Strangely Shaped Plasmonic Nanoparticles

Thomas A. Klar
Institute of Applied Physics, Johannes Kepler University Linz, 4040 Austria
thomas.klar@jku.at

Metallic nanoparticles are apt to modify the luminescence yield of fluorophores in their immediate nano-environment. They influence both the nonradiative and the radiative rate. The latter can be tuned that much that even Purcell-like changes of the fluorescence spectra are observable. Besides, nanoparticles have been identified to improve the intrinsic luminescence from gold by several orders of magnitude.

In order to gain deeper insight into the interaction of luminescence and fluorescence with localized plasmons, we investigated a range of gold nanoparticles of complex shape such as bipyramids, stars or sponges. We demonstrate applications of plain and silver-enhanced gold nanostars for random lasing or for increasing the electroluminescence in organic light emitting devices (OLEDs). In the case of random lasing, we have shown that nanostars can support random lasing over a very wide spectral range, spanning almost a full octave from the visible to the IR. As active materials, fluorophores in solution or in a solid matrix may be used, as well as pi-conjugated polymers and quantum dots.

Plasmons can also substantially improve the quantum efficiency of the intrinsic luminescence from gold stemming from the recombination of d-band holes with sp electrons. While the fluorescence yield of extrinsic fluorophores is inherently linked to the hot spots of localized plasmonic resonances just outside the nanoparticles (e.g. at the intimate surface of, or in between two almost touching nanoparticles), we have actually observed an anticorrelation of the intensity of the d-band luminescence with the intensity of the hot spots between two gold nanoparticles. It will be discussed that, instead of the hot spot intensity between two nanoparticles, it is the electric field intensity inside the nanoparticles as well as the spectral dispersion of the gold-intrinsic d-band hole recombination probabilities that matters. Besides, we also observed and simulated gold luminescence supported by higher order plasmonic modes.

In the case of three dimensionally percolated, sponge-like gold nanoparticles, we observe highly polarized light scattering, which excludes the assignment of an effective medium dielectric constant to the nanosponges. In contrast to the scattering response, however, we find far less polarization dependence for the intrinsic fluorescence from small gold nanosponges.

[1] E. Dulkeith *et al.*, "Fluorescence Quenching of Dye Molecules near Gold Nanoparticles: Radiative and Nonradiative Effects", Phys. Rev. Lett., **89,** 203002 (2002).
[2] M. Ringler, A. Schwemer, M. Wunderlich, A. Nichtl, K. Kürzinger, T. A. Klar, and J. Feldmann, "Shaping Emission Spectra of Fluorescent Molecules with Single Plasmonic Nanoresonators", Phys. Rev. Lett., **100,** 203002 (2008).
[3] G. T. Boyd, Z. Yu, and Y. R. Shen, "Photoinduced luminescence from the noble metals and its enhancement on roughened surfaces", Phys. Rev. B, **33,** 7923 (1986).
[4] E. Dulkeith, T. Niedereichholz, T. A. Klar, J. Feldmann, G. von Plessen, D. I. Gittins, K. S. Mayya, and F. Caruso, "Plasmon emission in photoexcited gold nanoparticles", Phys. Rev. B, **70,** 205424 (2004).
[5] D. Sivun, C. Vidal, B. Munkhbat, N. Arnold, T. A. Klar, and C. Hrelescu, "Anticorrelation of photoluminescence from gold nanoparticle dimers with hot-spot intensity", Nano Lett., **16,** 7203 (2016).
[6] J. Ziegler, M. Djiango, C. Vidal, C. Hrelescu, and T. A. Klar, "Gold nanostars for random lasing enhancement", Opt. Exp., **23,** 15152 (2015).
[7] J. Ziegler, C. Wörister, C. Vidal, C. Hrelescu, and T. A. Klar, "Plasmonic nanostars as efficient broadband scatterers for random lasing", ACS Photonics, **3,** 919 (2016).
[8] B. Munkhbat, J. Ziegler, H. Pöhl, C. Wörister, D. Sivun, M. C. Scharber, T. A. Klar, and C. Hrelescu, "Hybrid Multilayered Plasmonic Nanostars for Coherent Random Lasing", Journal of Physical Chemistry C, **120,** 23707 (2016).
[9] C. Vidal, D. Wang, P. Schaaf, C. Hrelescu, and T. A. Klar, "Optical Plasmons of Individual Gold Nanosponges", ACS Photonics, **2,** 1436 (2015).
[10] C. Vidal, D. Sivun, J. Ziegler, D. Wang, P. Schaaf, C. Hrelescu, and T. A. Klar, "Plasmonic Horizon in Gold Nanosponges", Nano Lett., **ASAP,** DOI: 10.1021/acs.nanolett.7b04875 (2018).
[11] C. Gollner *et al.*, "Random Lasing with Systematic Threshold Behavior in Films of CdSe/CdS Core/Thick-Shell Colloidal Quantum Dots", ACS Nano, **9,** 9792 (2015).
[12] B. Munkhbat, H. Pöhl, P. Denk, T. A. Klar, M. C. Scharber, and C. Hrelescu, "Performance boost of organic light emitting diodes with plasmonic nanostars", Adv. Opt. Mat., **4,** 772 (2016).