Engineering Single-Walled Carbon Nanotube Corona Phase for Molecular Recognition and Plant Nanobionics

by

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Submitted to the Department of Chemical Engineering
in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy in Chemical Engineering

Abstract

Single-walled carbon nanotubes (SWCNTs) exhibit unique optoeletronic and structural properties such as tunable bandgap transition energy, strong near-infrared (nIR) photoluminescence (PL), quasi-one-dimensionality with a high surface area to volume ratio, and versatile surface modifications. These attributes have positioned SWCNTs as a promising class of nanomaterials for diverse *in vivo* and *in planta* applications ranging from selective optical sensing to targeted biochemical cargo delivery. A variety of amphiphilic molecules can be functionalized onto the SWCNT surface to provide aqueous solubility. Engineering this adsorbed layer of molecules, termed as the corona phase (CP), through covalent or non-covalent conjugation of synthetic or natural heteropolymers, surfactants, or biomolecules such as oligonucleotide and peptide confers tailored functionality to SWCNTs. Upon adsorption to the nanotube surface, CP molecules adopt specific conformations that create selective artificial molecular recognition sites for target analytes. Binding of the analyte to the CP is transduced into modulations of SWCNT PL as emission intensity changes or wavelength shifts. These functionalized SWCNTs can be interfaced with living plants to impart non-native or enhance native functions to plants, enabling plant nanobionic applications such as real-time monitoring of plant physiological conditions and environmental pollutant uptake. These capabilities offer novel solutions to emerging agricultural challenges associated with climate change and environmental pollution.

This thesis presents the engineering of SWCNT CP for the development of optical sensors targeting viral oligonucleotide and environmental pollutants. Utilizing a single-stranded DNA CP, we probed oligonucleotide hybridization on the nanotube surface in the context of COVID-19 viral sensing. We explored the effects of CP sequence on hybridization responses and discovered enhancements in sensor specificity through the inclusion of a dummy-sequence anchor region in the CP, achieving nanomolar sensitivity and compatibility with biofluids. Additionally, we employed the Corona Phase Molecular Recognition (CoPhMoRe) concept with custom-designed synthetic polymers to develop the first SWCNT-based fluorescent nanosensor for detecting perfluorooctane sulfonate (PFOS), a toxic persistent environmental pollutant. By tailoring the CP composition, we demonstrate selective detection of PFOS against other perfluoroalkyl substances and robust sensitivity in real-world environmental water samples at part-per-billion concentrations. Advancement in sensor imaging technologies was also achieved via nIR fluorescent hyperspectral microscopy, further improving sensitivity by analyzing spatially and spectrally deconvoluted, chirality-specific sensor responses.

To facilitate *in planta* applications of functional SWCNTs, this thesis also investigates their uptake rate as a function of CP-mediated nanoparticle properties in model plant systems including protoplasts and chloroplasts, using an advanced hyperspectral, multimodal imaging microscope. The platform is able to measure nIR photoluminescence and Raman scattering of a sample within plant tissues, cells, organelles or the in-tact plant itself. We quantitatively analyzed the subcellular localization of SWCNT with high spatial and spectral resolution. Empirical models relating nanoparticle properties to the uptake results were formulated to provide design principles for achieving passive lipid membrane penetration capability and high subcellular uptake rates. Overall, this thesis demonstrates a comprehensive investigation of the SWCNT CP and their impacts on the functional performance of SWCNTs, paving the way for precision agriculture through next-generation nanobionic plant technologies *in-planta*.

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