Controlled Reduction of Photobleaching in Plasmon Enhanced Fluorescence Using Collapsible Nano-Fingers

B. Song[1], Z. Liu[1], Y. Wang[1], Y. Li[1], H. Yang[1], D. Meng[1], B. Chen[1], P. Hu[1], T. Ou[1], S. Cronin[1], A. Schwartzberg[2], S. Cabrini[2], and W. Wu[1*]
[1]University of Southern California
[2]Lawrence Berkeley National Laboratory
[*]E-mail: wu.w@usc.edu

Plasmonic nanostructures have recently received attention because of their ability to concentrate light to small volumes. This property gives rise to numerous potential applications in optical communication, disease diagnosis, and chemical sensing. We have reported a technology based on collapsible nano-fingers to fabricate down to sub-nanometer gap plasmonic structures with high precision, high reliability and high throughput deterministically [1]. The basic schematic is shown in Figure 1. Precisely controlled nano-gap arrays down to sub-nanometer in large area can be produced using collapsible nano-fingers. The gap size is well defined by twice the thickness of the ALD dielectric layer. Figure 2a and 2b are SEM images of the collapsible nano-fingers before and after collapse. Figure 2c is the TEM image of the dielectric nano-gap in the nano-fingers with 2 nm TiO_2 coating. Figure 2d, 2e and 2f are the corresponding EDS mappings of Au, Ti and O in this TEM image. Nano gap exist in Au mapping, while there is no gap in either Ti or O mapping. That indicates uniform and conformal ALD film provides reliable and accurate control on the gap size. This technology enables us to put active materials at the hottest part of optimally designed gap plasmonic hot spot, which is a great platform for optimally enhancing molecular fluorescence.

The physical approach to harvest more photons from fluorescent molecules is based on enhancing the radiative decay rate of the fluorophore k_r. As the molecule spends shorter times in the excited state before the emission of a photon, it can perform more excitation−emission cycles before undergoing photobleaching. The way to physically enhance k_r is based on Fermi's "golden rule". The key factor is the density of photon states at the emission frequency ν. A higher photonic mode density (PMD) of the right frequency and polarization facilitates a faster radiative decay of the excited fluorophore. Remarkably, most investigations on plasmonic enhancement of molecular fluorescence have focused on enhancing intensity and the emission directionality. Despite its fundamental practical significance, the possibility of increasing photostability of fluorophores by means of an enhanced PMD has remained rather unexplored. While a shorter distance between a fluorophore and metallic nanoparticles offers stronger electromagnetic coupling thus higher PMD, it also facilitates better energy transfer that further reduce photobleaching. However, quenching effect increases significantly as the distance between fluorophore and metallic nanoparticles reduces. The energy transfer mechanism to metallic nanoparticles in fluorescence quenching is short-ranged, which depletes the photon emission process in the vicinity of fluorophores. In the meanwhile, energy transfer in long range from fluorophore to metal could be further exploited to prevent photobleaching, which is essentially irreversible thermal destruction.

We propose a method to reduce photobleaching in plasmon enhanced fluorescence with ultrastrong fluorescence enhancement using collapsible nanofingers. A gold layer was deposited onto substrate before ALD process which inherently increase PMD by coupling between gold nanoparticles and gold substrates. Figure 3a shows the fluorescence intensity of Nile blue enhanced by collapsible nanofingers compared to non-collapsible nanofingers and plain glass, which shows ~2000 enhancement factor. Figure 3b shows the reduction of photobleaching using collapsible nanofingers with gold coated substrate. With the controlled reduction of photobleaching in this ultrastrong plasmon enhanced fluorescence, we pave the way for further accurate chemical detection and biological sensing. This is the ideal tool with high sensitivity and stability.

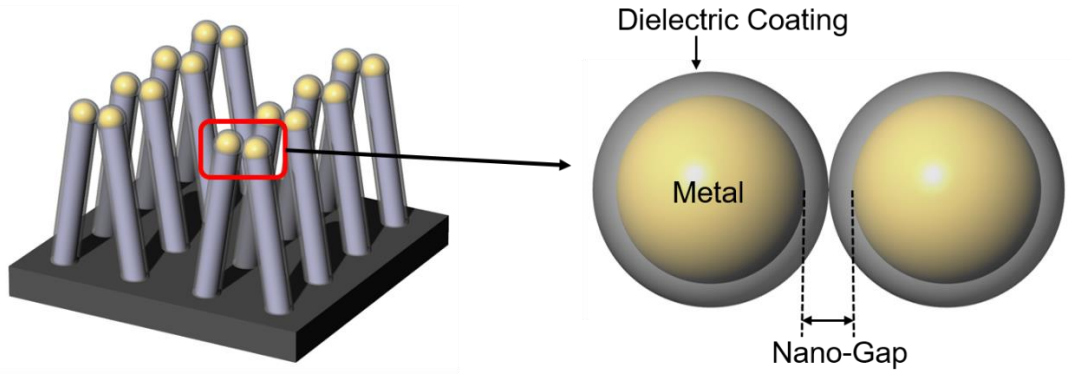

Figure 1. Schematic of controllable hot spots created using nano-fingers.

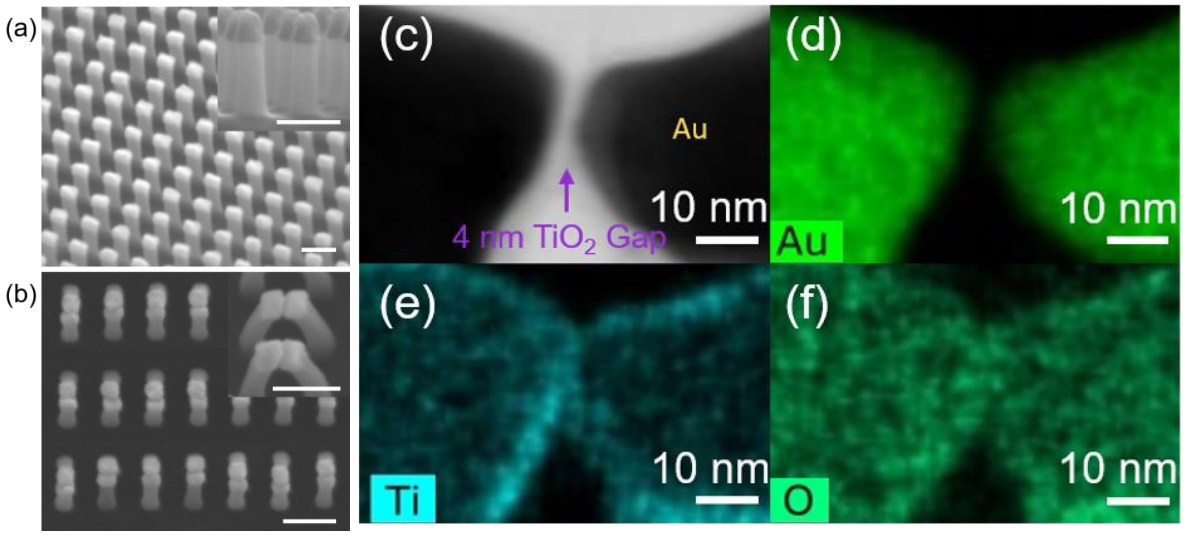

Figure 2. (a) SEM image of nano-fingers before collapse. (b) SEM images of nano-fingers after collapse. (c) TEM image of the dielectric nano-gap in the nano-fingers with 2 nm TiO2 coating. (d) (e) (f) EDS mapping of Au, Ti and O in the TEM image.

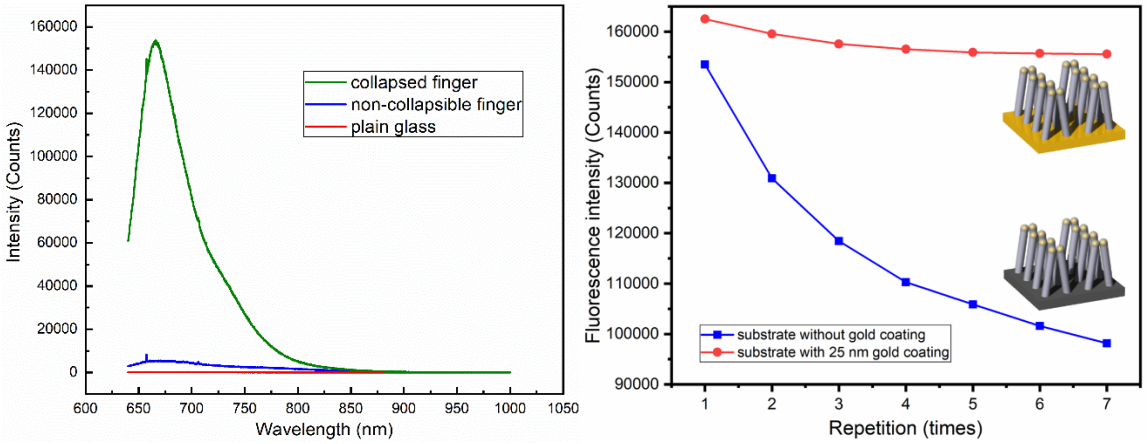

Figure 3. (a) Fluorescence intensity of Nile blue on collapsed nanofingers with 5 nm Al_2O_3 gap, non-collapsible nanofingers with same Al_2O_3 coating and plain glass. (b) Repeated fluorescence intensity measurement at same spot on nanofingers with and without gold coating on substrate.

References

[1] B. Song, Y. Yao, R. Groenewald, Y. Wang, H. Liu, Y. Wang, Y. Li, F. Liu, S. Cronin, A. Schwartzberg, S. Cabrini, S. Haas, W. Wu, Probing Gap Plasmons Down to Sub-Nanometer Scales Using Collapsible Nano-Fingers. *ACS Nano*. 2017 Jun 27;11(6):5836-5843.