

New Architectures of Photon Avalanching Nanoparticles for Sub-Diffraction Imaging

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Lanthanide-doped photon avalanching nanoparticles (ANPs) represent a unique and highly-nonlinear class of upconverting nanoparticles (UCNPs), which under lower-energy near-infrared (NIR) excitation emit higher-energy visible light. In ANPs a small increase in the laser excitation power (e.g. by 1%) can lead to a dramatic enhancement of the emission intensity (e.g. 100%). This is due to the exponential scaling of emission intensity with excitation power density ($I \sim P_s$) by a factor, s , which represents the nonlinearity of an upconversion process.

The nonlinearity factor, s , can reach values of 30 and higher for photon avalanching process vs. 2-5 for the conventional upconversion emission. Although avalanche-like processes in UCNPs have been observed early on [1], true ANPs, operating at room temperature conditions, were discovered only recently [2]. Due to the highly nonlinear excitation-emission characteristic of these ANPs, they were showcased as optical probes capable of breaking the diffraction limit of conventional laser scanning microscopes, allowing us to resolve structures below 100 nm.

Further development of ANPs is expected to open more possibilities in biomedical applications of sub-diffraction imaging, ultra-sensitive analyte detection, and precision drug delivery. Current research efforts are directed in developing ANPs of varied compositions and architectures – fine-tuned for these specific tasks. Particular improvements are being sought in creating libraries of ANPs for multiplexing applications, in reducing excitation power threshold to initiate photon avalanching processes, and in improving imaging speeds in laser scanning microscopy. These features can be obtained by creating heterostructured core/shell ANPs in which the photon avalanching properties of ions can be adopted by other ions within rationally engineered energy transfer networks. Here, we explore questions associated with developing such ANPs and present a library of heterostructured ANPs that could be fit for undertaking challenges beyond the reach of conventional UCNPs.

[1] E. S. Levy, C. A. Tajon, T. S. Bischof, J. Iafrati, A. Fernandez-Bravo, D. J. Garfield, M. Chamanzar, M. M. Maharbiz, V. S. Sohal, P. J. Schuck, B. E. Cohen, E. M. Chan, Energy-Looping Nanoparticles: Harnessing Excited-State Absorption for Deep-Tissue Imaging. *ACS Nano* **2016**, *10* (9), 8423–8433.

[2] C. Lee, E. Z. Xu, Y. Liu, A. Teitelboim, K. Yao, A. Fernandez-Bravo, A. M. Kotulska, S. H. Nam, Y. D. Suh, A. Bednarkiewicz, B. E. Cohen, E. M. Chan, P. J. Schuck, Giant Nonlinear Optical Responses from Photon-Avalanching Nanoparticles. *Nature* **2021**, *589* (7841), 230–235.