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Project Title: Photothermal and Charge-Transfer Dynamics of Aluminum Nanomaterials for Plasmon-Sensitized Photocatalysis

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Research efforts over the last year have focused on the following lines of inquiry:

1) *Investigation of size and surface-dependence of photothermal energy transfer mechanisms in solution-processed Al nanomaterials.* The photothermal properties of solution-processed aluminum nanoparticles, particularly how phonon energy transfer depends on particle size and surface

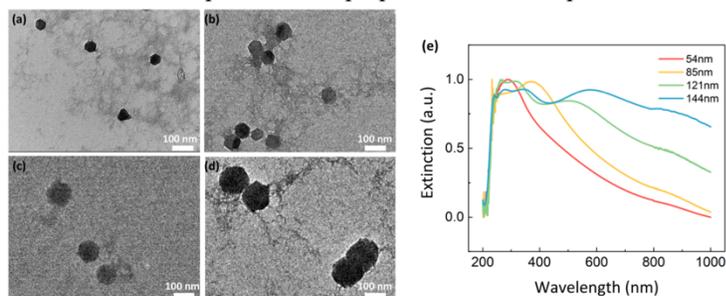


Figure 1: (a-d) TEM images of 54, 85, 121, and 144 nm Al particles with native oxide shell. (e) Visible/NIR Al particle solution-phase extinction spectra (normalized to peak intensity).

particles as a result of electron-to-phonon energy transfer and lattice expansion.¹ Periodic modulation in probe transmission associated with coherent phonon/acoustic vibrations were also resolved as was a slow thermal energy transfer from particles to the surrounding medium. A simple two-interface (Al/Al oxide/solvent) model revealed that the rate of local heating of the solvent is facilitated by the intermediary aluminum oxide, which quickly and efficiently mediates thermal energy transfer from the Al core to the surrounding medium.

In the last year, we completed a larger study of how photothermal energy transfer is impacted by both size and surface properties of these particles. This work used transient absorption spectroscopy (TAS), in combination with simulations of phonon and thermal energy dissipation, to investigate the photoresponses of aluminum nanoparticles of various diameters (54, 85, 121, and 144 nm) suspended in 2-propanol; images of particles and their extinction spectra are shown in Figure 1. In our TAS measurements, we observed signatures of coherent phonon vibrations in the time-dependence of optical spectra (Figure 2a) with periods and damping

transfer depends on particle size and surface properties, are critical for practical applications and are currently under-explored. We previously reported on the photothermal energy-transfer dynamics of solution-processed, single-crystal aluminum nanoparticles (~100 nm diameter) suspended in 2-propanol (IPA), observing rapid (sub-ps to ps) electron-phonon energy transfer followed by changes in the scattering cross-section of

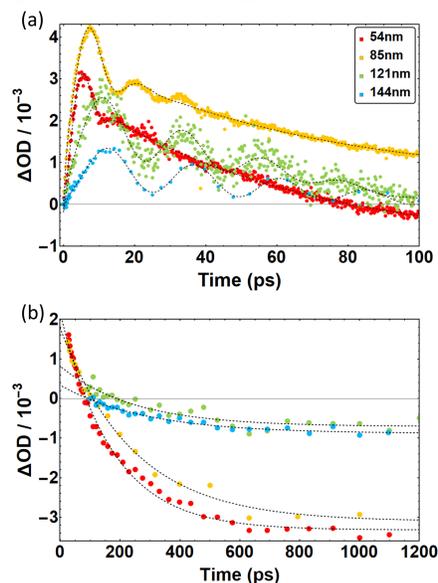


Figure 2: Time-dependence of near-IR Al particle extinction following plasmon excitation. (a) Signal evolution associated with coherent phonon breathing. (b) Signal evolution associated with thermal energy transfer to solvent.

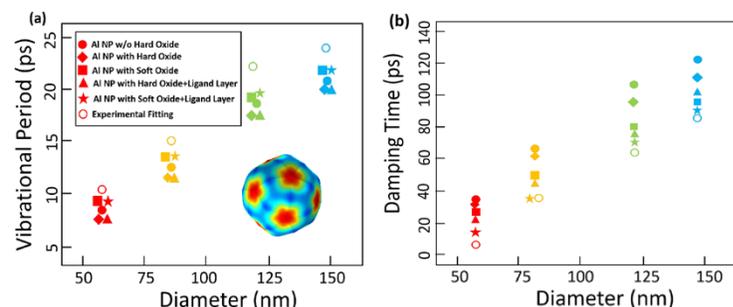


Figure 3: Comparison of experimental and finite element calculations for Al particle phonon vibrational period (a) and dephasing time (b). The inset of (a) illustrates the displacement of the fundamental radial mode for a 144-nm particle with a 4-nm oxide shell.

times decreasing with smaller NP sizes; homogeneous vs. inhomogeneous contributions to damping were differentiated from experimental data by accounting for sample dispersity as determined by TEM imaging. A series of finite element simulations was undertaken to analyze trends observed in experiment; results for damping and dephasing timescales are summarized in Figure 3a and 3b, respectively. Phonon models considered

particle sizes and the effects of the crystalline vs. non-crystalline nature of the native oxide shell as well as the presence of surface ligands. In total, we find the best agreement for vibrational period and dephasing time requires both a non-crystalline oxide shell and a ligand shell, although the oxide shell character dominates the vibrational period and the ligand shell dominates the dephasing time. We also observed fast (170-280 ps) heat transfer to solvent for NPs of all sizes (Figure 2b) mediated by the native oxide shell. This is substantiated by results of a two-interface model for heat transfer.

Thus, our study provides insight on the roles of surface composition and particle size on both the photothermal and photoacoustic properties of Al-based plasmonic NPs: by adding or subtracting “soft” surface components, such as oxide or polymer shells, phonon damping rates and thermal energy transfer times can be systematically increased or decreased. This effect could be useful for tuning nanoparticle properties “on demand” through prescriptive design for applications in photocatalysis, sensing, and medicine. This work is currently under review with *ACS Photonics* (Submitted August 2019).

2) Ligand replacement strategies for aqueous suspensions, electron transfer studies, and oxide shell growth.

In initial work, we synthesize oleic acid-capped Al nanoparticles suspended in 2-propanol via reduction of AlCl_3 by LiAlH_4 and titanium(IV) isopropoxide catalyzed reaction of $(\text{CH}_3)_2\text{C}_2\text{H}_5\text{NAlH}_3$ with 1,4-dioxane in tetrahydrofuran and oleic acid. Over the past year, we have been building on this work by exploring different ligand exchange processes to suspend the particles in water, perform electron transfer studies, and facilitate shell growth of metal oxides. Using aqueous suspensions of Al nanoparticles would give us the flexibility to explore hydrothermal growth methods for metal oxide shells of photocatalytic materials, including titanium dioxide. We are also interested in conducting experiments using organic electron acceptors as ligands anchored to the native Al oxide shell to explore whether electrons can efficiently tunnel through that shell, enabling the Al particles to act as hot electron plasmonic sensitizers.

To address whether hot electrons can tunnel through this surface oxide layer, we synthesized a phosphate-functionalized methyl viologen (MV^{2+}) derivative, referred to as PFMV, as a surface-bound ligand (Figure 4) and preliminarily used it to interrogate photoinduced electron transfer from TiO_2 . The spectro-electrochemistry of this ligand is similar to MV^{2+} : ligand reduction occurs promptly when TiO_2 is excited above its band gap, resulting in characteristic spectral features in the visible (630 nm) and near UV (350-400 nm). Next, we developed a ligand exchange procedure based on using a sequence of solvents with different polarities to attach PFMV directly to the Al nanoparticles, replacing some of the oleic acid ligands, and re-suspending the particles in water. Fourier Transform Infrared (FTIR) measurements show the presence of vibrational resonances associated with both phosphonic acid and imine stretches, indicating that the exchange was successful. Current efforts are focused on TAS studies of the PFMV-ligated particles to study electron transfer.

Additionally, we have been working on methods to grow titanium dioxide shells directly onto pre-synthesized aluminum nanoparticle cores. We are developing a ligand exchange method to replace the oleic acid ligands with citric acid-based ligands that should enable water solubility as a first step for TiO_2 shell growth. We are investigating two potential shell growth methods, inspired by previous methods for growing TiO_2 shells on metal nanoparticle cores.^{2,3} The first involves suspending the citric acid-capped Al nanoparticles in an aqueous l-arginine solution, then using a series of ligands with functional groups meant to enable TiO_2 shell nucleation. Titanium isopropoxide is the catalyst that initiates TiO_2 shell growth. The second method involves dispersing the Al nanoparticles in ethanol and adding tetrabutyl orthotitanate to initiate shell growth. We plan to test and refine these methods in the coming months, followed by TAS studies of photothermal and electron transfer processes on the core-shell particles. Successful metal oxide shell growth would broaden the range of applications for our plasmonic aluminum nanoparticle systems.

Educational impacts of activities: The work completed in the last year has involved 3 Ph.D. students, 1 Master’s and 1 undergraduate student. The publication described above will be a significant component of dissertation research for the two principle (graduate) student authors; both will be graduating within the coming year. One of the Ph.D. students was supported to present the results of this work at the 2019 Materials Research Society (MRS) Spring Meeting in Phoenix, AZ in the form of an oral presentation (“Size-Dependent Photoresponse of Plasmonic Aluminum Nanoparticles”). Opportunities such as this allow students to share their results with the field and gain a deeper understanding of and context for their research. Support of this research is helping to sustain a collaboration between the PI and co-PI that has made significant strides in the last year, including identification of promising future funding support for related work on plasmonic materials.

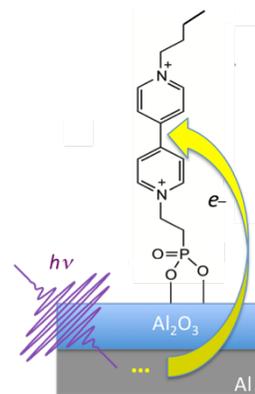


Figure 4: Phosphate-functionalized methyl viologen derivative for electron transfer

¹ K. J. Smith, Y. Cheng, E. S. Arinze, N. E. Kim, A. E. Bragg, S. M. Thon. *ACS Photonics* **5**, 805-813 (2018).

² W. L. Liu, F. C. Lin, Y. C. Yang, C. H. Huang, S. Gwo, M. H. Huang, J. S. Huang. *Nanoscale* **5**, 7953 (2013).

³ J. Shao, W. Sheng, M. Wang, S. Li, J. Chen, Y. Zhang, S. Cao. *Appl. Catal., B* **209**, 311-319 (2017).