Colloidal optics for advanced nanomaterials

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Keywords:
Colloidal synthesis, plasmonics, Raman spectroscopy, electron microscopy

Light-utilizing technologies are expected to play an increasingly important role to tackle large challenges our society faces, with applications in photocatalysis, harvesting solar power, and (bio)chemical sensing [1] [2]. The ability to efficiently direct optical signals to and from the functional parts of the advanced materials needed for these applications is crucial for the success of these technologies. However, conventional objectives used in laboratory settings are often bulky and expensive. In our research we explore the use of colloids as additional refractive elements to deliver high optical signals to and from functional materials at the nanoscale.

Our current focus is the use of colloidal optics in combination with plasmonic nanoparticles to obtain unprecedented surface enhanced Raman spectroscopy (SERS) signals [3]. State of the art SERS signals are achieved by confining an analyte between a gold nanoparticle (AuNP) and a gold mirror (figure 1b *left*). This geometry is limited by the shallow emission angle of the signal, which in combination with typical microscopy objectives leaves most of the light unused. We show effective re-angling of Raman emissions by growing a dielectric nanolens onto the surface of the AuNP (figure 1a and 2b *right*). The size of the nanolens can be reliably controlled (figure 1c), and we observe up to an order of magnitude increase in SERS signals with increasing nanolens diameter (figure 1d). This increased sensitivity allows for time-resolved measurements of the binding dynamics of small analytes to the gold surface [4], showcasing the systems potential use as a probe to investigate chemical reaction pathways.

Through synthesis and characterization of the colloidal system we aim to gain fundamental understanding of its (physical-)chemical properties. This knowledge is applied to direct synthesis pathways towards specific colloidal morphologies and create new functional nanomaterials. Our work is often validated and complimented by numerical simulations.

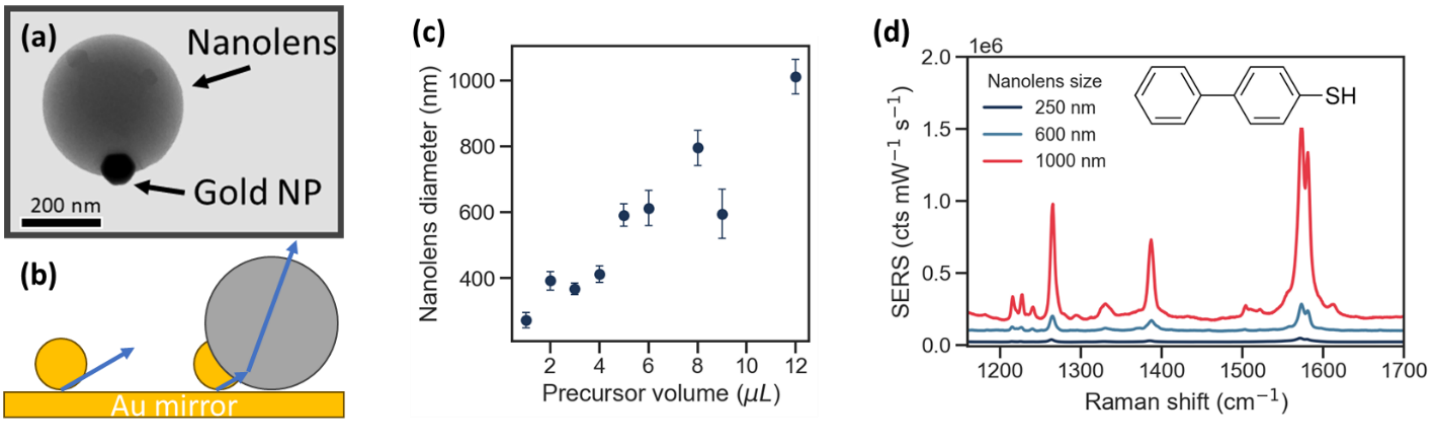

Figure 1: (a) TEM micrograph of a AuNP with a nanolens attached to its surface. (b) Schematic showing emission angles for a AuNP with and without nanolens. (c) Nanolens diameter as a function of the precursor volume. Size determined from TEM, error bars indicate the standard deviation of the lens size. (d) Typical SERS spectra of biphenyl-4-thiol for varying nanolens diameters. spectra for 600 nm and 1000 nm are offset for clarity.

References

[1] M. J. Groom, E. Miele, J. Pinnell, M. G. Ellis, J. B. McConnell, H. Sakr, G. Jasion, I. Davidson, N. Wheeler, Y. Jung, F. Poletti, S. Menkin, M. Kamp, J. J. Baumberg and T. G. Euser, "Microlens Hollow-Core Fiber Probes for Operando Raman Spectroscopy," *ACS Photonics*, vol. 11, no. 8, pp. 3167-3177, 2024.

[2] Q. Wang, C. Pornrungroj, S. Linley and E. Reisner, "Strategies to improve light utilization in solar fuel synthesis," *Nature Energy*, vol. 7, pp. 13-24, 2022.

[3] M. Kamp, B. De Nijs, N. Kongsuwan, M. Saba, R. Chikkaraddy, C. A. Readman, W. M. Deacon, J. Griffiths, S. J. Barrow, O. S. Ojambati, D. Wright, J. Huang, O. Hess, O. A. Scherman and J. J. Baumberg, "Cascaded nanooptics to probe microsecond atomic-scale phenomena.," *Proceedings of the National Academy of Sciences*, vol. 117, no. 26, p. 14819–14826, 2020.

[4] J. Huang, D.-B. Grys, J. Griffiths, B. d. Nijs, M. Kamp, Q. Lin and J. J. Baumberg, "Tracking interfacial single-molecule pH and binding dynamics via vibrational spectroscopy.," *Science Advances*, vol. 7, no. 23, 2021.