Plasmonic Aerosols

Jeffrey Geldmeier, Paul Johns, Nicholas J. Greybush, Jawad Naciri, and Jake Fontana
U.S. Naval Research Laboratory
4555 Overlook Ave. SW, Washington, D.C. 20375
(Dated: October 1, 2018)

Plasmonic nanoparticles resonantly couple to and confine light below the diffraction limit. This mechanism has enabled a modern renaissance in optical materials with potential applications ranging from sensing and circuitry to renewable energies and in medicines. Yet, these plasmonic materials are constrained to only a few phases of matter, typically as dilute liquids or solid two-dimensional surfaces, thereby limiting opportunities. Here, we introduce the concept of a plasmonic aerosol and experimentally realize this phase of matter by transitioning liquid suspensions of gold nanorods into the gas phase and simultaneously measuring their optical spectra. The plasmonic aerosol absorption peaks are sharp and well-defined with quality factors as large as 2.5. We show by controlling the aspect ratio of the nanorods that the aerosol absorption peaks are broadly tunable over 2,500 nm, from visible to mid-wave infrared wavelengths. We find for large aspect ratio gold nanorods that the aerosol absorption peak wavelength is extraordinarily sensitive (≈ 4,000 nm per refractive index unit) to changes in the refractive index of the gas and this sensitivity depends linearly on the aspect ratio. This work establishes a novel phase of plasmonic matter, potentially enabling exciting opportunities for fundamental and applied research.

PACS numbers: 71.45.Gm, 42.68.Jg, 78.67.Qa, 64.70.Nd

The relationship between aerosol particles and cloud systems is a poorly understood nonlinear process and is the largest uncertainty to accurately predicting climate and extreme weather events.1,2 Aerosol particles serve as nucleation sites for water molecules to condense into droplets, forming clouds. Recent work posited that aerosol particles from the exhaust of ships enhanced the intensity and electrification of storms, showing that the aerosol particles from the exhaust of ships enhanced the formation, but have recently been shown to significantly intensify the convective strength of cloud systems.3 Moreover, ultrafine aerosol particles (diameter < 50 nm) where once thought to be too small to influence cloud formation, or remote sensing.4 Yet, these plasmonic materials remain aerosolized indefinitely. Gold is also an inert metal, making it bio-compatible and environmentally friendly. Additionally, recent gram-scale gold nanorod synthesis breakthroughs have now made these materials accessible.5

Plasmonic aerosols are promising candidates for benchtop aerosol studies. They couple strongly to light, leading to the capability to optically detect them in dilute concentrations and they are also sensitive to changes in their surrounding environment. The imaginary electric susceptibility of a plasmonic nanoparticle is, \( \chi = \beta\omega_p^2/((L\omega_p^2 - \omega^2)^2) \), where \( \beta \) is the dampening constant, \( L \) is the depolarization factor, \( \omega_p \) is the plasma frequency and \( \omega \) is the frequency. The imaginary susceptibility, and consequently the absorption, is a maximum at resonance, \( \omega = \sqrt{L}\omega_p \), yielding, \( \chi_{\text{max}} = \omega_p/(\beta\sqrt{L}) \).6,7,8

In this Letter, we aerosolize gold nanorods from liquid suspensions into a gas phase and measure their optical spectra at bench-top scales, thereby demonstrating a novel phase of plasmonic matter. By tailoring the aspect ratio (length, \( l \), to diameter, \( d \)) of the nanorods, we show that the aerosol absorption peaks are tunable from visible to mid-wave infrared wavelengths. We find the sensitivity of the longitudinal absorption peak wavelength to the refractive index of the host medium depends linearly on the nanorod aspect ratio and can be estimated from the geometric and material properties of the nanorod. Utilizing this sensitivity dependence, we show changes of the host refractive index of 10\(^{-4}\) may be detectable, suggesting plasmonic aerosols may be useful for environmental or remote sensing.

In Fig. 1(a) we present the conceptual experimental apparatus to transition aqueous suspensions of gold nanorods from the liquid phase into the gas phase and simultaneously measure the optical response (see Sup-
FIG. 1. Conceptual experimental apparatus to aerosolize and optically measure gold nanorods in the gas phase in situ is shown in (a). The absorbance spectra of high aspect ratio gold nanorods in the gas, (b), and liquid phase, (c). A representative transmission electron microscopy image is shown in (d) and the corresponding aspect ratio statistics in (e). The scale bar in (d) is 500 nm.

The gold nanorods were synthesized using wet-seed mediated synthesis approaches, tuning the aspect ratio from 1.5 to 38.9–11 Transmission electron microscopy was used to measure the polydispersity of the nanorods, yielding less than 10% for aspect ratios smaller than 20 and 25% for larger aspect ratios. To aerosolize the nanorods, a Venturi tube was used to drive high velocity air over a reservoir of gold nanorods in a liquid suspension, pulling the suspension into the airstream and then through a small orifice. Upon exiting the orifice, the liquid suspension breaks apart into an aerosol containing liquid droplets (diameter ∼ 300 nm) with embedded nanorods. The droplets then enter a dehumidifier chamber, evaporating the water droplets from the nanorods, thereby creating a suspension of dry nanorods in the gas phase.

To measure the in situ absorbance spectra of the gold nanorods in the gas phase, a 10 m optical path length Herriott cell was placed at the exit of the dehumidifier. The Herriott cell was integrated into a Fourier transform infrared spectrometer, enabling the optical signatures of the plasmonic aerosols to be measured. The absorbance spectrum of gold nanorods in the gas phase was measured in Fig. 1(b), revealing a well-defined absorption peak at 3.3 µm. The relatively large Q-factor ($\lambda_0/\text{FWHM}$) of 1.3 in Fig. 1(b) strongly supports the nanorods not being flocculated or aggregated in the gas phase.

FIG. 2. Experimental spectra of gold nanorods with aspect ratios ranging from 1.5, 2.5, 3, 4.5 in water to 10, 15, 30 in toluene, (a), and 5, 15, 30 in air, (c). Three dimensional finite element simulation spectra in (b) and (d) mimicking the experimental parameters and phases in (a) and (c).
sorbance spectrum to be measured in the liquid phase, Fig. 1(c). Transmission electron microscopy, Fig. 1(d), and corresponding statistics, Fig. 1(e), determined the aspect ratio of the nanorods to be 32.3 ($l = 646 + 156 \text{ nm}$, $d = 20 + 4 \text{ nm}$).

The aspect ratio of the gold nanorods were varied from 1.5, 2.5, 3, 4.5 in water to 10, 15, 30 in toluene in Fig. 2(a), demonstrating nearly a decade in wavelength tunability from 0.6 to 5 $\mu$m in the liquid phase. The optical response of gold nanorods in the gas phase with aspect ratios of 5, 15 and 30 are shown in Fig. 2(c), spanning over 2.5 $\mu$m in wavelength tunability.

Three dimensional finite element simulations (COMSOL Multiphysics) in Fig. 2(b) and Fig. 2(c) were used to replicate the experimental spectra, showing good agreement of the absorbance peak wavelength as a function of aspect ratio and host solvent. The Q-factor from the simulated spectra are larger than the experimental spectra due to experimental variations in the aspect ratio of the nanorods.

To understand the spectroscopic evolution of the evaporating water-nanorod droplets, further simulations were carried out in Fig. 3. Initially, a nanorod ($l = 60 \text{ nm}$, $d = 25 \text{ nm}$) was surrounded with water, yielding an extinction peak wavelength at 670 nm (red curve), Fig. 3(a). The nanorod was then embedded into a water droplet of diameter, $D = 200 \text{ nm}$ and surrounded by air (orange curve). The peak wavelength remained constant, however the magnitude of the peak increases by $\sim 1/3$ due to the increased scattering contribution to the extinction from the water droplet. As the diameter of the water droplet radially decreased to 61 nm, mimicking evaporation, the peak wavelength blue shifted to 624 nm (green curve). The extinction peak then jumped to 582 nm when $D = l = 60 \text{ nm}$, Fig. 3(b), due to the ends of the nanorod being exposed to air. For droplet diameters less than the length of the nanorod the extinction peak remains constant, only slightly increasing in magnitude once all the water is removed.

Fig. 3(c) shows the extinction, scattering and absorption cross sections of a large aspect ratio gold nanorod ($l = 450 \text{ nm}$, $d = 20 \text{ nm}$) as the diameter of the water droplet decreases from $D = 1,000 \text{ nm}$ to $D = l = 450 \text{ nm}$. The most striking feature as the water droplet evaporates is the decrease in the visible wavelength scattering. The albedo ratio, scattering to extinction cross sections, are 0.066 for the $l = 60 \text{ nm}$ nanorods and 0.366 for the $l = 450 \text{ nm}$ nanorods.

The longitudinal absorption peak wavelength is related to the refractive index of the host medium, $n_m$, by 

$$\lambda = \lambda_p \left[ 1 + (1 - L_{||}) (n_s^2 - n_m^2) f + \left( \frac{1}{L_{||}} - 1 \right) n_m^2 \right]$$  \hspace{1cm} (1)

where $\lambda_p$ is the plasma wavelength of gold, $n_s$ is the dielectric constant of the ligand shell coating the nanorods, and $f$ is the ellipsoidal volume fraction of the inner nanorod to the outer ligand shell. The depolarization factor of the long axis of the nanorod is $L_{||} = ((1 - e^2)/e)((1/2e)(\ln(1-e)/(1+e)) - 1)$, where $e = \sqrt{1 - (l/d)^2}$.

If the nanorods are very long ($1/L_{||} >> 1$) and there is no ligand shell ($n_s = n_m$), then Eq. 1 can be differentiated with respect to $n_m$ and series expanded about $L_{||}$ to approximate the sensitivity,

$$\frac{\partial \lambda}{\partial n_m} \approx \frac{\lambda_p}{\sqrt{L_{||}}}$$  \hspace{1cm} (2)

This result implies from the geometric, $L_{||}$, and material, $\lambda_p$, properties of the nanorod, the shift in the absorption peak wavelength can be estimated as the host medium surrounding the nanorods is varied.

To validate Eq. 2, we carried out experiments and simulations measuring the absorbance peak wavelength as the aspect ratio of the gold nanorods was varied from 7.5, 13, 16.8, 33 and 38 in toluene and air, Fig. 4(a). As anticipated, the simulations showed the absorbance peak wavelength depends linearly on the aspect ratio of the nanorods, $\lambda_{toluene} = 0.135(l/d) + 0.422$ and $\lambda_{air} = 0.0883(l/d) + 0.359$, and the peak red-shifts as the refractive index of the host medium increases.\[14\] The experimental data agrees well with the simulation data, within experimental uncertainty.

In Fig. 4(b) we find the sensitivity also depends linearly on the aspect ratio, $\partial \lambda/\partial n_m = 0.098(l/d) + 0.133$, where $n_m$ is the refractive index of the host medium.\[13\]
FIG. 4. Evolution of the absorbance peak wavelength and sensitivity as the nanorod aspect ratio and host refractive indices are varied are shown in (a) and (b), respectively. The simulated absorbance spectra for plasmonic aerosols as a function of host gases is shown in (c).

for the data retrieved from the simulations (solid line). This result is supported by the good agreement with the experimental data. For smaller aspect ratios, the relationship in Eq. 2 is confirmed (dashed line), providing a straightforward means to predict the sensitivity. For larger aspect ratios, Eq. 2 begins to diverge from the simulation data (e.g., 18% at aspect ratio = 45) showing the limitations of the simple relationship.

The absorbance peak wavelength shifts are ~ \( \mu m \) per refractive index unit (RIU) in Fig. 4(b). This large sensitivity implies very small changes in the host medium can be detected. To investigate this possibility, simulations of gold nanorods with an aspect ratio of 30 were performed in He, Air, and CO\(_2\) gases, Fig. 4(c). The absorbance peak wavelength shifted from 3,275.94 nm for He to 3,277.25 nm for CO\(_2\), showing that changes of \( \Delta n_m \approx 10^{-4} \) may be detectable at atmospheric transmission window wavelengths.[15]

In conclusion, we united the fields of plasmonics and nanoparticle aerosols by efficiently transitioning gold nanorods into the gas phase and measuring the optical response, demonstrating for the first time a plasmonic aerosol. We suggested at mid-wave infrared wavelengths that plasmonic aerosols may be useful in aiding geoengineering challenges. The full consequences of transitioning liquid and solid phase plasmonic properties to the gas phase remains an open question and warrants future investigations.

We thank Kyoungweon Park, Richard Vaia, Tiffany Sutton, Jerold Bottiger and Brendan Delacy for useful discussions. This material is based upon work supported by the Office of Naval Research under (N0001418WX00122). See Supplemental Material at https://journals.aps.org/prl/.

---

* ASEE-NRL Postdoctoral Fellow
† NRC-NRL Postdoctoral Fellow
‡ Corresponding author: jake.fontana@nrl.navy.mil

[1] I. P. O. C. Change, *Climate Change 2013: The Physical Science Basis* (Cambridge University Press, 2013).
[2] C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley-VCH, New York, NY, 1988).
[3] J. A. Thornton, K. S. Virts, R. H. Holzworth, and T. P. Mitchell, *Geophysical Research Letters* 44, 9102 (2017).
[4] J. Fan, D. Rosenfeld, Y. Zhang, S. F. Giangrande, Z. Li, L. A. T. Machado, S. T. Martin, Y. Yang, J. Wang, P. Artaxo, H. M. J. Barbosa, R. C. Braga, J. M. Comstock, Z. Feng, W. Gao, H. B. Gomes, F. Mei, C. Phlker, M. L. Phlker, U. Pschl, and R. A. F. de Souza, *Science* 359, 411 (2018).
[5] J. W. Keith, *Proceedings of the National Academy of Sciences* 107, 16428 (2010).
[6] L. V. Besteiro, X.-T. Kong, Z. Wang, F. Rosei, and A. O. Govorov, *Nano Letters* 18, 3147 (2018).
[7] V. B. Koman, P. Liu, D. Kozawa, A. T. Liu, A. L. Cottrill, Y. Son, J. A. Lebrón, and M. S. Strano, *Nature Nanotechnology* (2018), 10.1038/s41565-018-0194-z.
[8] O. D. Miller, C. W. Hsu, M. T. H. Reid, W. Qu, B. G. DeLacy, J. D. Joannopoulos, M. Soljaini, and S. J. Johnson, *Physical Review Letters* 112, 123903 (2014).
[9] K. Park, M.-s. Hsiao, Y.-J. Yi, S. Iozor, H. Koerner, A. Jawaid, and R. A. Vaia, *ACS Applied Materials & Interfaces* 9, 26363 (2017).
[10] Y. Takenaka and H. Kitahata, *Chemical Physics Letters* 467, 327 (2009).
[11] B. P. Khanal and E. R. Zubarev, *Journal of the American Chemical Society* 130, 12634 (2008).
[12] J. Fontana, G. K. B. da Costa, J. M. Pereira, J. Naciri, B. R. Ratna, P. Palffy-Muhoray, and I. C. S. Carvalho, *Applied Physics Letters* 108, 081904 (2016).
[13] J. Yang, J. C. Wu, Y. C. Wu, J. K. Wang, and C. C. Chen, *Chemical Physics Letters* 416, 215 (2005).
[14] J. Fontana, R. Nita, N. Charipar, J. Naciri, K. Park, A. Dunkelberger, J. Owutsaka, A. Piquu, R. Vaia, and B. Ratna, *Advanced Optical Materials* 5, 1700335 (2017).
[15] F. Neubrech, A. Pucci, T. W. Cornelius, S. Karimi, A. Garca-Etxarri, and J. Aizpurua, *Physical Review Letters* 101, 157403 (2008).