Investigation of Plasmonic Enhancement of Molecular Fluorescence Using Collapsible Nano-Fingers

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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. Last year, 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.

Metallic nanoparticles are known to dramatically modify the spontaneous emission of nearby fluorescent molecules and materials. Here we examine the role of the gap plasmon resonance on the molecular fluorescence enhancement. Considering quenching effect, the distance between fluorescent molecules and gold nanoparticles should not be too small in order to obtain strongest enhancement. In that sense, to fully exploit plasmonic enhancement on the fluorescent molecules, an appropriate gap size should be kept between the molecule and each metallic nanoparticle, which separates molecules away from the metal to avoid quenching effect. The ALD-defined gap plasmonic nano-finger structure facilitate direct and precise control on the gap size between the molecule and metallic nanoparticle by simply changing ALD film thickness that has atomic precision. This makes collapsible nano-fingers the ideal structure for the optimization of molecular fluorescence enhancement. We examined both oxazine 1 (OX-1) and IR-140 by soaking 2 nm TiO_2 coated nano-finger samples into 1 μM ethanol solution of corresponding molecules. After samples drying in air, the fluorescence spectra were examined. By comparing them to the results obtained from repeating the experiment with plain glass plates, the enhancement coefficients were calculated. (OX-1 is 43-fold, and IR-140 is 57-fold.)

We propose a simple, phenomenological model to describe the electric field enhancement and scattering cross section at the gap center point between two nanoparticles for different separation distances in order to interpret and correlate the experimental observations with quantum based model incorporating electron tunneling and nonlocality, which can effectively guide better understanding of the role of strong gap plasmon on molecular fluorescence enhancement and related design of potential applications.

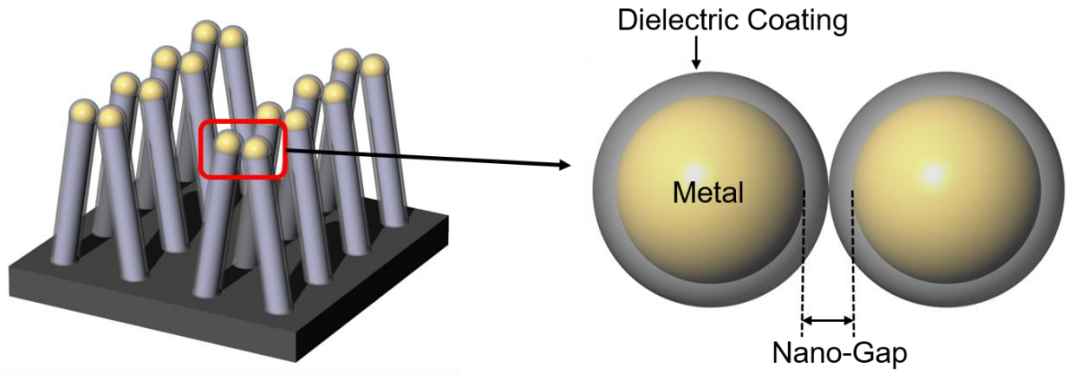

Figure 1. Schematic of controllable hot spots created using nano-fingers.

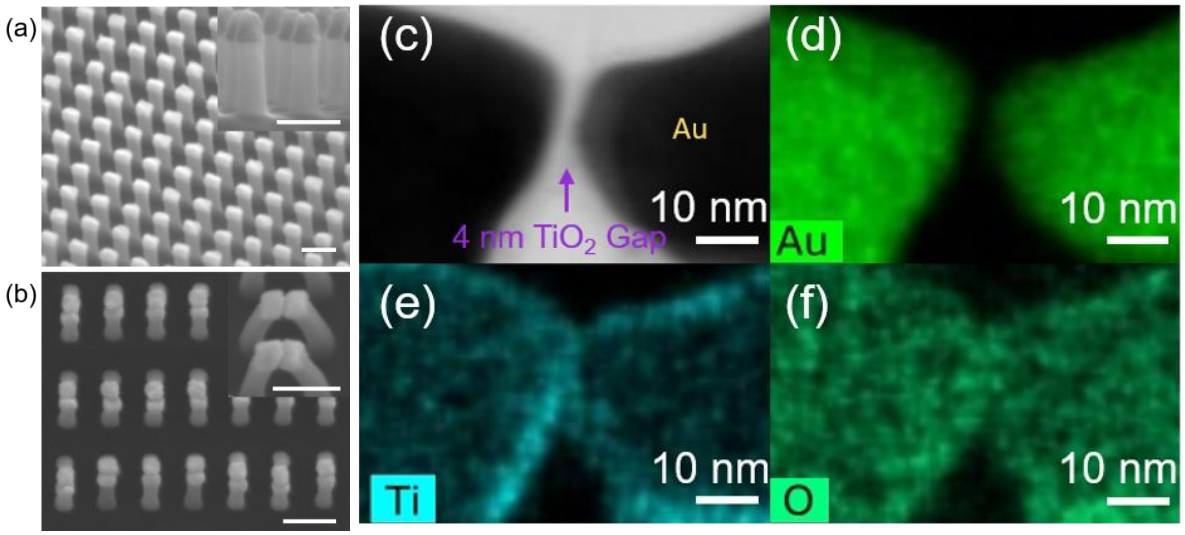

Figure 2. (a) SEM image of nano-fingers before collapse. (b) SEM images of nano-fingers after collapse. (c) TEM image of the dielectric nano-gap in the nano-fingers with 2 nm TiO2 coating. (d) (e) (f) EDS mapping of Au, Ti and O in the TEM image.

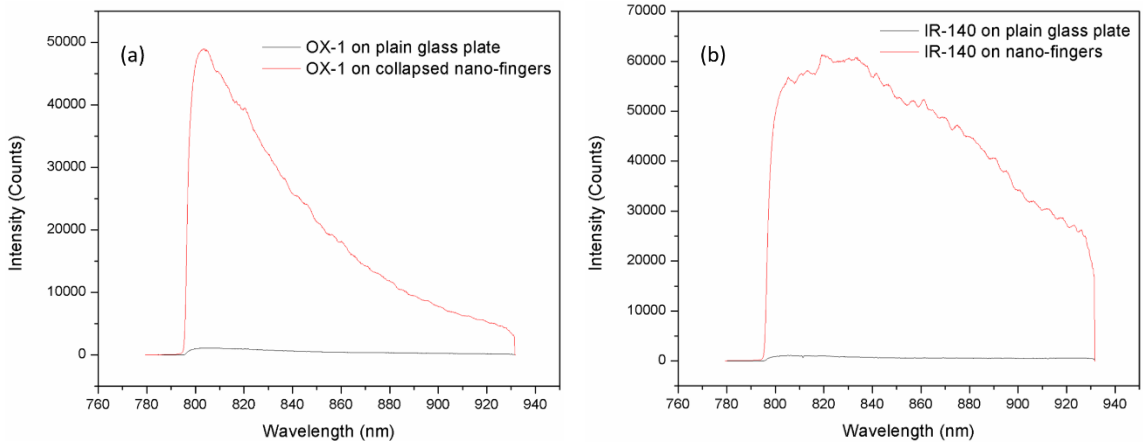

Figure 3. (a) Fluorescence intensity of OX-1 on collapsed nano-fingers and on plain glass plate. (b) Fluorescence intensity of IR-140 on collapsed nano-fingers and on plain glass plate.

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.