Coffee-ring Effect in Concentrating Analytes in 3D Cavity Array for Ultra-sensitive Detection

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In assay detection of a targeted maker (i.e. analyte), often a liquid sample is dropped on a surface of an assay plate, and dries, before being measured (Fig. 1). Recently, plasmonic nanostructures patterned on an assay surface have been used to enhance the signal detection in fluorescence or surface Raman scattering assay. It becomes a very important question: Can just the surface topology of the nanostructures alone, without any plasmonic structures, enhance the assay signal over a flat assay plate? [1] Here, we report our experimental study which shows that indeed just the surface topology alone can enhance the assay signal.

The particular assay we studied is the D2PA (disk-coupled dots-on-pillar antenna-array) assay we invented, which has a surface topology of a mushroom in a cavity (Fig. 2)[2]. To isolate nanostructure topology effects from plasmonic effects, we have fabricated several structures that have similar topology as the D2PA, but do not contain any plasmonic materials and hence have no plasmonic effects. These samples include (i) SiO_2 straight nanopillar (SP), (ii) mushroom-shaped nonmetallic nanopillar (MNP) with cavity, (iii) sealed mushroom shaped nanostructure (SMNP), which has additional shadow-deposited materials that make the mushroom size larger than MNP but the cavity sealed off, and (iv) the mushroom removed nanopillar (MRNP), which has the mushroom top of MNP removed, leaving a shallow cavity around the pillar foot (Table 1). A flat SiO_2 surface was used as the baseline reference sample.

In fabrication, an array of SiO_2 straight nanopillar (SP) of 5μm pitch, 150nm diameter, and 130nm height was first created using nanoimprint lithography (NIL) and reactive ion etching (RIE)[3]. Then MNP was fabricated by evaporating 60nm thick SiO_2 on top of SP. SMNP was fabricated from MNP by 4 shadow evaporations of 15nm thick SiO_2 each from 4 different directions (90 degree apart). MRNP was fabricated by removing the evaporated SiO_2 mushroom from the MNP.

In testing, 2 μL of 10 μM indocyanine green (ICG) in ethanol was dropped in each sample and was left to dry in a closed petri dish. All samples were cut to the same area to make average molecule density the same. In fluorescence imaging (setup in Fig. 2 and results in Table 1), we found that while the flat surface, SP and SMNP show uniform fluorescence intensity, the MNP and MRNP show bright fluorescence dot array with the same pitch as the pillar array, indicating that they come from their nanostructures. Compared to the flat surface reference, the intensity of each bright dot was enhanced by 6.8 fold for MNP and 4.68 fold for MRNP. This means that, as we suspected[1], the nano-cavity on an assay plate surface can enhance the signal. The experiment offers new understanding and paths to enhance an assay by topology.

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[1] S. Y. Chou, unpublished, 2011
[2] W. Li, F. Ding, J. Hu, and S.Y. Chou. Opt. Express **19**, 3925 (2011)
[3] S. Y. Chou, P. R. Krauss, W. Zhang, L. Guo, and L. Zhuang, J. Vac. Sci. Technol. B **15**, 2897 (1997)

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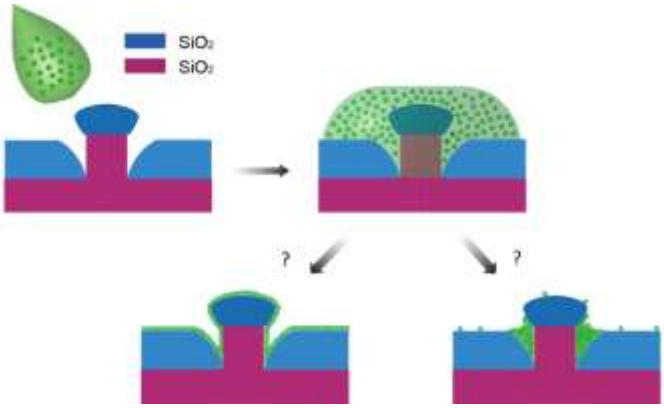


Fig. 1. Schematic of analyte distribution indicating two possible scenarios after solvent evaporation.

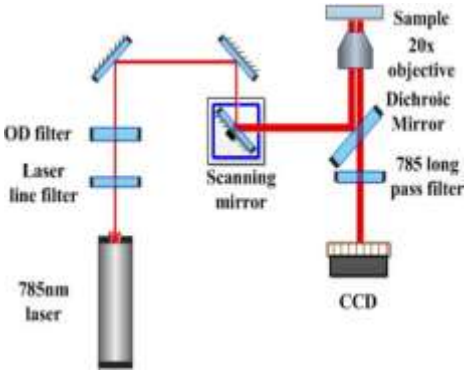
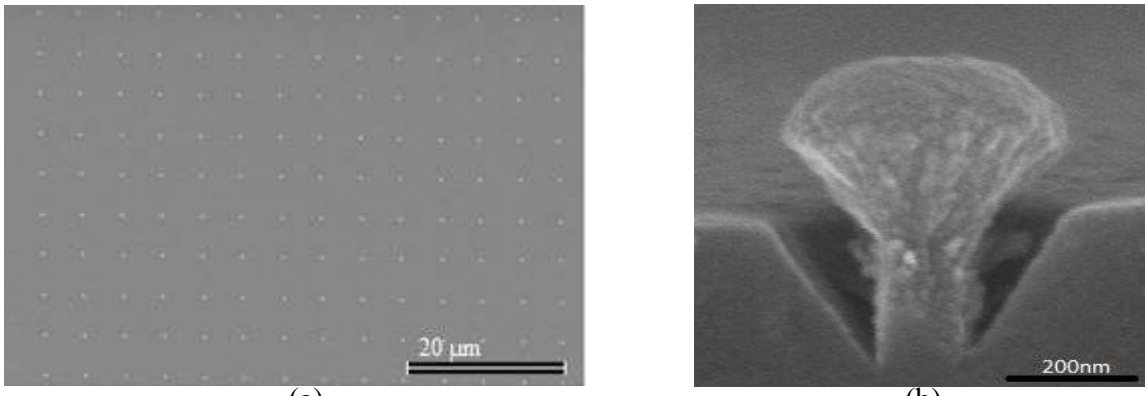


Fig. 2. Optical setup for fluorescence measurement.



(a) (b)

Fig. 3. SEM of (a) MNP array of 5µm pitch, and (b) cross-section of an individual MNP.

Sample	Flat SiO_2	SiO_2 pillar	MNP	SMNP	MRNP
Schematic (crosssection)					
Fluorescence Intensity	1.44×10^7	1.58×10^7	9.8×10^7	1.55×10^7	6.74×10^7
Enhancement*	1	1.09	6.8	1.07	4.68
Fluorescence Picture					

Table 1. Fluorescence intensity from different types of samples. *Enhancement is the ratio of fluorescence intensity from the nanostructured surface to that from flat surface sample.

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