Probing the Mechanisms of Strong Fluorescence Enhancement in Plasmonic Nanogaps with Subnanometer Precision

B. Song[1, 2], Z. Jiang[2], Z. Liu[2], Y. Wang[2], H. Yang[2], D. Meng[2], B. Chen[2], P. Hu[2], T. Ou[2], S. Cronin[2], A. Schwartzberg[3], S. Cabrini[3], S. Haas[2] and W. Wu[2*]
[1]Huazhong University of Science and Technology
[2]University of Southern California
[3]Lawrence Berkeley National Laboratory
[*]E-mail: wu.w@usc.edu

Fluorescence has many useful applications, including single molecule detection, biological labelling, and optoelectronic devices. Since the fluorescence of molecules can be strongly enhanced by increased excitation electromagnetic (*EM*) field intensity, plasmon-enhanced fluorescence (PEF) technology is now widely adopted, utilizing the enhancement of *EM* fields in the vicinity of metal nanostructures. However, while many attempts have been made in recent years to further improve the performance of PEF in applications that require high sensitivity and precision, progress has been fundamentally limited by fluorescence quenching effects in the emission process.

It has recently been demonstrated that ultra-strong *EM* fields can be realized in-between pairs of plasmonic nanostructures, which are formed by metallic nanoparticles with sub-nanometer inter-particle gaps. Here, precise control of the physical gap at the sub-nanometer scale is critical to form strong and stable plasmonic hotspots. On the other hand, fluorescence quenching in the molecular emission process has been demonstrated at sub-5 nm scales. Two main factors pose serious obstacles to understanding the mechanisms leading to fluorescence quenching experimentally. One key factor that determines fluorescence quenching is the distance between the molecule and the metal. In order to experimentally investigate the mechanism behind the continuous transition from fluorescence enhancement to fluorescence quenching, one thus needs to vary molecule-metal distance continuously with sub-nanometer precision in the vicinity of the optimally designed plasmonic hotspots. Furthermore, since experimentally measured fluorescence intensities are simultaneously affected by the local field enhancement and fluorescence quenching mechanisms, they cannot be directly used to study the contributions from both physical processes independently.

We demonstrated a technology to experimentally investigate plasmon enhanced fluorescence at the sub-nanometer scale, where strong fluorescence quenching occurs. We have experimentally identified optimal gap sizes for maximum plasmon enhanced fluorescence with tunable dielectric spacers. This technology enables us to position fluorophore molecules in the hottest region of gap plasmonic hotspots, resulting in ultra-strong field enhancement (Figure 1). The nanofinger fabrication results including SEM and TEM images are shown in Figure 2. Using this approach, we have simultaneously observed fluorescence and the Raman signal in the same spectra, which enables the interpretation and analytical modeling of the leading fluorescence quenching mechanism at small gap sizes. (Figure 3) This platform provides an opportunity to analyze plasmon enhanced fluorescence with in-situ monitoring of the local field enhancement, which enables the exclusion of the field enhancement contribution, thus isolating the quantum mechanical quenching mechanism. These results provide the guidance for the future design of plasmon enhanced applications, such as chemical sensing and biological labeling which require ultra-high sensitivity and accuracy.

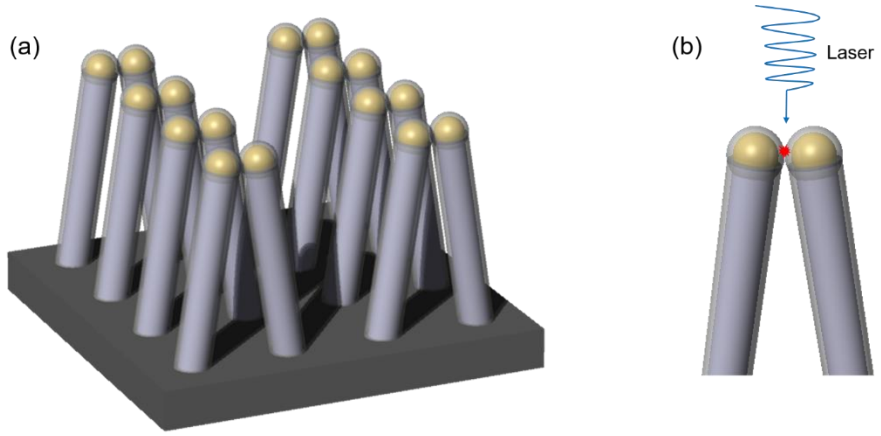

Figure 1. Schematic diagram of controllable plasmonic hot spots for fluorescence enhancement created by collapsible nanofingers.

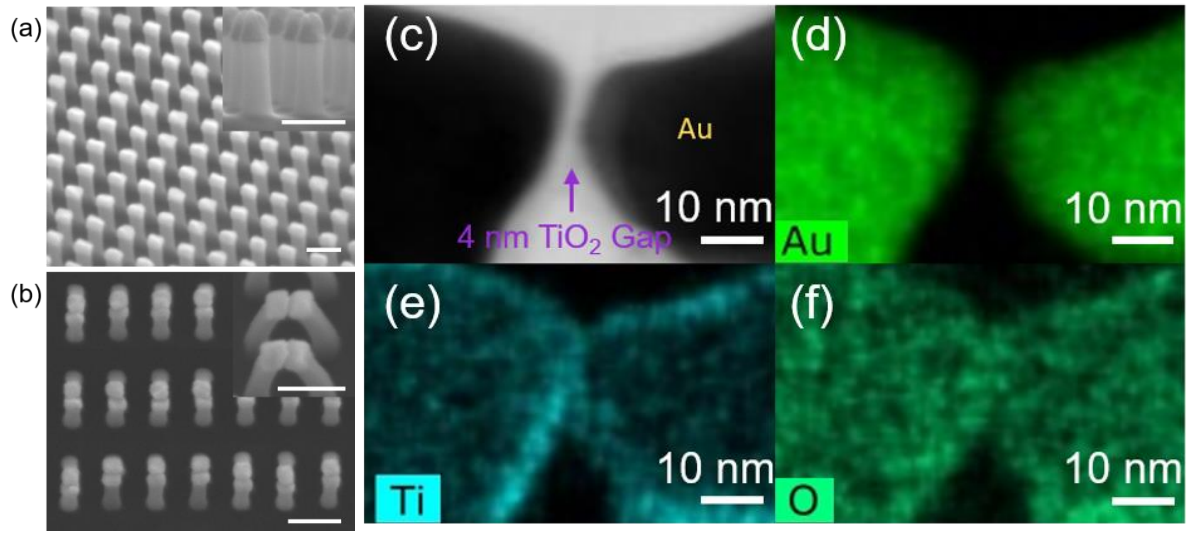

Figure 2. (a) SEM image of nano-fingers before collapse. (b) SEM images of nano-fingers after collapse. (c) TEM image of the dielectric nano-gap in the nano-fingers with 2 nm TiO2 coating. (d) (e) (f) EDS mapping of Au, Ti and O in the TEM image.

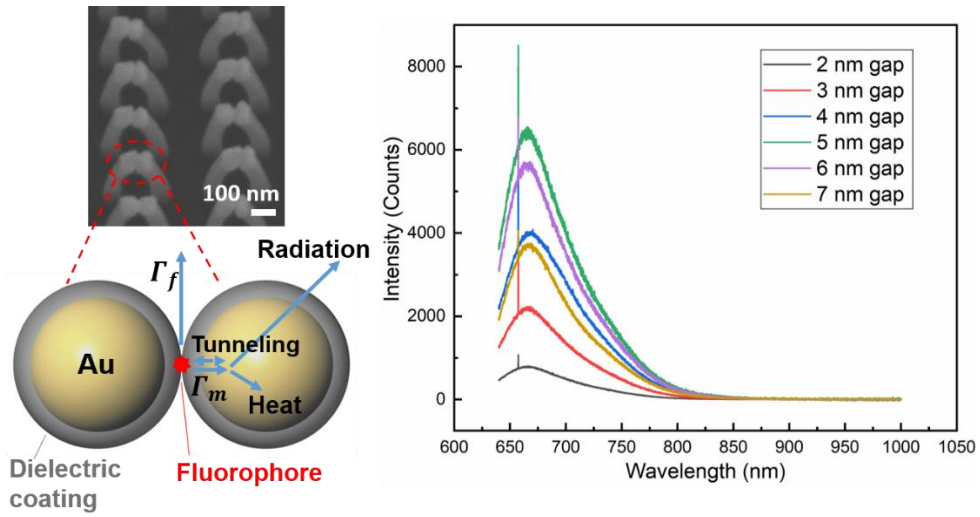

Figure 3. Schematic of quantum mechanical fluorescence quenching mechanism and typical spectra of Nile Blue enhanced by collapsed nanofingers exhibiting fluorescence and Raman signals simultaneously.