Plasmonic Optoelectronic Interactions (NBIT III)

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“Plasmonic Optoelectronic Interactions (NBIT III):

Hybrid plasmonic interaction: collective and spin-coupled plasmonic systems”

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Abstract:
During the past four years, the Mirkin Group has successfully developed template-assisted syntheses that can be used to generate nanomaterials with new structures and compositions. In particular, the invention and development of on-wire lithography (OWL) and coaxial lithography (COAL) have enabled the syntheses of solution-dispersible nanowires with architectural control over both the axial and radial dimensions, such that core-shell semiconductor nanowire–plasmonic nanoring structures can be realized. In addition to electrochemical synthesis, the Mirkin group also has reported a template-assisted solution-based process for the preparation of uniform nanostructured metal-halide perovskites. This class of materials has recently emerged as a promising material in photovoltaic, optoelectronic, and other energy harvesting devices.

Also, based on expertise in nanoparticle assembly techniques using chemically modified oligonucleotides, the Mirkin group has realized plasmonic photonic crystals composed of inorganic nanoparticles uniformly arranged into crystalline lattices. In addition, fluorescent dye molecules also can be attached to the DNA to incorporate them into these plasmonic photonic crystals, where the collective effect of plasmon (nanoparticle) - exciton (dye) interactions can be studied. Moreover, the Mirkin group has continued to work with magnetic nanoparticles functionalized with oligonucleotides, assembling them into lattices even in conjunction with plasmonic nanoparticles as a means to realize yet-to-be-studied magnetically active colloidal crystals.

The Jang Group has continued to elucidate the mechanism of plasmonic photocurrent enhancement in semiconducting nanowire (NW) systems by metal nanoparticles (NPs), carrying out in-depth characterization utilizing advanced scanning probe microscopy. As a result, it was found that the energy band-matching between the metal NP and the semiconductor NW is important in determining the role of the metal NP as either an electron donor or acceptor during plasmonic excitation. In the extended research period, wavelength-
and spin alignment-dependent charge carrier transfer in ferromagnetic NWs with a plasmonic excitation structure (Au double rings) was investigated and demonstrated to show spin-coupled plasmonic phenomena. Importantly, this work is based upon the close collaboration of the Mirkin group (USA) and the Jang group (Korea) in which protocols, samples, and personnel have been extensively exchanged.

**Introduction:**

Compared to their bulk counterparts, nanomaterials are known to exhibit unique properties that can be exploited to fabricate optoelectronics devices that display enhanced performance. However, it is essential to understand light-matter interactions at the nanoscale and be able to synthesize novel (and complex) nanostructures, assemble them into well-defined arrays and probe their properties with high resolution. As a part of the NBIT collaborative research of the Mirkin and the Jang groups, light-matter interactions of different classes of materials (i.e., semiconducting, metallic, or magnetic) as well as their hybrid structures were investigated and this knowledge was applied to the fabrication of functional optoelectronic devices.

For the past decade, the Mirkin group has employed anodized aluminum oxide (AAO) templates to synthesize multicomponent nanowires within parallel and cylindrical nanopores, typically via electrochemical deposition. The library of materials that can be synthesized in this fashion include metals (e.g., Au, Ni, Ag, Pd), simple inorganic semiconductors (e.g., ZnO, MnO₂, CdS), and polymers (e.g., polypyrrole, polyaniline, polythiophene, their derivatives). During the earlier stage of the NBIT funding period, we reported a novel technique, termed coaxial lithography (COAL), which enables one to synthesize core-shell nanostructures. Briefly, post-deposition polymer contraction leaves a small gap between it and the pore wall and subsequent electrodeposition then occurs as a shell around the polymer core. As a result, COAL enables the synthesis of semiconducting nanowires surrounded by metallic nanorings, a type of plasmonic-optoelectronic hybrid structure, and solution-dispersible 2D cavity structures, complementing the 1D cavity structures synthesized by on-wire lithography (OWL).

Moreover, the porous AAO membranes have been utilized for fabricating nanostructured metal-halide perovskites, expanding the library of materials that can be prepared via template-assisted synthesis to those that can be cast from solution (i.e., spin-coating a precursor solution and evaporating the solvent). Over the past few years, metal halide perovskites (of which the most studied composition has been of the chemical formula CH₃NH₃PbI₃) have emerged as a promising class of low-cost, solution-processable semiconductors with highly desirable properties as components in photovoltaics (e.g., due to efficient visible light absorption and long charge diffusion lengths), LEDs, and lasers. Nanostructuring this perovskite material within AAO could offer benefits including improved crystallinity (compared to bulk films), reduced charge separation distances for more efficient charge extraction, and the unique opportunity to controllably interface perovskite nanowires with other functional materials (e.g., plasmonic nanorings).

The Mirkin group also used DNA-mediated nanoparticle assembly to realize the construction of plasmonic-semiconducting and plasmonic-magnetic hybrid nanostructures. Throughout the past decades, colloidal crystallization using surface-immobilized DNA has been advanced to generate single-crystalline superlattices of nanoparticle cores of different sizes, shapes, and compositions. The interparticle distances and lattice parameters are highly controllable in these structures, enabled by the rigidity of DNA, and optically functional molecules, such as fluorescent dyes can be incorporated at specific locations on a DNA strand using click chemistry. In these structures, unusual optical properties were observed that derive from the microscale geometries of the crystalline superlattices and the strong
interactions between the plasmonic and excitonic components.

In parallel to the development of the synthetic platform by the Mirkin Group, the Jang group focused on the characterization and nanoscale visualization of the effect of the plasmonic optoelectronic interactions. In addition to the previously reported measurement schemes, light-irradiated Kelvin Probe Force Microscopy (KPFM) was introduced to the library of analytical tools that could be used to probe nanostructures. Systematic control over nanostructured metal/semiconductor junctions enables one to access an ideal testbed to explore light-matter interactions. As a complementary investigation of the light-matter interactions of COAL-based nanowires, metal nanoparticles (NPs) coordinated to semiconductor NW devices have been used for a plasmonically enhanced photocurrent study. We previously reported that Au NPs attached to p-type polypyrrole NWs cause plasmonic enhancement of photocurrent generation, and we employed light-irradiated KPFM to inform the mechanism by which this enhancement occurs. In addition to magnetic force microscopy (MFM), light-irradiated KPFM has been used as a tool to characterize spin-coupled plasmonic interactions in Fe NWs with plasmonic Au double ring structures. We propose that the metal NP can work as either an electron donor or acceptor depending on the type of semiconductor NW (p-type or n-type) using light-irradiated KPFM with Au NPs attached to PPy NWs. In case of spin-coupled plasmonic interactions, the surface potential difference as a result of the plasmonic excitation in the Fe NWs with Au rings is relatively large when the external field-aligned magnetic moment of the Fe NW is perpendicular to the electrical component of the applied light. Our demonstration reveals that the bandgap-matching of the metal and the semiconductor is important for determining the direction of the electron movement in the nanostructured metal/semiconductor junction.

It is worth emphasizing that while the synthetic work was primarily done by the Mirkin group, the architectures of interest were chosen through close collaboration with the Jang group. We have leveraged the collaboration formalized by this grant to characterize the properties of the wires utilizing the advanced optoelectronic measurement set-up constructed by the Jang group, including light-irradiated KPFM and MFM. These coordinated optical and electrical measurements are a powerful and necessary part of realizing new architectures for studying light-matter interactions as well as investigating spin-coupled plasmonic interactions.

**Experiment:**

1. **Synthetic advances through template-assisted synthesis (Mirkin group)**

As mentioned briefly above, coaxial lithography (COAL) is a technique by which core-shell nanowires can be synthesized in a high-throughput manner with sub-10 nm resolution, and compositional control in both the axial and radial dimensions. This method is enabled by polymer electrodeposition (polyaniline was often used in this study); the polymer contracts inside the pores when it dries after deposition. Then, through the small gap between the polymer core and the AAO pore wall, further deposition can be performed to grow multi-segmented shell layers, composed of, for example, Au or Ni, around the core (Figure 1). It is noteworthy that the metal segments or the polymer core can be selectively removed, and based on this, many variations of the structure can be made.
Figure 1. (a) General scheme showing the synthesis of metal nanorings around an organic core. Blue: organic core. Yellow: target material (Au). Grey: sacrificial material (Ni). On top of the first Au segment, polymer is deposited that subsequently shrinks when exposed to vacuum. Around the polymer core, the shell layers can be deposited from the bottom. (b) STEM images in secondary electrons (SE) and z-contrast (ZC) modes show typical NWs before (left) and after etching (right) the sacrificial Ni shell to generate Au rings (outer diameter: 340 nm) around a polypyrrole (PPy) core (diameter: 280 nm).

An example would be the generation of solution-dispersible nanorings made of various metals with tailorable dimensions (Figure 2). Here, before the deposition of the shell layers (i.e., nanorings), the template and the polymer core can be carefully etched using the appropriate etchants: the AAO template can be dissolved using 0.5 M NaOH and the polyaniline core can be slowly dissolved using a mixture of ethanol and water, allowing for precise control over the outer and the inner diameters, respectively, of the final ring structure. Also, the height of the rings can be controlled as a function of the amount of charge passed during the electrochemical deposition of the shell layers. Then, following the steps to completely remove the AAO template (3 M NaOH), polyaniline core (acetone), and sacrificial metal layers (respective oxidants), the nanorings can be released into solution. By tailoring the dimensions and compositions, the localized surface plasmon resonance (LSPR) of the nanorings can be controlled (Figure 2). The fabrication of single nanowire-based optoelectronic devices with plasmonic nanorings also was demonstrated. As mentioned, the polymer core (polyaniline) and sacrificial Ni segments can be selectively removed, leaving Au nanorings in the pores of the template. Then, semiconducting materials (e.g., MnO₂ or CdSe) are electrochemically deposited in the core (Figure 3).
Figure 2. Characterization of nanorings composed of different materials. STEM images (left) and elemental maps via energy-dispersive X-ray spectroscopy (EDS, right) of single component (a) Au, (b) Ag, (c) Pt, (d) Ni, and (e) Pd nanorings and a multicomponent (f) Au–Ni–Pt nanotube. STEM images in (a), (c), (d), and (e) are false-colored to match the EDS color mapping. (g-i) Control over all three architectural parameters of Au nanorings. STEM images (left), measured extinction spectra (middle), and calculated extinction spectra (right) of the nanorings are presented. (g) The outer diameter was enlarged from 156 to 179 nm by increasing the duration of the pore-widening step from 3 to 18 min (maintaining constant inner diameter and aspect ratio), which corresponds to a 50 nm blue-shift in the most intense LSPR wavelength. (h) The inner diameter was reduced from 95 to 64 nm (maintaining constant outer diameter and aspect ratio) through the introduction of the polymer-thinning step; this corresponds to a 192 nm blue-shift in the LSPR wavelength. (i) The height was increased with the amount of charge passed through the electrodes during the electrodeposition step. By increasing the applied charge from 350 to 1750 mC, the aspect ratio was increased from ∼0.4 to ∼1.8 (maintaining constant outer and inner diameters), which corresponds to a significant red-shift in the lowest frequency plasmon resonance wavelength by 478 nm. Scale bars are 100 nm in all of the electron microscopy images. The blue curves in all of the extinction spectra correspond to the control nanoring sample.
As a demonstration for how COAL-synthesized structures can be used to study light-matter interactions, the Mirkin group synthesized nanoring-embedded hybrid core-shell semiconductor NWs. The target architecture consisted of a p-type semiconducting core surrounded by a Au ring at a deliberately programmed location. This entire structure was surrounded by a n-type semiconducting shell with pure Au segments affixed to either end of the wire. This novel NW architecture was not only chosen for its complexity, but also because it should enhance the absorption of visible light without significantly blocking the electron-hole flow through the wire. COAL was used to initially make Ni and Au rings around a polymeric core (polyaniline, Figure 1). Then, the polymer was dissolved with acetone, and the Ni segment was etched with aqueous 3% FeCl₃ to generate a Au ring within the pores at a deliberately chosen location (Figure 4a). P-type poly(3-hexylthiophene) (P3HT) was then polymerized within the pores, and the pores were subsequently widened by slow dissolution with aqueous 0.5 M NaOH. The n-type semiconductor (CdSe) was then electrochemically deposited to surround the ring-encased p-type semiconductor. At the end of this wire, a Au segment was electrodeposited as an electrical contact to generate the target device architecture. A z-contrast image of a typical NW consisting of a P3HT core (diameter: 120 nm) surrounded by a 175-nm wide, 75-nm long Au ring, further encased in CdSe (outer diameter: 235 nm) clearly shows that all components are where they were programmed to be (Figure 4b).
Figure 4. Integration of a plasmonic Au ring within a hybrid junction composed of an organic p-type core (P3HT) and an inorganic n-type shell (CdSe). (a) Scheme illustrating the modified synthesis steps. From left to right: dissolution of the PANI core (shown in blue), etching of the sacrificial segments (grey) within the AAO template, deposition of the P3HT core (green), pore widening step, growth of the CdSe shell (red) around the P3HT core and the Au ring (yellow), deposition of the top Au segment and dissolution of the AAO template. (b) SE and ZC STEM images, and elemental maps of the P3HT core/CdSe shell NWs with a Au ring (yellow: Au, blue: Cd, and green: Se). Scale bars are 100 nm for all of the images. (c) Comparison of the average Ion/Ioff ratios as a function of wavelength of the NWs with (red circles) and without a ring (black triangles). Three NWs were measured in each case (with and without a ring). The error bars correspond to the standard errors of the experimental measurements. The red and black lines are only guides for the eye. (d) Simulated electric-field intensity maps of the metal segments (NW shown in b), without (left) and with (right) a ring, recorded at 532 nm (logarithmic scale). The maps were generated using an excitation source polarized in the direction parallel to the longitudinal axis of the NWs. The dotted line corresponds to the location of the semiconductor segments.

The effect of the embedded plasmonic ring on the photoconducting properties of the core/shell NW was investigated by performing electrical measurements under vacuum. NWs made in this manner and similar structures without Au rings were irradiated using a Xe lamp with a monochromator while the I-V characteristics were measured (Figure 4c). The plasmonic nanoring was found to modify the photoresponse of the NWs as evidenced by the rise in photocurrent at the LSPR wavelength of the Au ring (Figure 4d). Indeed, Ion/Ioff at this wavelength was on average 45% higher than for structures without the Au rings (3 wires averaged for each condition). FDTD simulations suggest that this enhancement arises from the greatly increased electric field within and around the Au ring at 532 nm (for simplicity, the semiconductor segment was not included in the model; however, a red shift is expected
due to the higher dielectric constants of the semiconductors compared with vacuum).

The generation of vertically aligned perovskite (CH$_3$NH$_3$PbI$_3$) nanowires with controlled diameters have been demonstrated. To form CH$_3$NH$_3$PbI$_3$ nanowires in these templates, a CH$_3$NH$_3$PbI$_3$ precursor solution in dimethylformamide (DMF) was added and allowed to penetrate the pores of the AAO, followed by a removal of excess liquid from the template surface via spin-coating and annealing (Figure 5a, I). While this step results in crystalline perovskite nanowires, solvent evaporation from the AAO surface during annealing led to material contraction such that much of the perovskite material within the template did not touch the bottoms of the pores. In addition, a thin perovskite film remained on the surface of the AAO. To address these synthetic issues, we employed a surface-cleaning step, where a syringe pump dispensed a solution of dimethyl sulfoxide (DMSO) and chlorobenzene on the top of a rapidly rotating AAO template (Figure 5a, II). This solvent mixture dissolved the perovskite (as evidenced by a color change from dark red to transparent), removed residual material from the AAO surface, and drew liquid into the pores via capillary and centrifugal forces. Subsequent annealing led to perovskite recrystallization (as evidenced by the return to a dark red color) and nanowire formation at the bottoms of the pores. In this process, the high surface area at the pore bottoms relative to the pore walls likely favors preferential nucleation and materials growth at these locations, contributing to the formation of CH$_3$NH$_3$PbI$_3$ nanowires that conform to the cylindrical shape of the AAO pores. Importantly, this synthetic procedure can be used to generate large-area nanowire arrays (Figure 5b) over 75 cm$^2$ with uniform nanowires across the sample.

To test whether this procedure is amenable to size control, templates with different pore diameters were prepared. Indeed, CH$_3$NH$_3$PbI$_3$ nanowires with diameters ($D$) ranging from 50 - 200 nm (Figure 5c-g) can be easily synthesized. Importantly, the dispersity in $D$ was <10% for most samples, as measured by SEM.

![Figure 5. Synthesis of perovskite nanowire arrays in AAO. (a) A CH$_3$NH$_3$PbI$_3$ precursor solution penetrates the AAO pores, followed by spin coating and annealing (I); the sample is exposed to a DMSO:chlorobenzene solution followed by a short annealing step (II). (b) Photograph of a ~9 x 9 cm nanowire array. Cross-section SEM images of nanowires with diameters of (c) 50.3 ± 6.5 nm, (d) 70.0 ± 6.8 nm, (e) 107 ± 9.4 nm, (f) 155 ± 13 nm, and (g) 199 ± 19 nm. Nanowire lengths are consistently ~425 nm. Scale bars are 500 nm.](image-url)
2. DNA-mediated assembly of nanoparticles (Mirkin group)

The colloidal crystallization of DNA-modified nanoparticles has been heavily investigated by the Mirkin group and others. More than 500 colloidal crystals in ~40 different lattice symmetries have been realized via DNA-mediated crystallization. When identical nanoparticles are functionalized with two types of DNA that are complementary to each other, they form body-centered cubic (bcc) symmetries, and by a slow cooling crystallization process, these superlattices can grow into microscale rhombic dodecahedral single crystals (Wulff shape of bcc, Figure 6a). As part of the NBIT program, the optical properties of these faceted colloidal crystals have been studied, where strong light-plasmon interactions were observed. Significantly, modes at two different length-scales exist within a single crystal. At the micron-scale, Fabry-Perot type photonic modes exist, which can be tuned by controlling the size and shape of NP, and the volume fraction of the crystal. On the nano-scale, plasmonic modes are produced by individual nanoparticle building blocks and can be controlled by the nanoparticle size, shape, and composition. The two types of modes interact strongly with each other, giving rise to a polaritonic band gap (Figures 6c and d-f), which opens the door to studying exciton-photon coupling in novel photonic plasmonic cavities and exploring new directions in cavity QEDs, quantum optics, and quantum many-body dynamics.

In order to make use of this unique class of metamaterials and illustrate its potential as a novel cavity, excitonic elements can be added into the crystals. Alexa fluor dye molecules can be attached onto the DNA strand by incorporating amino modifier C6 dT at any designated position of the DNA sequence (Figure 7, d1, d2, and/or d3). Each DNA can contain either one dye or multiple dyes. For our initial investigation, only one dye was attached to each DNA strand. The process of attaching fluorophore-labeled DNA onto the NPs and assembling fluorophore-DNA-coated NPs into superlattices can be performed in the same way as when using DNA strands without dye molecules. With this technique, the distance between the dye molecules and the nanoparticle can be tuned with sub-nanometer precision, allowing for the systematic study the interaction between the photonic, plasmonic, and excitonic modes.
Figure 6. A polaritonic photonic crystal (PPC) made by DNA-programmable assembly. (a) Three-dimensional illustration of a plasmonic PPC, in the shape of a rhombic dodecahedron, assembled from DNA-modified gold nanoparticles. Red arrows indicate light rays normal to the underlying substrate, impinging on and backscattering through a top facet of the crystal (Fabry-Perot cavity modes, FPMs). The blue arrows represent light rays entering through the slanted side facets and leaving the PPC through the opposite side, not contributing to the FPMs. The top right inset shows the top view of the crystal with two sets of arrows defining two polarization bases at the top and side facets. The bottom right inset shows an SEM image of a representative single crystal corresponding to the orientation of the top right inset. (Scale bar, 1 μm.) (b) A 2D scheme showing the geometric optics approximation of backscattering consistent with the explanation in (a). The hexagon outline is a vertical cross-section through the gray area in the top right inset of (a) parallel to its long edge. The box enclosed by a dashed line depicts the interaction between localized surface plasmons and photonic modes (red arrows; FPMs) with a typical near-field profile around gold nanoparticles. The contribution of backscattering through the side facets (blue arrows) to FPMs is negligible. (c) Schematic energy diagram for plasmon polariton formation. The localized surface plasmons (yellow bar) strongly couple to the photonic modes (red bars; FPMs). (d-f) Experimental and theoretical backscattering spectra of PPC1–3, having different volume fraction of Au. (d) SEM image (top left) and optical bright field reflection mode image (bottom left) of PPC1 on a silicon substrate. (Scale bar, 1 μm.) On the right, measured backscattering spectrum (red solid line) of PPC1 from the center red spot in the optical micrograph. Calculated backscattering spectra are based on two infinite slab models with BCC crystal geometry (blue solid line) and EMT approximation (blue dashed line). FPMs are indicated by markers. (e,f) The corresponding datasets for PPC2 and PPC3 as in (d). The optical images show bright spots at the center owing to backscattering from the top and bottom facets. All scale bars are 1 μm.
Figure 7. Scheme showing the 3D microcavity geometry (blue, Bottom Right) and a dye-coupled gold nanoparticle (magenta, Top) of dye-functionalized singlecrystal bcc superlattices. An SEM image shows a representative superlattice (Bottom Left). The superlattice is drop-cast onto a glass substrate leading to a facet facing up orientation (Bottom Right). Its RD shape can lead to 3D microcavity properties. L is defined as a vector connecting two vertices (two red dots) with the largest intervertex distance (blue arrow aligned with y axis, Bottom Right). Three Ls can be defined in an RD, and they all pass through the center of the structure. The gold nanoparticles at the lattice sites in the superlattice (Top) are surrounded by multiple dye molecules forming a layer, and the distance between the gold surface and the dye layer is controlled by selecting a dye binding site among three sites (purple circles; denoted d1, d2, and d3 from left to right) on DNA strands. The dye molecules are chosen based on the spectral positions of their emission with respect to that of the surface plasmons, depending on the intended use.

3. Light-irradiated Kelvin probe force microscope (KPFM) (Jang group)

KPFM has been developed to monitor the surface charge state of sample. In KPFM (Figure 8) (reference: Lee et al. Surface Science Reports 66 (2011), 1-27), a conducting cantilever is scanned over a surface at a constant height to map the work function of the surface. When a tip-probe contacts the sample surface, a potential difference ($V_{\text{CPD}}$) is generated owing to difference between the work functions of the sample and KPFM tip-probe. $V_{\text{CPD}}$ can be detected by applying bias ($V_{\text{DC}}$) to the tip-probe using a lock-in amplifier (Figure 8b). $V_{\text{CPD}}$ decreases when the work function of the sample increases (with in-letting electrons). Hence, the change of the surface charge state of sample is sensitively measured by KPFM.

Figure 8. (a) Scheme of Kelvin probe force microscopy (KPFM) and (b) energy band diagram during KPFM measurement. The difference between the work functions of sample and tip is represented as $V_{\text{CPD}}$, which can be detected by applying bias ($V_{\text{DC}}$) to the tip-probe.
Plasmonic excitation will change the surface charge state of sample, and it can be measured by KPFM. Therefore, we set-up a light-irradiated KPFM system (Figure 9). An additional light source, such as a wavelength tunable laser, is implemented to a KPFM spectrometer. One can observe the change of the surface charge state due to the plasmonic excitation of sample by varying the irradiated light wavelength. Therefore, the wavelength-dependent surface charge state of sample (i.e., plasmonic excitation) can be monitored with nanoscale spatial resolution. The light-irradiated KPFM system was established with introducing blue (λ = 450 nm), green (λ = 550 nm), and red (λ = 620 nm) lasers (500 mW) to a multimode atomic force microscope (Dimension ICON, Bruker Inc.). The blue light irradiated KPFM we are using is displayed in Figure 9b.

![Figure 9](image)

**Figure 9.** (a) Schematic diagram of light-irradiated KPFM. V_{CPD} is monitored at the same time with wavelength tunable light irradiation to the sample. (b) A snapshot image of light irradiated KPFM; KPFM measurement is being carried out under irradiation by a blue laser.

4. **Plasmonic nanoparticle-decorated semiconducting nanowires (Jang group)**

Ferromagnetic NWs with plasmonic structures have been fabricated by changing the core materials during COAL. After formation of Au ring structures during COAL, core materials can be chosen to be ferromagnetic. Fe has been deposited inside the empty holes of the AAO, where the Au rings are stuck on the walls inside the holes of the AAO; hence, ferromagnetic NWs decorated by plasmonic structures (Au double rings) were obtained (Figure 10a). Energy-dispersive X-ray spectroscopy (EDS) mapping of the plasmonic structure (the boxed area of Figure 10a) is displayed as an inset and indicates that a Au double-ring structure has been prepared. To control the magnetic moment of the ferromagnetic part of the NW, Fe NWs with Au double rings were drop-dispersed on a substrate with markers (to note the orientation of the NWs). Two directional alignments of the magnetic moments, parallel and perpendicular directions corresponding to the NW axis, are established as shown in Figure 10b. As the next step, the magnetic moment aligned Fe NWs with Au double rings has been characterized by light-irradiated KPFM and MFM for investigating spin-coupled plasmon excitation.
Results and Discussion:

1. Template-assisted synthesis of perovskite nanowires (Mirkin group)

To better understand the effect of nanowire diameter on crystallinity, each sample was characterized by X-ray diffraction (XRD). These measurements confirmed that the target perovskite crystal structure was achieved for each of the nanowire samples (Figure 11). Subsequently, Williamson-Hall (WH) analysis was used to evaluate the relative crystallinity of each sample. This analysis separates the contributions of lattice strain ($\varepsilon_{WH}$) and crystallite size to peak breadth. To perform this analysis, the full-width at half maximum of five diffraction peaks characteristic of the CH$_3$NH$_3$PbI$_3$ perovskite crystal were plotted versus the diffraction angle ($\theta$). For each sample, the data fit well to a linear model, as expected. Interestingly, $D = 110$ nm nanowires reproducibly exhibited the smallest absolute $\varepsilon_{WH}$, with greater $\varepsilon_{WH}$ at both larger and smaller $D$ (Figure 12a). This property is consistent with reduced defect density, which is directly related to the rate of charge recombination.

In order to elucidate structure-function relationships in perovskite nanowires, time-resolved photoluminescence spectroscopy experiments were performed to analyze charge transport dynamics. Decay curves were fit to a biexponential function, such that two distinct populations of excited charge carriers (i.e., those that undergo fast surface recombination vs. slow bulk recombination) could be described. For this comparative study, we report the overall characteristic lifetime ($\tau_c$, which accounts for both populations of charge carriers) as a concise metric to evaluate charge transport within each nanowire sample (Figure 12b,c). As expected from WH analysis, $D = 110$ nm exhibited the longest $\tau_c$ (~60 ns), with reductions in $\tau_c$ observed with both increased and decreased $D$. The correlation between $\varepsilon_{WH}$ and $\tau_c$ suggests that charge carrier lifetime is largely controlled by defect-driven lattice strain in these experiments.
Figure 11. Representative powder XRD patterns of CH$_3$NH$_3$PbI$_3$ nanowires of controlled diameter. Five peaks characteristic to the CH$_3$NH$_3$PbI$_3$ perovskite crystal (space group: I$\bar{4}$mcm) are noted above the pattern for 200 nm nanowires (blue trace), which are consistent among each sample. The full-width at half maximum values of these peaks are subsequently used for Williamson-Hall analysis.
Figure 12. Structure-function relationships in CH$_3$NH$_3$PbI$_3$ nanowire arrays. (a) Estimated strain from WH analysis for different nanowire diameters (negative values signify lattice contraction). (b) Average $\tau_c$ for different nanowire diameters. (c) Representative PL decay curves.

Figure 13. Compositional generality in the templated synthesis of perovskite nanowires. Cross-section SEM images of (a) CH$_3$NH$_3$PbBr$_3$ and (b) Cs$_2$SnI$_6$ nanowires. Scale bars are 500 nm. (c) Powder XRD patterns of CH$_3$NH$_3$PbBr$_3$ and Cs$_2$SnI$_6$ nanowires.
In order to demonstrate the general nature of this approach, perovskite nanowires with a variety of compositions were synthesized. In particular, halide substitution is known to enable bandgap tunability in organolead halide perovskites (~1.55 – 2.3 eV). Use of the appropriate precursor solution and surface cleaning conditions indeed led to CH$_3$NH$_3$PbBr$_3$ nanowires with similar uniformity (Figure 13a). Beyond organolead halide perovskites, Cs$_2$SnI$_6$ has been investigated more recently as an inorganic, air-stable, lead-free alternative. After the synthesis of Cs$_2$SnI$_6$ powder, an analogous method was employed to deposit Cs$_2$SnI$_6$ nanowires from a single precursor solution (Figure 13b). XRD confirmed the expected crystal structures for both CH$_3$NH$_3$PbBr$_3$ and Cs$_2$SnI$_6$ nanowires (Figure 13c), and to the best of our knowledge, Cs$_2$SnI$_6$ nanostructures have not yet been synthesized using any other method.

The work presented here describes a new method for the synthesis of composition general perovskite nanowires with controlled diameter. The substrates used for synthesis (TiO$_2$/fluorine-doped tin oxide (FTO)-bound AAO) should enable a facile transition from fundamental nanowire characterization to array photovoltaic device fabrication, as TiO$_2$, FTO, and AAO can act as a hole-blocking layer, transparent anode, and stabilizing scaffold, respectively, in an operational device. Moreover, the use of AAO in this way provides a unique opportunity to exploit the established synthetic abilities of the Mirkin Group. Specifically, the use of coaxial lithography (COAL) enables the synthesis of shell structures (i.e., rings and tubes) around nanowires with controlled placement and dimensions. We will employ COAL methodology to precisely place plasmonic Au nanorings around functional nanowires (i.e., semiconducting, magnetic; Figure 14a,b) in order to systematically elucidate the effects of plasmonic nanostructures on their optical, electronic, or magnetic properties. Importantly, core-shell nanowire constructs will be connected in parallel as an array; bulk electronic measurements can then be made via contact with the FTO substrate. Indeed, COAL can be executed within thin AAO templates, in which metallic segments (e.g., Ni and Au) can be electrodeposited around a contracted polyaniline core (Figure 14c). Subsequent dissolution of sacrificial segments followed by deposition of the desired nanowire material will enable the synthesis and testing of plasmon-enhanced semiconducting (i.e., photovoltaic) and magnetic nanowire array devices. Future work will focus on the optimization of these syntheses and device testing in which nanowire diameter and nanoring dimensions (outer diameter, inner diameter, and height) and position along the nanowire are systematically varied.
2. Plasmon-exciton interactions in DNA-nanoparticle superlattices (Mirkin group)

The incorporation of dye molecules into the single crystalline nanoparticle superlattices allows the study of interactions among photonic, plasmonic, and excitonic modes. On one hand at the nanoscale, the interaction between the dye dipoles and surface plasmons can be finely tuned by positioning the dye molecules to specific sites of the DNA particle-linker strands, thereby modulating dye-nanoparticle distance, as briefly mentioned in the previous section. On the other hand, the microscopic anisotropic geometry of the superlattices, as represented as the rhombic dodecahedral crystal habit, couples with photonic modes to give directional light emission. DNA-mediated colloidal crystallization offers individual control of these two aspects, and interesting coupling behavior was probed by an experiment performed by the Mirkin group (Figure 15). By using a laser with a wavelength that matches the absorption peak of the dye, in this case 504 nm, dye molecules in the superlattices are excited, and they fluoresce at 550 nm. However, light emitted or transmitted through the center of the superlattice is absorbed by Au nanoparticles, and thus, only the light emitted at the vertices of the rhombic dodecahedral crystal can be observed when the focal plane of the objective lens is at the center of the superlattice (Figure 15a, top). Due to the interaction with Au nanoparticles, the dye molecules also fluoresce at longer wavelength (~650 nm). Since the extinction of Au nanoparticles is less significant at λ=650 nm, light at this wavelength passes through the superlattice and can be detected 3 μm below the superlattice (Figure 15a, bottom). Without the absorption of Au nanoparticles, the superlattice acts as an uncoupled ensemble of dye molecules, as can be seen in the control sample where the Au nanoparticles were etched away (Figure 15c,d). These initial proof-of-concept structures unambiguously show that one can obtain plasmonically modulated directional light emission. The DNA-guided approach to superlattice microcavities described herein provides a versatile platform for building photonic architectures with exciton emission behavior that can be modulated in the spatial, spectral, and time domains for various nano-/microphotonic
applications. In addition, the use of magnetic nanoparticles, for example, magnetite ($\text{Fe}_3\text{O}_4$), as the core materials for this type of colloidal crystallization, enables researchers to investigate the spin- and surface ligand-guided interactions between the magnetic nanoparticles themselves, or more interestingly, magnetoplasmonic interactions when co-crystallized with plasmonic nanoparticles.

Figure 15. Spatio-spectral analysis of microcavity dye emission. Laser pulses ($\lambda = 504$ nm, pulse width $\sim 100$ ps, spot size of $\sim 5 \sim 10$ μm) were used in transmission mode and focused through a 100х objective lens to excite a single superlattice. (a) Spatio-spectral emission profile (Left) of a superlattice ($L \sim 5$ μm, Inset) compared with the theoretical prediction (Middle). The top images were formed with the focal plane located around the center of the superlattice, and the bottom images with the focal plane 3 μm below it (see the scheme in the (b)). Emitted light was collected with a slit cutting through the center of the superlattice (white arrow in (b)) where spatial (vertical axis of the profile, 30 μm) and spectral information (horizontal axis of the profile) were collected simultaneously. (c) Comparable data for a Au-etched control superlattice were investigated to analyze the effect of plasmonic absorbers. The Au-etched control superlattice is transparent under optical microscope due to lack of nanoparticle scattering (Inset). These results of emission behaviors of superlattices in (a) and (c) are described in schemes in (b) and (d), respectively. (Scale bar, 5 μm.)

3. Direct observation of PICS in metal NP/semiconductor NW hybrid system (Jang group)

To evaluate role of the AgNP at a junction between a AgNP and a p-type PPy NW, KPFM measurement on AgNP-attached PPy NWs (PPY$_{AgNP}$ NW) were carried out (Figure 16). A surface potential ($V_{CPD}$) image in dark mode (normal KPFM) of the PPy$_{AgNP}$ NW is displayed with a simultaneously observed topographic image. A line-profile of surface potential at the interface between the AgNP and PPy NW of the PPy$_{AgNP}$ NW is displayed with that of the PPy NW and Ag NP. The blue arrow indicates that the surface potential of PPy NW decreases at the interface, while that of the AgNP increases (indicated by the red arrow). This means that negative charges (electrons) increase at the interface of the PPy NW, and negative charges (electrons) decrease at the interface of the AgNP.

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Figure 16. (a) Topographic image and KPFM images of PPY\textsubscript{AgNP} NW. (b) Surface potential line-profiles of PPY\textsubscript{AgNP} NW, PPy NW, and AgNP. Changes of surface potential at junction and non-junction of AgNP and PPy NW are displayed as red and blue arrows, respectively.

The surface potential of PPY\textsubscript{AgNP} NW in plasmonic excitation was measured by KPFM with blue light (λ=450 nm) irradiation. Because the plasmonic absorption peak of the AgNPs and absorption peak of the PPy NWs exist between 400 nm – 500 nm, plasmonic excitation of the AgNP as well as excitonic excitation of the PPy NW will occur with blue light irradiation. Surface potential line-profiles of the AgNP, PPy NW, and PPY\textsubscript{AgNP} NW are displayed in Figure 17b. The blue arrow indicates that the surface potential of PPy NW increases at the interface, while that of AgNP decreases (red arrow). On the contrary, in the dark for the PPY\textsubscript{AgNP} NW system, negative charges (electrons) decrease and increase at the interface of PPy and AgNP, respectively. This implies that the AgNP works as an “electron donor” in initial contact with PPy NW and works as an “electron accepter” in the plasmonic excitation mode.

Figure 17. (a) Topographic image and blue light irradiated KPFM image of PPY\textsubscript{AgNP} NW. (b) Surface potential line-profiles of PPY\textsubscript{AgNP} NW, PPy NW, and AgNP. Changes of surface potential at junction and non-junction of AgNP and PPy NW are displayed as red and blue arrows, respectively.

As a control experiment, light-irradiated KPFM measurements of AuNPs attached to n-type ZnO NWs (ZnO\textsubscript{AuNP} NW) were carried out. To lower the Fermi energy, an n-type ZnO NW was introduced, where upward bending of the energy band of the semiconductor NW is anticipated at the interface with AuNP. A KPFM image of a ZnO\textsubscript{AuNP} NW in the dark (normal KPFM) and the change of surface potentials of the ZnO NW and AuNP at the junction are displayed in Figure 18b. The blue arrow indicates that the surface potential of ZnO NW increases at the interface, which means the amount of negative charges (electrons)
decreases. Whereas, the surface potential of the AuNP decreases at the interface (red arrow), which means that negative charges (electrons) increase at the interface of the AuNP.

Figure 18. (a) Topographic image and KPFM image of ZnO_{AuNP} NW. (b) Surface potential line-profiles of ZnO NW, ZnO_{AuNP} NW, and AuNP. Changes of surface potential at junction and non-junction of ZnO NW and AuNP are displayed as red and blue arrows, respectively.

The surface potential of the ZnO_{AuNP} NW in plasmonic excitation by green light (λ = 550 nm) irradiation was measured (Figure 19a). The plasmonic absorption peak of the AuNPs exists around 550 nm. Figure 19b shows that the surface potentials of ZnO NW and AuNP oppositely change in plasmonic excitation mode. The blue arrow indicates the decreasing surface potential of ZnO region, while the red arrow indicates the increasing surface potential of the AuNP region in the ZnO_{AuNP} NW by green light irradiation. This result means that negative charges (electrons) decrease and increase, respectively, in the ZnO region and the AuNP region in plasmonic excitation mode of ZnO_{AuNP} NW.

Figure 19. (a) Topographic image and green light irradiated KPFM image of ZnO_{AuNP} NW. (b) Surface potential line-profiles of ZnO_{AuNP} NW in dark mode and in plasmonic excitation mode (green light irradiation). Changes of surface potential in the ZnO and AuNP region by plasmonic excitation are displayed as blue and red arrows, respectively.

In Figure 20, the changes of surface potential of the PPy_{AgNP} NW and the ZnO_{AuNP} NW in the dark and plasmonic excitation modes are summarized as bar graphs. For the PPy_{AgNP} NW system, the AgNP initially (dark mode) works as “electron donor” and then works as an “electron accepter” in plasmonic excitation mode by blue light irradiation. However, the AuNP in the ZnO_{AuNP} NW works as an “electron accepter” in the initial dark mode and works as an “electron donor” in the plasmonic excitation mode (green light irradiation). Hence, we can conclude that metal NPs behavior as either electron donors or acceptors depending on the type of semiconductor NW used.
The Jang group has characterized the role of the metal NP in the metal/semiconductor nanostructured junction with plasmonic excitation of the metal NP. The type of the semiconductor NW is important to determine whether the metal NP works as an electron donor or acceptor. This discovery demonstrates a way to control electron movement in metal/semiconductor nanostructured junctions by means of matching the energy bandgaps of the metal and semiconductor.

4. Spin-coupled plasmonic interactions (Jang group)

In the case of the characterization of the spin-coupled plasmonic interactions of the Fe NW with Au double rings, the surface potential difference of the NW depending on the alignment of the magnetic moment in the NW has been characterized by light-irradiated KPFM measurement. In Figure 21, schemes of two different alignments of the NW are displayed with MFM images; the +z direction represents the magnetic moment alignment perpendicular to the NW axis (μ || +z), while the +y direction represents magnetic moment alignment parallel to the NW axis (μ || +y). Line profiles of surface potential along with the NWs in three different conditions (dark, LSPR on and off) are summarized in Figure 21b-c. When the magnetic moment alignment is perpendicular to the NW axis (μ || +z), the difference between the surface potentials in dark and light irradiation (ΔVCPD) are relatively larger than the ΔVCPD when the magnetic moment alignment is perpendicular to the NW axis (μ || +y) (Figure 21d-f). In the result, we noticed that the surface potential difference reveals three insights: ΔVCPD at the Au double rings is smaller than that at the Fe NW region, ΔVCPD under LSPR is larger than that in the LSPR off condition, and ΔVCPD when the H-field compartment of the irradiating light is perpendicular to the magnetic moment of the NW (μ || +y) is smaller than that when the H-field compartment of the irradiating light is parallel to it (μ || +z). From these observations, spin-coupled plasmonic interactions can be characterized, providing a way to manipulate plasmonic excitations by controlling the spin alignment of the sample system.
Figure 21. (a) Scheme of aligning magnetic moment and surface potential mappings of Fe NW with Au double rings. (b, c) line profiles and (d, f) bar graphs of surface potential and its difference depending on magnetic moment alignment.

List of Publications and Significant Collaborations that resulted from your AOARD supported project: In standard format showing authors, title, journal, issue, pages, and date, for each category list the following:

The Mirkin Group


The Jang Group


**Mirkin-Jang Collaboration**


b) papers published in peer-reviewed conference proceedings,

Nothing to report.

c) papers published in non-peer-reviewed journals and conference proceedings,

Nothing to report.

d) conference presentations without papers,

*Chad A. Mirkin*


3. NCI Alliance in Cancer Meeting, Bethesda, MD; “Spherical Nucleic Acids (SNAs) for the Treatment of Glioblastoma” (2013).


12. The Scientific Research Society (Sigma Xi), Student Research Conference, Raleigh, NC; (2013).


22. American Chemical Society, Dallas, TX; “Nucleic Acid-Modified Nanostructures as Programmable Atom Equivalents: Forging a New ‘Table of Elements’” (2014).
25. American Association for the Advancement of Science, Chicago, IL; “Convergence Science: A Revolution for Health Solutions” (2014).
31. The Sixth International Symposium on Bioanalysis, Biomedical Engineering, and Nanotechnology, Hunan University, Changsha, China; “Intracellular Fate of Spherical Nucleic Acid Nanoparticle Conjugates” (2014).
34. The Twelfth International Conference on Nanostructured Materials, Moscow, Russia; “Spherical Nucleic Acid (SNA) Nanostructures as Intracellular Probes and Gene Regulation Agents” (2014).
35. NBIT Program Review and Nanoscience Technical Exchange, University of California, Berkeley, CA; “Plasmonic Optoelectronic Interactions” (2014).
42. Fermilab Arts & Lecture Series, Batavia, IL; “Nanotechnology: Learning to think big in a field focused on the small” (2014).
43. NCI Alliance for Nanotechnology in Cancer Annual Investigator’s Meeting, Rockville, MD; “Nanomaterials for Cancer Diagnostics and Therapeutics” (2014).
44. SmithGroupJJR Distinguished Lecture, Beckman Institute for Advanced Science and Technology, UIUC, Urbana, IL; “The Nature of the DNA Bond” (2014).
46. Multidisciplinary Chemistry Without Borders, Porto Alegre, Brazil; “Revolutionizing the field of medicine through advances in nanotechnology” (2014).
51. Korean Academy of Science and Technology, Distinguished Lecture, Seoul National University, Seoul, South Korea; “Programmable Atom Equivalents from Nucleic-Acid Modified Nanostructures: Constructing a New ‘Table of Elements’” (2014).
52. Korea Academy of Science and Technology, Prestige Workshop, Seoul National University, Seoul, South Korea; “Biological Properties of Spherical Nucleic Acids” (2014).
53. Korean Academy of Science and Technology, Pioneers in Photonic Nanostructures and Nanophotonics Symposium, Seoul National University, Seoul, South Korea; “Plasmonic Nanostructures and Assemblies Based Upon Them” (2014).


63. Phi Lambda Upsilon-Rho Chapter Award Lecture, University of Nebraska – Lincoln, Lincoln, NE; “The Nature of the DNA Bond” (2015).


66. CIC biomaGUNE Seminar, San Sebastian, Spain; “Programmable Atom Equivalents from Nucleic Acid-Modified Nanoparticle Constructs” (2015).


69. GRC Nucleosides, Nucleotides & Oligonucleotides, Salve Regina University, Newport, RI; “Programmable Materials and the Nature of the DNA Bond” (2015).

70. IARPA Bio Intelligence Chips Program PI Meeting, Livermore, CA; “Biodiagnostic Approaches to Human Profiling Through Nanomaterial Indicators” (2015).

71. Karle Symposium, University of Michigan, Ann Arbor, MI; “Programmable Materials and the Nature of the DNA Bond” (2015).

72. ACS Fall National Meeting, Boston, MA; “Nature of the DNA Bond” (2015).


75. Frontiers Seminar, Case Western University, Cleveland, OH; “Programmable Materials and The Nature of the DNA Bond” (2015).

76. President’s Science Symposium, Bowdoin College, Brunswick, ME; “Nanotechnology: A Small World with Big Potential” (2015).


79. Peking University, Beijing, China; “Nanocombinatorics Through Scanning-Probed Based Chemistry and Biology” (2015).
80. MRS Fall Meeting, Boston, MA, “Programmable Materials and the Nature of the DNA Bond” (2015).
82. MRS Fall Meeting, Boston, MA, “Liposomal SNAs as Immunomodulatory Agents for Cancer Vaccines” (2015).
85. DOE Energy Frontier Research Centers Center for Bio-Inspired Energy Science Mid-Term Review, Gaithersburg, MD, “Pluripotent Nanoparticles: Reconfigurable Programmable Atom Equivalents” (2016).
89. ACS Spring 2016 Conference, San Diego, CA, “Pluripotent nanoparticles with programmable and responsive DNA bonds” (2016).
92. Baylor University Medical Center at Dallas Internal Medicine Grand Rounds, Dallas, TX, “Realizing the Promise of Nanomedicine” (2016).
93. Baylor University Medical Center at Dallas Internal Medicine, Dallas, TX, “Spherical Nucleic Acids: A New Platform in Immunotherapy” (2016).
95. Royal Society of Chemistry Centenary Prize Lecture Series, Glasgow University, Glasgow, Scotland, “Programmable Atom Equivalents and the Nature of the DNA Bond” (2016).
100. Wuxi University, China, "Programmable Materials and the Nature of the DNA Bond" (2016).
102. The 7th International Symposium on Bioanalysis, Biomedical Engineering and Nanotechnology, Hunan University, Changsha, China, “Nanostructures for Tracking RNA in Live Cells with Single Cell Resolution” (2016).
139. ARO Chemical Sciences Division Program Review, Durham, NC, “Infinite Coordination Polymer Particles from Polymeric Coordinating Precursors” (2017).
145. Sixth International Conference on DNA Nanotechnology, Beijing, China, “Crystal Engineering with DNA” (2017).

The Jang Group
Congress of Nano Science & Technology, Qingdao, China; “Tunable Phase Transition above the Percolation Threshold” (2014).


e) manuscripts submitted, but not yet published

Mirkin-Jang Collaboration


f) provide a list any interactions with industry or with Air Force Research Laboratory scientists or significant collaborations that resulted from this work.

- This work in part led to the Center of Excellence for Advanced Bioprogrammable Nanomaterials (C-ABN), Northwestern-AFRL, FA8650-15-2-5518, June 2015-June 2020.
- The Mirkin group has published three papers with AFRL researchers: