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Electronic Relaxation Dynamics in Isolated and Aggregated Hollow Gold Nanospheres

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Nanoparticles often display strikingly different chemical and physical properties than their bulk counterparts. Perhaps more intriguingly, these properties vary widely with particle size and shape. One example exhibited in metal nanoparticles is the surface plasmon resonance (SPR), which provides selective enhancement of molecular spectroscopies such as surface-enhanced Raman spectroscopy (SERS)[1] and metal-enhanced fluorescence (MEF).[2] Potential surface plasmon contributions to nano-optics include three-dimensional photon delivery in nanoscale devices.[3] Carefully prepared, closely spaced nanoparticles will undergo near-field coupling and provide a nanostructured waveguide that promotes the coherent propagation of electromagnetic radiation for particles smaller than the wavelength of light. Hollow gold nanospheres (HGNs) and dielectric core−shell particles can be used to extend the flexibility of device design based on plasmonic materials; the SPR spectral position can be tuned across the visible and near-infrared region by varying the shell diameter/thickness aspect ratio.[4,5] We demonstrate that interparticle electromagnetic coupling enhancement can be achieved by using aggregates of HGNs.

Here, we report for the first time on the electronic relaxation pathways of HGNs and examine electromagnetic coupling in aggregates of these particles. Comparisons of both the electron−electron and electron−phonon scattering processes of HGNs and HGN aggregates are made using femtosecond time-resolved transient absorption measurements. Experimental details and HGN synthesis and characterization are described in the Supporting Information. TEM and optical absorption measurements indicated the particles had an outer diameter of 48 ± 5 nm and a shell thickness of 7 ± 1 nm. Nanoparticle aggregation was induced by addition of KCl to the colloidal HGN suspension while stirring, which results in particle necking. Absorption, HRTEM, and TEM-EDS analyses confirmed HGN integrity following aggregation. Dynamic light scattering (DLS) measurements indicate the aggregate diameter is 800 ± 300 nm.

The absorption spectra of colloidal and aggregated HGN are shown in Figure 1A. The colloidal HGN solution yielded a single SPR peak at 605 nm, consistent with previous characterizations of similarly sized particles.[4] The HGN absorption was monitored from 350 nm to 2 μm, and no other additional peaks were observed. The single SPR results from the particle's spherical symmetry, which makes all transitions degenerate. The SPR spectral position depends directly on the HGN diameter/thickness aspect ratio.[4a] Upon aggregation, the absorption unexpectedly shifted to bluer wavelengths, approaching the 520-nm solid nanosphere value. This effect was reproduced on multiple hollow nanosphere samples. The observed shift appears small, but it indicates that the plasmonic

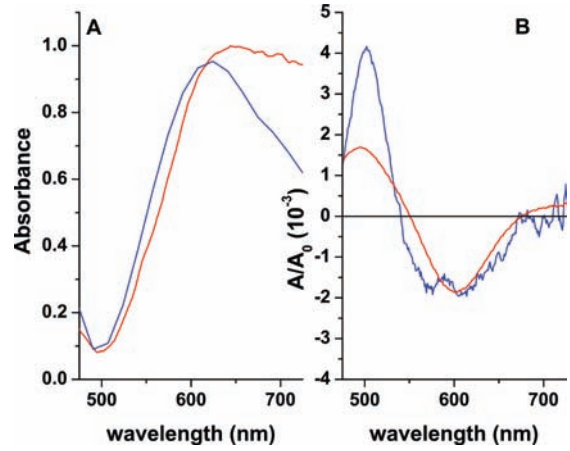

Figure 1. (A) Absorption spectra of colloidal HGNs (red) and hollow gold nanoparticle aggregates (blue). A clear blue shift in the aggregate spectrum is apparent. (B) Femtosecond transient absorption spectra of HGNs (red) and hollow gold nanoparticle aggregates (blue) (HGN-agg). The nanospheres are excited with 405 nm (500 nJ/pulse) and probed at 500 fs time delay with a white-light continuum probe. The aggregate spectrum contains two negative amplitude (bleach) features centered at 550 and 605 nm.

nature of the nanospheres was retained upon aggregation. To our knowledge, this is the first-ever report of blue-shifted absorption upon metal nanoparticle aggregation. Previous spectroscopic measurements on small gas-phase Au and Ag nanoclusters and subsequent single-particle measurements revealed SPR that is blue-shifted with respect to Mie theory-based approximations.[6] This effect was attributed to electron "spill-out", or confinement, in these small nanoclusters. Previous[7] and current (see Supporting Information) examination of solid MNPs indicated that aggregation led to red-shifted and extended absorption profiles. Interestingly, when hollow NPs were substituted for solid NPs, aggregation resulted in both a blue-shifted SPR and a retention of peak width, suggesting preserved plasmon coherence in the aggregates.[8] The observed absorption blue shift could result from delocalization over multiple particles, forming new SPR, and this is supported by finite-difference time-domain (FDTD) calculations (Supporting Information). Time-resolved transient absorption measurements were used to further investigate the cause of the blue shift in HGN aggregates.

For both systems, the 5d electrons of gold were excited using the 405-nm second harmonic of an amplified Ti:sapphire laser, and the relaxation dynamics were tracked with a white-light continuum probe that monitors the SPR bleach at 550 and 605 nm for the HGN-agg and HGN, respectively. The transient absorption spectra recorded at a 500-fs probe temporal delay for both HGN and HGN-agg are shown in Figure 1B. The transient absorption spectrum of the aggregate system clearly shows two distinct regions of bleach-

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ing, corresponding to two different transitions (populations). The bleach at 605 nm arises from the negative amplitude of HGN differential SPR absorption following electronic excitation; the 550-nm bleach may be a new resonance resulting from particle−particle interactions.

The kinetic traces for HGN-agg and HGN were obtained by temporal integration of the 550-nm and 605-nm regions of the transient bleach spectrum. The time domain data are shown in Figure 2A. Both the electron−electron and electron−phonon scattering events occur more rapidly for HGNs than for the aggregate system or similarly sized spherical particles.[9,10] In fact, both processes are remarkably fast in HGN. To quantify this effect, the electron−electron scattering lifetimes are determined to be 150 ± 70 fs (HGN) and 300 ± 50 fs (HGN-agg) by convoluting the fit function with the instrument response. The electron−phonon coupling step of the relaxation process was treated with the well-established two-temperature model to determine the electron−phonon coupling constant (g) for these systems.[11] The electron−phonon coupling time as a function of relative excitation pulse energy is shown in Figure 2B. The y-intercept of these linear fits was taken as the electron−phonon coupling lifetime for each system. Note that care was taken to ensure all data was taken in a low-power, linear excitation regime. For HGN a T^0_{el-ph} of 300 ± 100 fs was observed; a longer T^0_{el-ph} of 730 ± 140 fs was determined for HGN-agg, in contrast to solid nanospheres.[7a] These lifetimes correspond to HGN $g_{HGN} = 6.6 \times 10^{16}$ W m^{-3} K^{-1} and $g_{HGN\text{-}Agg} = 2.7 \times 10^{16}$ W m^{-3} K^{-1}.

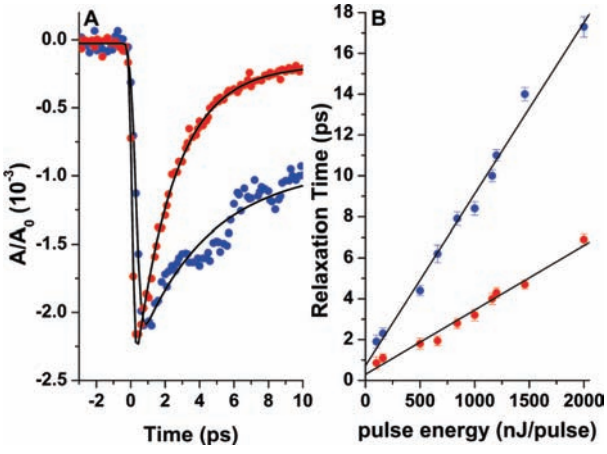

Figure 2. (A) Femtosecond transient absorption bleach recovery comparison of HGN (red) and HGN aggregates (blue) obtained with the same excitation conditions. The HGN bleach recovery is much slower for the aggregate system. (B) Electron−phonon scattering lifetime plotted as a linear function of relative laser power. The laser pulse energies used spanned 100 nJ/pulse to 2 μJ/pulse. The y-intercept provides the electron−phonon coupling lifetime of the HGN (red) and aggregate (blue) systems. Details of the fitting procedures are provided in Supporting Information.

We demonstrated that the electron−phonon coupling lifetime of colloidal HGNs was remarkably fast, whereas the aggregate system has a lifetime that approaches the 750-fs value of solid spherical nanoparticles and bulk systems.[9c,f] For comparison, our results from examination of solid 50-nm particles are provided in the SI. The short electron−phonon coupling time we observed for HGN was 40% of the value obtained for HGN aggregates. Previous studies on silver and gold nanoparticles showed electron−phonon coupling times of small (2−5 nm) nanoclusters can be as short as 35%−50% of bulk values.[11] Our observations reported here, along with previous work on small nanoclusters, suggest that the ultrafast electron−phonon coupling times of HGN are surface/volume effects, resulting from spatial confinement of electrons in the very thin shell of the HGN. The SPR-spectral shifts and relaxation lifetimes approaching values of large spherical particles and bulk solution that are demonstrated by the HGN aggregates indicate the presence of interparticle coupling. That is, prompt electron scattering occurs over multiple particles, and subsequent electron−phonon coupling occurs over a larger bath. Similar observations have been made on small gold nanoparticles.[13,14] This can be viewed as delocalization of the Fermi-gas across many particles in an aggregate, resulting in electron and phonon scattering through the entire system.

Important future experiments include a systematic study of the dependence of interparticle coupling on the particle aspect ratio. These first experiments on HGN aggregates show promise for controlled energy transport over nanometer-length scales that can arise from the spatial confinement properties of thin-shell hollow particles that spread the metal atoms over a larger area of space.

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Supporting Information Available: Complete ref 12; synthetic protocol and characterization, including TEM images, XRD, DLS, and FDTD calculations; description of the femtosecond TA apparatus and fitting procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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