Giant and Uniform Fluorescence Enhancement of Organic Dye by 3D Plasmonic NanoCavity Array

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Fluorescence plays a key role in many important disciplines. Metallic nanostructures can enhance fluorescence signals, but previous reported enhancements are low in average (over an area), and relatively high only at a few random "hot spots". Here, we report the a new plasmonic nanostructure -- the disk-coupled dots-on-pillar antenna array (D2PA) -- which has demonstrated an unprecedented high fluorescence enhancement of an IR dye indocyanine green (ICG): 3,000-fold enhancement for an area average, 4×10^6-fold for a single dye molecule at a "hot spot", and an excellent uniformity (for the average fluorescence) of a spatial variation < 15% over a large-area. The result is two and three orders of magnitude larger than the previous reported enhancement for the area-average and a single molecule at a hot spot, respectively. [1,2]

The D2PA substrate we proposed and demonstrated is an array of 3D plasmonic nanocavity (Fig. 1), which consists of a periodic non-metallic pillar array, metal disks and a metal back-plane on top and base of the pillars respectively, dense metallic nanodots on the pillar wall, and nanogaps between the metal components.[3] The D2PA substrates were fabricated by nanoimprint, self-alignment, and self-assembly, which allows a fabrication of D2PA in a simple process and is well suited for mass production. In fabrication (Fig. 2), SiO_2 nanopillars were first patterned with nanoimprint and reactive ion etching (RIE), and then Au nanodisks, backplane and nanodots on the nanopillar sidewall were all formed within one step of Au evaporation. Finally, a thin layer of SiO_2 was deposited on the Au surface conformally using plasma-enhanced chemical vapor deposition (PECVD) to avoid the quenching effect (i.e. signal losses caused by the coupling of the fluorescence emission to the nonradiant modes of the metal substrate). The ICG dye was deposited on D2PA by precise dropping.

The area-average enhancement of the fluorescence was measured using a commercial laser scanning confocal spectrometer with a 785 nm laser excitation. We observed that (Fig. 3) the fluorescence signal on D2PA substrate is 3,000 times higher than the signal observed on a flat Si substrate which were covered by the same amount of ICG molecule. This result is two orders of magnitude better than previously reported.[1] Furthermore, fluorescence mapping was also performed, showing a <15% spatial variation over a 2.5 mm × 2.5 mm area (Fig. 3). In addition, using a low dye concentration (34 μm^2), we observed extraordinarily strong emissions (4.5×10^6 times larger than that on the Si substrate) from single molecules at "hot spots". This indicates a great potential for further improving the average fluorescence enhancement by increasing the density of such "hot spots". The giant enhancement and excellent uniformity, plus ease of manufacturing, will opens up opportunities for wide range of applications, such as bio-imaging, sensing and solar energy harvesting.

[1] R. M. Bakker, et al. New J. Phys. **10**, 125022 (2008)
[2] A. Kinkhabwala, et al. Nat. Photonics, **3**, 654 (2009)
[3] W. Li, et al. Opt. Express, **19**, 3925 (2011)

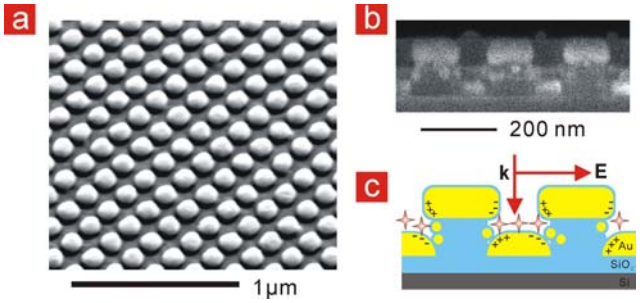

Figure 1: (a) and (b) SEM images of D2PA, from 45 degree and side, respectively.(c) Schematic of D2PA covered by a SiO_2 spacer and dye molecules.

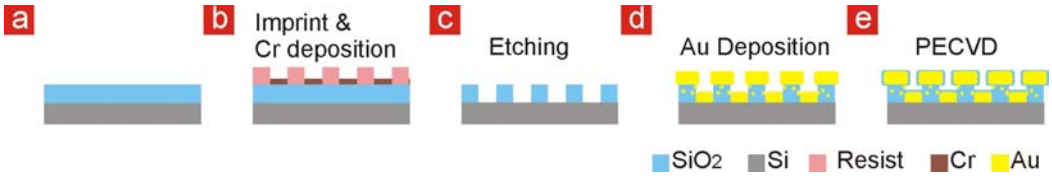

Figure 2: Fabrication process of D2PA: (a) forming an oxidized layer, (b) imprint and Cr evaporation, (c) RIE etching, (d) Au deposition and (e) growth of SiO_2 spacer using PECVD.

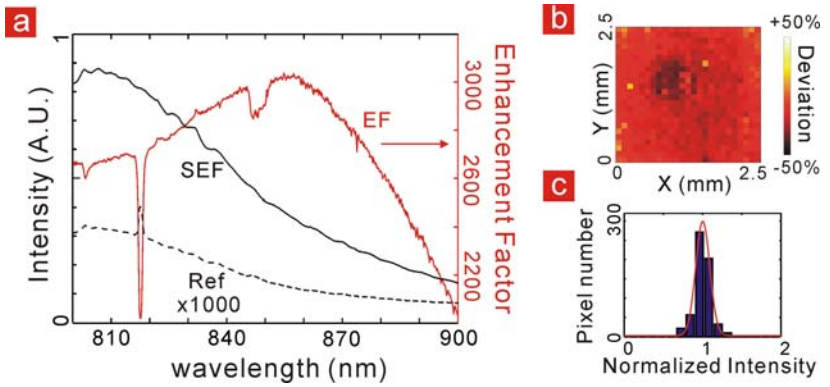

Figure 3: Surface-enhanced fluorescence on D2PA. (a) Fluorescence spectra on a D2PA and a ref substrate (Si substrate). Fluorescence mapping on a D2PA substrate (b) and the corresponding histogram (c).