The Chinese University of Hong Kong
Department of Biomedical Engineering

Graduate Seminar – PhD Oral Defence

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Date	**:**	28 June 2019 (Friday)
Time	**:**	10:00 a.m.
Venue	**:**	Room 215, William M.W. Mong Engineering Building

Title: Polydopamine-Based Plasmonic Nanostructures for Intracellular Applications

Polydopamine (PDA), a bioinspired polymer derived from the self-polymerization of monomeric dopamine (DA), is gaining ever-growing attention as an adhesive coating material. However, the exploration of PDA as a building block for assembling plasmonic nanostructures remains limited. In this thesis, we demonstrate that PDA allows for the facile preparation of plasmonic nanostructures, namely, nanoshells and nanoworms, both of which exhibit a sharp plasmon peak in biological near-infrared (NIR) windows and hold great promise in plasmon-driven intracellular applications.

Plasmonic nanoshells (NSs), classically comprising gold (Au) as the metallic component and silica as the dielectric material, are important for fundamental studies in nanoplasmonics. They also empower a myriad of applications, including sensing, energy harvesting, and cancer therapy. Yet, laborious preparation precludes the development of next-generation NSs with structural complexity, compositional diversity, and tailorable plasmonic behaviors. We present an efficient approach to the bottom-up assembly of concentric NSs. By employing PDA as the dielectric material and exploiting its intrinsic adhesiveness and pH-tunable surface charge, the growth of each shell only takes 3–4 hours at room temperature. A series of PDA-based concentric NSs with programmable nanogap thickness, elemental composition [Au and silver (Ag)], and geometrical configuration (number of layers) is prepared, followed by extensive structural characterization. Four of the Ag-containing nanostructures are newly reported. Systematic investigations into the plasmonic properties of concentric NSs as a function of their structural parameters further reveal multiple Fano resonances and local-field “hot spots”, infrequently reported plasmonic features for individual nanostructures fabricated using bottom-up wet chemistry.

Plasmonic nanochains, derived from the one-dimensional assembly of individual plasmonic nanoparticles (NPs), remain infrequently explored in biological investigations due to their limited colloidal stability, ineffective cellular uptake, and susceptibility to intracellular disassembly. We report the synthesis of PDA-coated plasmonic nanoworms (NWs) by sonicating citrate-capped Au (Cit-Au) NPs in a concentrated DA solution under alkaline conditions. DA mediates the assembly of Cit-Au NPs into Au NWs within 1 min, and subsequent self-polymerization of DA for 60 min enables the growth of an outer conformal PDA shell that imparts stability to the inner Au NW structure in solution, yielding “core–shell” Au@PDA NWs with predominantly 4–5 Au cores per worm. Our method supports the preparation of monometallic Au@PDA NWs with different core sizes and bimetallic PDA-coated NWs with Au and Ag cores. The protonated primary amine and catechol groups of DA, with their ability to interact with Cit anions via hydrogen bonding and electrostatic attraction, are critical to assembly. When compared to unassembled PDA-coated Au NPs, our Au@PDA NWs scatter visible light and absorb NIR light more intensely and enter HeLa cancer cells more abundantly. Au@PDA NWs cross the cell membrane as intact entities primarily via macropinocytosis, mostly retain their inner NW structure and outer PDA shell inside the cell for 24 h, and do not induce noticeable cytotoxicity. We showcase three intracellular applications of Au@PDA NWs, including label-free dark-field scattering cell imaging, delivery of water-insoluble cargos without pronounced localization in acidic compartments, and photothermal killing of cancer cells.

Facilitated by PDA chemistry, we have not only established materials design rules for engineering complex plasmon-based systems originating from the integration of multiple plasmonic elements into defined locations within a compact nanostructure, but also expanded the experimental toolbox available for preparing 1D plasmonic nanoassemblies to foster their utilization in biomedical engineering.

***** ALL ARE WELCOME *****

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