a conductor and paper as a substrate. A crystalline nanocellulose ink is developed that is compatible with nanotube and graphene inks and can be written onto a paper substrate using room-temperature aerosol jet printing. The addition of mobile sodium ions to the dielectric improves the thin-film transistor on-current (87 $\mu A\ mm^{-1}$) and subthreshold swing (132 $mV\ dec^{-1}$), and leads to a faster voltage sweep rate (by around 20 times) than without ions. The devices also exhibit stable performance over six months in ambient conditions and can be controllably decomposed, with the graphene and carbon nanotube inks recaptured for recycling (>95% recapture efficiency) and reprinting of new transistors. We have demonstrated the utility of the thin-film transistors by creating a fully printed, paper-based biosensor for lactate sensing.

Single-Walled Carbon Nanotubes: from Fundamental Electronic Structures to On-Demand Optoelectronic Properties, Y. Bai and M. J. Therien, *J. Am. Chem. Soc.* Submitted.

Abstract: Single-walled carbon nanotubes (SWNTs), with outstanding mechanical properties, ballistic transport capabilities, and extensively tunable electronic bandgaps, have long been attractive for crafting novel optoelectronic functionality. The past decade has witnessed rapid developments in nanotube growth, purification, and dispersion techniques that have made possible isolation of electronically and morphologically homogeneous SWNT ensembles. At this stage, with such materials control capabilities, to fully exert the potential of SWNTs in next-generation optoelectronics, it is vital to actively manipulate SWNT electronic structures near the Fermi level, as it is the low-energy excitations that determine the common optoelectronic properties of a given material. In this regard, we delineate the microscopic origins of SWNT low-energy excitations, and subsequently chart key strategies to program on-demand optoelectronic properties at a fundamental level. These approaches are made possible with contemporary SWNT processing techniques. With concerted efforts that leverage theoretical insight and synthetic design, many more emergent and unique functionalities of SWNTs will be crafted, making possible new classes of SWNT-based optoelectronic materials and applications.

Low Energy Band Gap Opening and Metal to Semiconducting Phase Transitions in Metallic Carbon Nanotubes, G. Bullard, A. Nayak, F. Mastrocinque, N. X. Williams, Z. X. Widel, A. D. Franklin, and M. J. Therien. Manuscript in preparation.

Abstract: Single chain helical wrapping of metallic single-walled carbon nanotubes (m-SWNTs) with a chiral polyanionic semiconducting polymer breaks carbon nanotube sublattice symmetry in a controllable manner via the uniform nature of polymer-SWNT electronic interactions. Wrapping (11,11) SWNTs with the *S*-PBN(b)-Ph_4 polymer exfoliates, individualizes and disperses these m-SWNTs via a single-chain helically chiral wrapping mechanism, assuring morphological homogeneity of *S*-PBN(b)-Ph_4-[(11,11) SWNT] polymer−SWNT superstructures that maintain a fixed polymer helical pitch length (10 nm) on the SWNT surface. Polymer-nanotube electronic mixing in these well-defined assemblies shifts the SWNT Dirac points away from the quantization lines, and drives m-SWNT band gap opening. Raman spectroscopic data evince G+ and G- band relative intensities congruent with a semiconducting SWNT (s-SWNT) electronic structure. Corresponding infrared (IR) spectroscopic data highlight a new transition at 2500 cm^{-1} for *S*-PBN(b)-Ph_4-[(11,11) SWNTs] relative to simple surfactant-dispersed (11,11) SWNTs, indicating that a 0.3 eV band gap has been opened in these m-SWNTs. Circular dichroism (CD) data evidence chiro-optic confirmation of symmetry breaking, and underscore that M_{11} band electronic excitation drives displacement of excited-state electron density along a helically chiral path. Field effect transistors (FETs) fabricated from these *S*-PBN(b)-Ph_4-[(11,11) SWNT] superstructures demonstrate both semiconducting behavior as well as source-drain currents three orders of magnitude smaller than those exhibited by analogous devices fabricated from pristine metallic (11,11) SWNTs. Because the degree of polymer-SWNT electronic interactions may be highly regulated via tuning the relative energetics between polymer frontier orbital energies and m-SWNT Fermi levels, these studies establish a compelling approach to engineer novel low bandgap materials.

Work in Progress:

Ongoing work includes: (1) Refining a scalable technique that provides diameter-sorted SWNTs of a single helical handedness. Towards this goal, we have developed a simple, robust, two-step, enantioselective ATP-like protocol that has allowed for the first time the isolation of single-diameter SWNT enantiomers. This process utilizes a novel chiral, binaphthalene-based surfactant that discriminates SWNT helical handedness. This experimental work has been carried out in concert with molecular dynamics simulations, which help guide next-generation chiral surfactant designs optimized for a specific nanotube diameter and helical handedness. The ability to now isolate single-diameter SWNT enantiomers opens up entirely new strategies to generate and propagate spin currents in polymer-wrapped/SWNT assemblies that take advantage of the chirality-induced spin selectivity (CISS) effect. (2) Characterizing the nonlinear optical responses of pristine and polymer-wrapped nanotube assemblies based on single-chirality, enantioenriched m- and s- SWNTs. This work leverages new opportunities enabled by our recently developed approaches to open band gaps via symmetry breaking in polymer-wrapped chiral m-SWNTs. (3) Determining the Fermi level energies (E_F values) of m-SWNTs via electrochemical and spectroelectrochemical methods. These efforts are important as they inform polymer designs that regulate the extent and nature of polymer-

m-SWNT electronic interactions, control hyperpolarizabilities in these polymer-SWNT superstructures, and modulate the magnitude of band-gap opening via symmetry breaking. (4) Exploiting larger single diameter (~1.9 nm) semiconducting and metallic nanotubes in polymer-SWNT superstructures. These larger diameter nanotubes have only now been made accessible via aqueous two-phase (ATP) extraction techniques developed in our lab. These large, single-diameter nanotubes feature unique electronic structures that have been heretofore uncharacterized, and offer new platforms to realize novel optical, electro-optic, and spintronic functionality. (5) Developing a series of new rylene-based polymers that give rise to polymer-wrapped/SWNT assemblies. These compositions possess lowest-energy transitions that are highly polarized along the conjugated polymer axis, and provide critical tests of how semiconducting polymer electronic structure can be exploited to regulate the extent of m-SWNT symmetry breaking.

Executive Summary:

This program develops novel materials that enable high-resolution vision and identification in near and total darkness, ultrafast signal processing, flexible sensors that operate in unique spectral regimes at ambient temperature, and processing and delivery of information at high frequency and low voltage operation costs. Such materials will ultimately enable new Air Force-relevant technologies that detect, identify, and target, as well as those that provide fast, secure, and novel means of high-speed communication. Towards these broad goals, this program designs, synthesizes, and characterizes novel functional hybrid materials based on semiconducting polymers, metallic single-walled carbon nanotubes (m-SWNTs), and semiconducting single-walled carbon nanotubes (s-SWNTs), that have unique optical, electro-optic, and spintronic functionalities. Semiconducting polymer-carbon nanotube hybrid materials were developed for objectives that spanned short wavelength infrared detection, active refractive index control, and spin current propagation. Spectroscopic, electrical, transport, and excited-state dynamical studies elucidate critical structure-property relationships that broadly inform molecular and nanoscale design criteria central for these applications.