Nanocrystal Assembly for Bottom-Up Plasmonic Materials

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Plasmonic materials are emerging as key platforms for applications that rely on the manipulation of light at small length scales. Sub-wavelength metallic features support surface plasmons that can induce huge local electromagnetic fields at the metal surface, facilitating a host of extraordinary optical phenomena.[1] In this dissertation, Ag nanocrystals and nanowires are used as building blocks for the bottom-up fabrication of plasmonic materials for photonics, spectroscopy, and chemical sensing. To begin, faceted Ag nanostructures are synthesized using a colloidal approach to regulate nucleation and crystallographic growth direction. Next, new methods of nanoscale organization using Langmuir-Blodgett compression are presented in which 1-D and 2-D assemblies can be constructed with impressive alignment over large areas. Using this method, plasmon coupling between Ag nanostructures can be controlled by varying spacing and density, achieving for the first time a completely tunable plasmon response in the visible wavelengths. Lastly, these assemblies are demonstrated as exceptional substrates for surface-enhanced Raman sensing by achieving high chemical sensitivity and specificity, exhibiting their utility as portable field sensors, and integrating them into multiplexed "lab-on-a-chip" devices.

Shape-Controlled Synthesis

Because metal nanostructures generate plasmon-mediated evanescent fields near their surfaces when irradiated with light, Ag nanocrystals and nanowires are ideal building blocks for rationally designed plasmonic materials. Ag structures with anisotropic shapes produce electromagnetic field enhancements due to the excitation of highly polarized surface plasmons. Most work in this area has focused on top-down lithographic methods for generating such structures.[2] Colloidal synthesis is advantageous because it can achieve exceptional yields and high monodispersity. The use of adsorbate molecules that bind preferentially to a certain crystal face regulates growth kinetics at the crystallographic level, resulting in well-defined shapes with sharp corners, edges, and facets.[3] In this thesis, poly(vinyl pyrrolidone) is demonstrated as an excellent shape-control agent for Ag colloids, producing rods, wires (Figure 1), cubes,

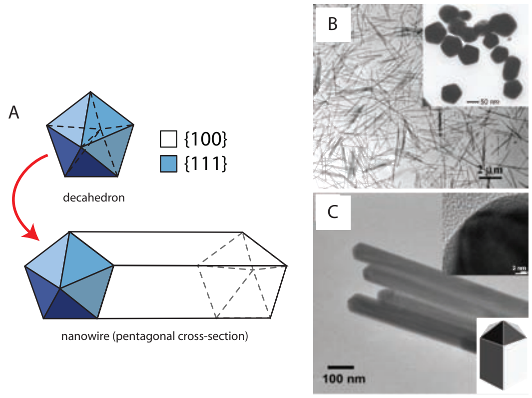

Figure 1. (A) Schematic depiction of nanowire growth from a decahedral seed particle. (B) Uniform solution of wires with a microtomed cross-section shown in the inset. (C) TEM image of nanowires with a high resolution image of the wire tip.

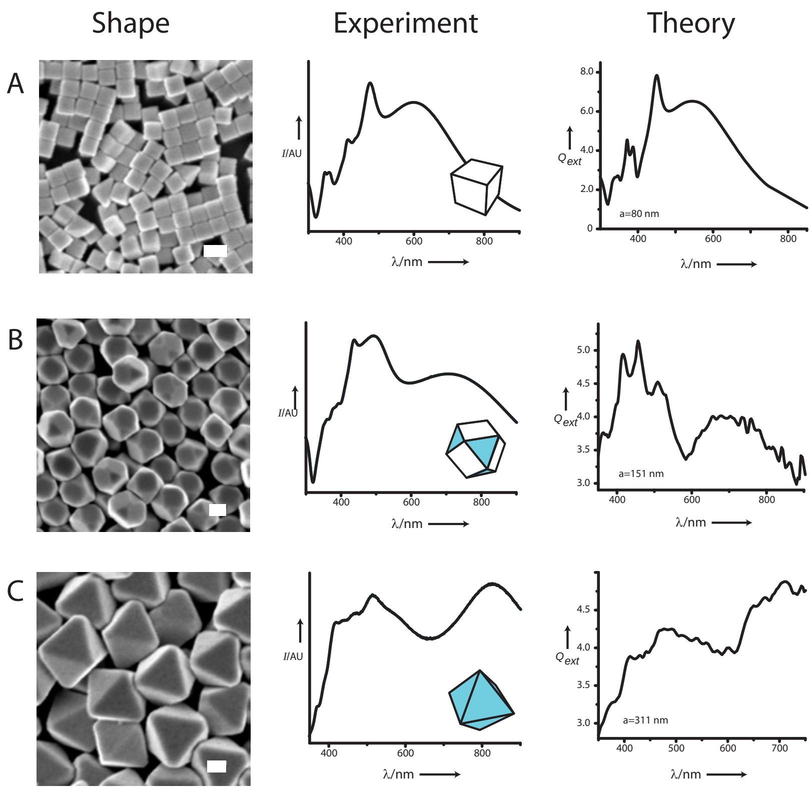

Figure 2. From left to right: SEM images of Ag nanocrystals, UV-Vis spectra of colloidal solutions, and theoretical discrete dipole approximation scattering for (A) cubes, (B) cuboctahedra, and (C) octahedra. Scale bar = 100 nm. In depictions, blue areas represent {111} facets, white areas represent {100} facets.

octahedral (Figure 2), tetrahedra, and other polyhedra.[4] Crystalline and bound entirely by {100} and {111} crystal facets, each structure gives rise to distinct plasmon resonances that correlate with particle size and shape.[5] These localized plasmon modes are able to spatially confine light to the nanocrystal volume.

Langmuir-Blodgett Assembly

Controlled positioning of nanoparticles using a self-assembly method is highly desirable for its simplicity and compatibility with device integration processes.[6] For plasmonic materials, the bottom-up organization of metal nanostructures is largely unexplored. Nanowires and nanocrystals are model anisotropic building blocks for assembly into Langmuir-Blodgett (LB) monolayers. The LB technique is a general and versatile method of organizing colloidal structures at an air/water interface that enables transfer to an arbitrary substrate, making it a powerful tool for nanoscale assembly. Simple manipulation of the

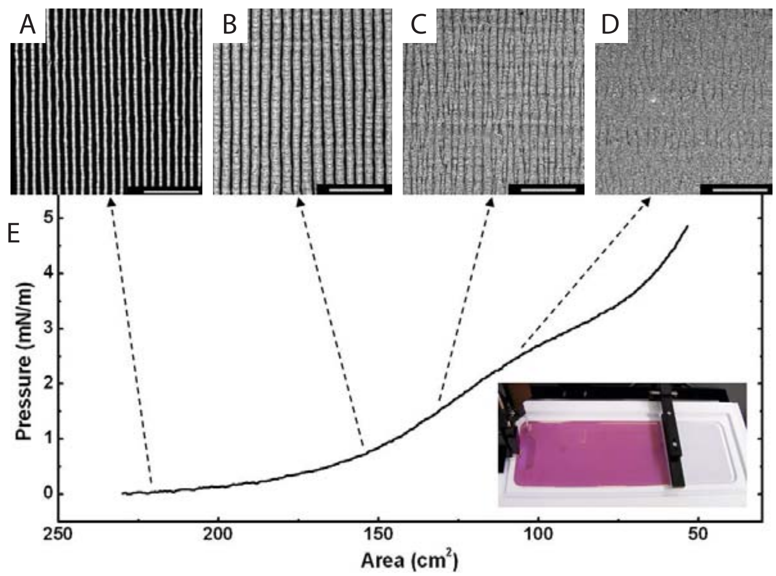

Figure 3. Stripe formation upon monolayer dewetting. From (A) to (D), substrate dip-coating is performed at increasing monolayer surface pressures, as shown on isotherm curve. Inset: LB trough with nanocrystal monolyer on water surface.

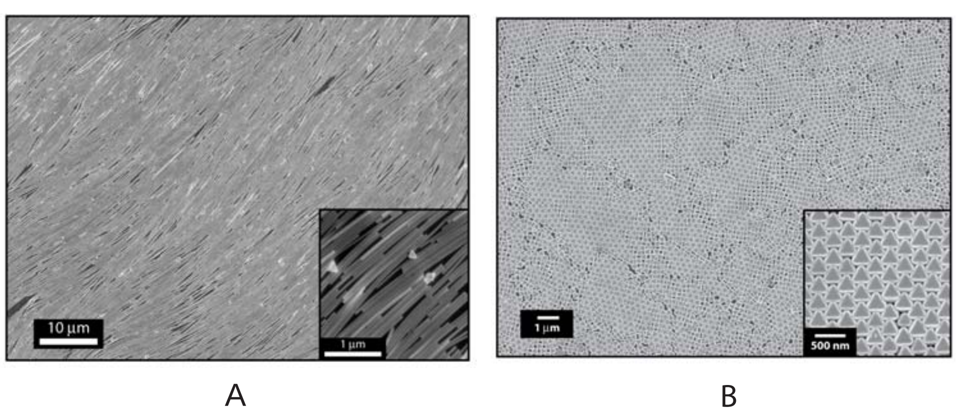

Figure 4. SEM of dense arrays of (A) Ag nanowires and (B) Ag octahedra assembled by Langmuir-Blodgett compression. Insets show a close-up of superlattice packing.

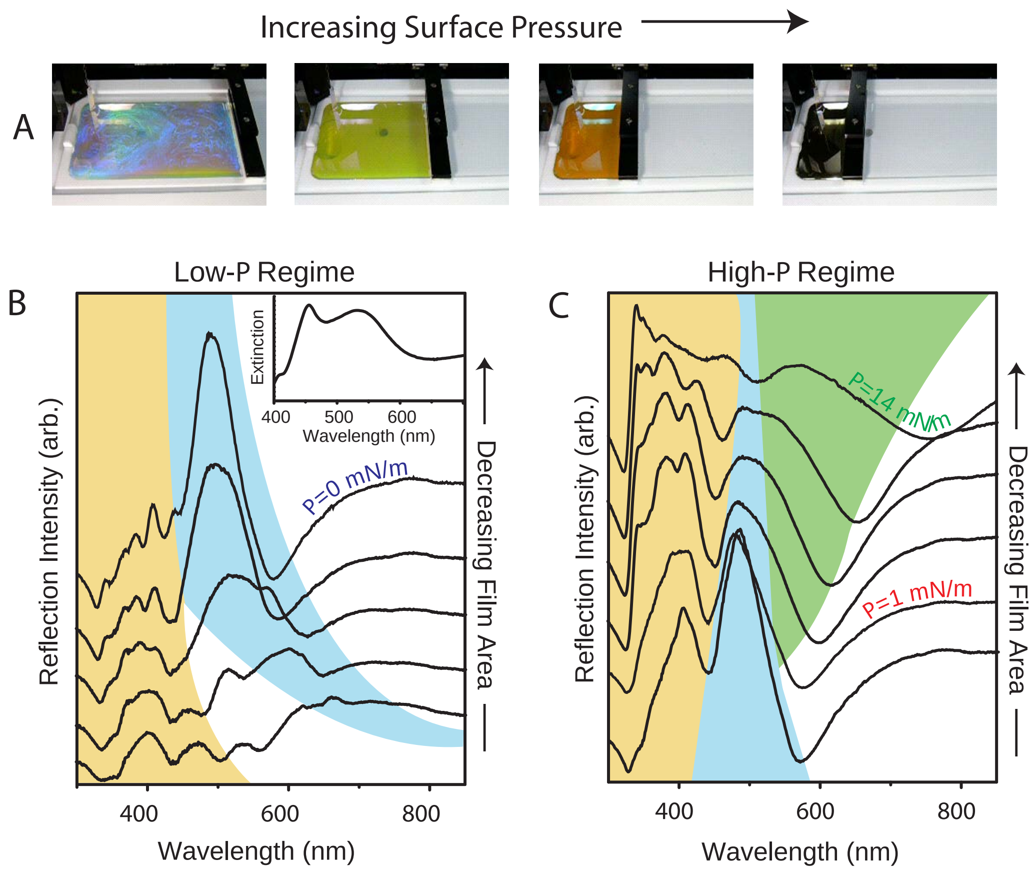

Figure 5. Tunable plasmonic response of Ag nanocrystal monolayers. (A) Images of the nanocrystal monolayer as surface pressure is increased. (B) Reflection spectra of the low surface pressure regime showing strong peak due to Bragg scattering. Inset: UV-Vis of the colloidal solution. (C) Reflection spectra of the high surface pressure regime, showing evolution of the optical response as plasmon coupling ensues.

interface can give rise to complex patterns, such as stripes[7] and single-particle lines[8] with tunable widths, particle densities, and spacing. (Figure 3)

LB assembly produces highly ordered monolayers,[9] where packing symmetry can be determined by building block shape. For anisotropic structures like Ag nanowires, the assembly process is a microscopic version of "logs-on-a-river:" as the nanowires are compressed at the air-water interface they align side-by-side along their long axis.[10] (Figure 4a) This achieves large-scale nematic ordering with unprecedented nanowire packing density, allowing the fabrication of high density nanoscale interconnects and sensor arrays. For polyhedral Ag nanocrystals, LB assembly can produce unique 2-D superlattices.[11] (Figure 4b) These assemblies promote electromagnetic coupling between nanocrystals, leading to narrow plasmon bands and intense field enhancement in the interstitial spaces between neighboring particles. Because coupling is distance-dependent, plasmon resonances can be continuously tuned across the visible range. (Figure 5)

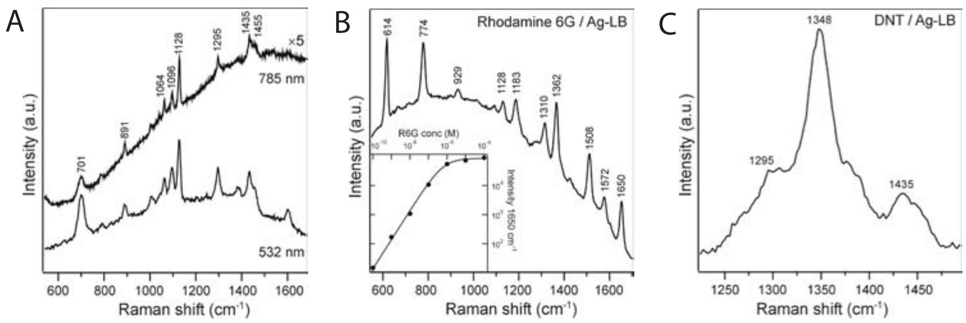

Figure 6. SERS response from a nanowire monolayer for (A) a molecular monolayer of hexadecanethiol, (B) adsorbed Rhodamine 6G, and (C) adsorbed 2,4-dinitrotoluene, an analyte molecule for explosives.

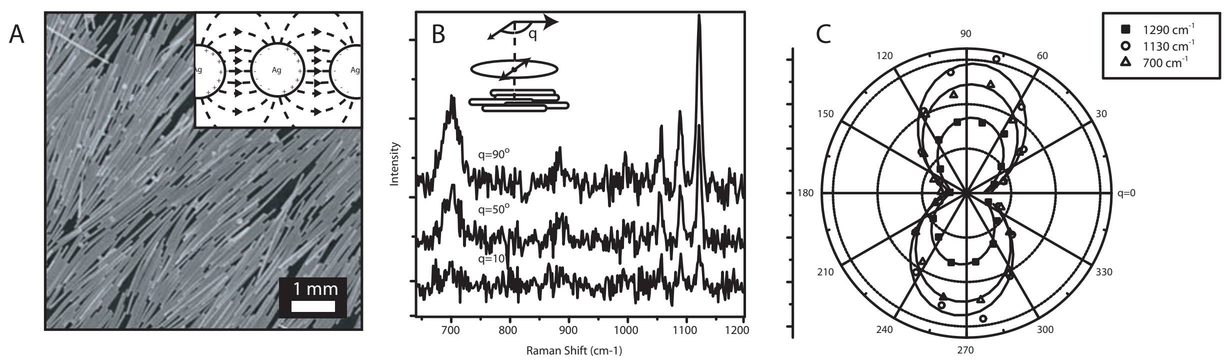

Figure 7. Polarized SERS response of a nanowire monolayer. (A) SEM of monolayer and schematice of localized electromagnetic fields between wires. (B) SERS spectrum as a functional of polarization angle for the excitation source. (C) Polarized SERS response for different Raman bands.

Controlling the density and strength of near-field interactions has important consequences for applications such as optical spectroscopy, light focusing, energy transfer, or integration into optoelectronic devices.

Anisotropic Structures for Surface-Enhanced Raman Spectroscopy

Surface-enhanced Raman spectroscopy (SERS) is an ideal sensing technique because it provides chemically-specific vibrational signatures and detection in aqueous environments.[12] The assemblies described in the previous section are advantageous SERS substrates because their unique morphologies facilitate the intense electromagnetic field amplifications responsible for Raman enhancement. For example, Ag nanowire films assembled by the LB method have been shown to yield high Raman intensities orders of magnitude higher than traditional substrates.[10] (Figure 6) Plasmon coupling between nanowires is responsible for SERS “hot spots” in the interstitial spaces between adjacent wires, where field localization occurs.[13] (Figure 7) These assemblies can be used for molecular detection in either air-borne or solution

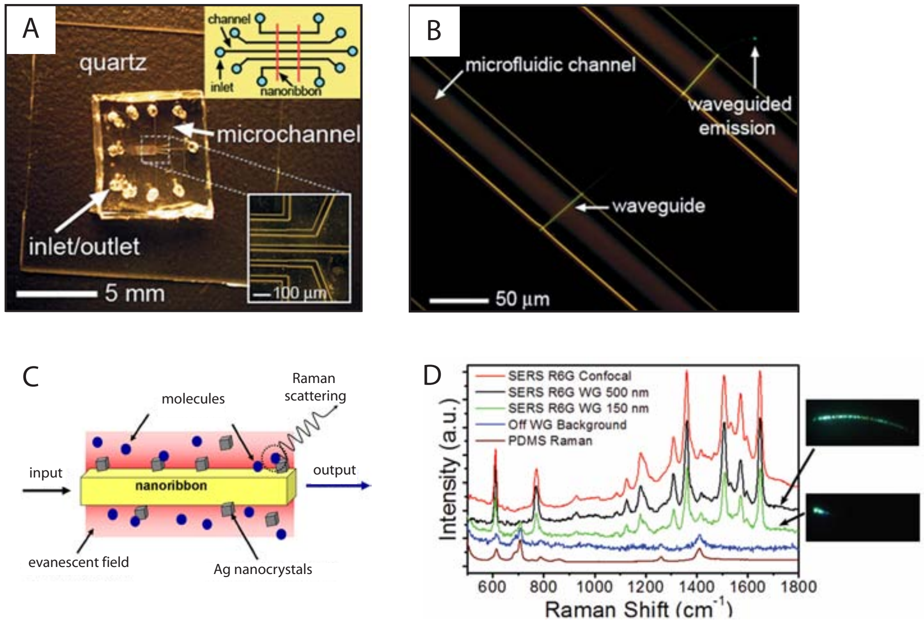

Figure 8. Lab-on-a-chip device. (A) Microfluidic platform with multiple channels for analyte flow. (B) Close-up of nanowire waveguides crossing channels. (C) Schematic of SERS sensing strategy, where Ag nanocrystals are attached to the nanowire and then exposed to the analyte solution. (D) SERS spectra for Rhodamine 6G solutions.

environments, which has significant implications in chemical warfare detection and medical diagnostics. LB assemblies of octahedral Ag nanocrystals have been utilized as SERS substrates for the identification of arsenic in water down to ppb concentrations.[14] Lastly, a microfluidic sensing platform has been developed for on-site field detection, integrating semiconductor nanowires waveguides and shaped Ag nanocrystals.[15] This photonic sensor, shown in Figure 8, is capable detection by SERS, fluorescence, and absorbance. Such a multifunctional sensor with the ability to analyze extremely small sample volumes is necessary for deconvoluting complex mixtures.

Conclusion

This dissertation pioneers the bottom-up engineering of plasmonic materials for application in sub-wavelength optics, field-enhanced spectroscopy, and chemical sensing. It highlights the exciting prospect of utilizing assembled nanostructures in fundamental and applied studies.

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