Ultrafast Dynamics and Real-Time Spatial Imaging of Plasmonic Excitations in Strongly-Coupled Gold Nanowire Arrays

your name

Scientific Objectives

- **General:** to study the influence of near-field plasmon coupling on the rate and spatial pattern of energy dissipation in arrays of gold nanowires.
- **Specific Aim 1:** Study the relationship between nanowire array plasmon cooling time and plasmon coupling in the full ensemble of nanowires.
- **Specific Aim 2:** Track the spatial propagation of nanowire plasmon energy dissipation following localized excitation of the nanowire array.

Background, Previous Work and Significance of the Research

** *Note: the background and research proposal sections of this example are organized by Specific Aim, but this organizational scheme is not required.* **

- *with respect to Aim 1*:
    - Ultrafast control of light-matter interactions on the nanoscale via plasmonic excitations is of interest for applications including field-enhanced time-resolved spectroscopies and all optical switching.[1-7]
    - The coupling of plasmon oscillations in neighboring nanostructures via near-field dipole interactions is known to influence the extinction spectrum of plasmonic nanostructures.[8-10]
    - Electron-phonon scattering dictates plasmon cooling dynamics on the picosecond timescale, but the effect of near-field coupling on this process has only been investigated in aggregates of gold nanoparticles, and not in a controlled system of ordered nanostructures.[11,12]
    - Coupling between nanostructures on the hundred nanometer length scale is still an active area of inquiry. Is the nature of this interaction entirely dipole-mediated (i.e., any contributions from higher order multipoles)? Can it be modeled in the fashion of excitonic coupling as put forward by Jain, Halas, and Nordlander?[11,13]

- *with respect to Aim 2*:
  - Plasmon energy migration has been studied extensively in the context of surface plasmon polariton propagation in single-direction waveguides.[5,14]
  - No analogous studies have studied the velocity and pattern of plasmon energy diffusion in nanowire arrays.
  - Studying plasmon energy diffusion in a 2D array of strongly coupled nanowires is a way to elucidate the design parameters for waveguides and filters based on propagating surface plasmons with nanoscopic spatial control.

Proposed Research

- *with respect to Aim 1*:

Experimental Plan

- Fabricate arrays of Au nanowires separated by dielectric medium.
  - Close-packed wire arrays typically fabricated by electrodeposition of gold into anodized aluminum oxide templates (~60 nm diameter, ~40 nm spacing, ~400 nm long).[15,16]
- Vary plasmon dipolar coupling.
  - Change wire spacing.
  - Alter dielectric of wire matrix (ie quartz, ZnO, etc instead of alumina).
- Systematically vary electronic heat capacity of Au nanowire plasmon
  - Surface chemistry of gold modifies rate of plasmon cooling.[17]
  - Amine vs thiolated polymer or small molecule.
- Monitor change in plasmon dynamics with respect to both variables, determine whether wire spacing has a significant influence relative to dielectric medium heat capacity.
  - Use transient absorption to follow change in plasmon extinction after excitation of Au nanowire plasmon mode.
  - Previous work from Jain suggests that greater coupling should result in faster cooling – coupling between nanowires will increase the rate of energy dissipation.[11,12]

Experimental Challenges and Contingency Plans

- Potentially difficult to independently vary electronic heat capacity and near field plasmon coupling.
  - Dope quartz/silica to change dielectric while minimally changing heat capacity.
  - Use polymer systems with similar backbone, different binding groups (all organic materials have dielectric ~1-2, change in binding group will influence electronic heat capacity of gold).
- Plasmon heat dissipation may degrade organic materials.
  - Focus on inorganic dielectric environment.

- *with respect to Aim 2*:

Experimental Plan

- Excite plasmonic nanowire array at a diffraction limited spot, follow spatial motion of energy dissipation between nanowires via transient absorption microscopy (TAM).[18,19]
  - Excite coupled, longitudinal mode of gold nanowire array.[16]
  - Probe plasmon extinction as a function of both space and time.
- Track velocity, propagation length, and pattern of energy dissipation as a function of nanowire spacing.
  - In a 2D array of nanowires, does plasmonic excitation move as a random walk?
  - Is this motion instead entirely dictated by momentum of initiating laser pulse?
  - Closer wire spacing may lead to faster plasmon propagation, but ultimately lower the total propagation length due to enhanced rate of energy loss.
- Test the extent to which coupling is broken between nanowires at the interface of excited and ground state nanowires.
  - Coupling between nanowires dictated in part by overlap in plasmon frequency, which changes upon excitation and electron heating.

    - Probe at the interface – does the plasmon extinction spectrum change depending on whether the plasmonic nanowires are no longer coupled as strongly?

Experimental Challenges and Contingency Plans

- It would be most instructive to record transient spectra of the entire plasmon spectrum, and transient absorption microscopy with white light probe is technically challenging.
    - May be impossible to achieve diffraction limited white light spot.
    - At best, will have difficulties with varying focus volumes depending on probe wavelength.
    - Potentially mitigated by using reflective focusing optics rather than lenses and choosing a probe spot based on the reddest probe wavelength (ie not entirely diffraction limited at all WL).
    - Could also construct spectra one probe wavelength at a time by probing with white light filtered through a monochromator.
- Spatial resolution of TAM may not be sufficient to see emergent patterns in plasmon energy propagation.
    - New electron microscopy techniques based on the photoemission of electrons from plasmonic nanostructures may offer necessary space and time resolution.[14,20]
    - Could track energy diffusion by coating nanowires with fluorescent molecules and following PL intensity. Would reveal path of energy diffusion, but would not show the motion of plasmonic excitation as a function of time.[21]

References (at least 15; not included in the page count)

see formatting instructions in the Graduate Program Guide.