Universal Enhancement of Raman Scattering Sensing by Plasmonic Nanotubes Coupled with Photonic Crystal Slab

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Abstract: We experimentally demonstrate 2-D photonic crystal slab-coupled plasmonic nanocapsules for surface enhanced Raman spectroscopy (SERS). A strong Raman signal enhancement can be unambiguously detected even with a low concentration 10 nM dye molecules.

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Surface enhanced Raman scattering (SERS), which has a history about 40 years[1], has demonstrated single-molecule-detection capability[2] and becomes more and more attractive as its significant potential in chemical and medical applications[3-5]. Nevertheless a peak enhancement factor (EF) as large as 10¹⁴ can be generated from the random “hot spots” that are formed by metallic nanoentities[2], the density of “hot spots” is extremely low thus makes the single-molecule-detection event unpredictable. Therefore, a comprehensive enhancement mechanism that can provide a universal increase of the Raman signal intensity across the entire substrate is highly desirable for biomolecule detection. Recently, innovative approaches using Fano resonance in 2D photonic crystals to enhance and localize electromagnetic filed have been investigated extensively[6]. Thanks to the Fano resonance principle in photonic crystals and materials, local electromagnetic field enhancement also can be realized in uniform dielectric photonic crystal slabs which does not require precise placement of designed nanoentities onto the substrates[7].

Fig. 1 (a) Schematic of 2D photonic crystal microcavity array (b) COMSOL simulation result of 2D photonic crystal microcavity array with optimized parameters (c) SEM image of 2D photonic crystal microcavity array

In this paper, we design and fabricate a Si₃N₄ 2D photonic crystal slab with rectangular air hole array on fused silica substrate providing about 10 times electromagnetic filed enhancement due to the Fano resonance at the center wavelength of 633nm. Later Ag nanocapsules with densely assembled silver nanoparticles on theirs outside silica cells are dispersed on the Si₃N₄. Here each individual nanocapsule is an assembly of densely packed “hot spots,” which can provide a constant and stable enhancement in addition to existing SERS effect. As shown in Fig. 1(a), the 2D photonic crystal microcavity array is fabricated in a thin layer Si₃N₄ with thickness of t=230 nm, which is deposited onto a fused silica substrate by LPCVD. The diameter of microcavity and the lattice constant of the 2D photonic crystal are optimized by numerical simulation with Rsoft DiffractMod. Fig. 1(b) shows the electromagnetic field profile with optimized parameter of lattice constant p=425 nm and the hole diameter d=213nm. Those air holes were first patterned by Ebeam lithography then transferred into Si₃N₄ layer by reactive ion etching (RIE). To minimize the charging effect caused by the poor conductive silica substrate, commercial available conductive polymer Espacer 300Z was applied before exposure. Fabrication results were characterized by SEM to confirm that desired dimensions are reached. A SEM image of 2D photonic crystal microcavity array is shown in Fig. 1(c).
To achieve the plasmonic Ag nanocapsules, we first synthesized Au nanowires (300 nm in diameter, 9.5 μm in length) by electrodeposition in nanoporous anodized aluminum oxide membrane which serves as a mold and will be dissolved in NaOH solution later. Next, controlled hydrolysis of tetraethyl orthosilicate was applied to coat Au nanowires with 220 nm amorphous silica thin films. The last step is to grow Ag nanoparticles on the silica cells by incubating Au nanowires with a reactant mixture made of silver nitrate, ammonia, and polyvinylpyrrolidone (PVP) ethanol solution. Finally, large arrays of Ag NPs grew uniformly on the surface of the nanowires as shown in Fig. 2(a) and 2(b).

![Fig. 2(a) (b) Scanning electron microscopy images of Au nanocapsules. (c) Representatively Raman spectra of 10 nM Nile blue detected from a flat silicon nitride substrate (in red) and from the silicon nitride photonic crystal device (in black). (d) Statistic Raman signal analysis of 10 nM Nile blue.](image)

Nile blue, a standard SERS characterization dye, was selected as the detection probe for evaluating the SERS enhancement function of the photonic crystal device. A custom Raman microscope equipped with a 633 nm laser was used for Raman spectroscopy measurement. Nile blue molecules with a concentration as low as 10 nM in ethanol were uniformly dispersed on the nanocapsules. In each measurement, the laser was focused on only one nanocapsule to ensure the reproducibility. The Raman signals of the Nile blue can be readily detected from nanocapsules on a flat Si₃N₄ substrate (in red) and on the photonic crystal device (in black), respectively, as shown in Fig. 2(c). Although not all the characteristic Raman peaks of Nile blue are clearly observed, The Raman shift at 596 cm⁻¹ showed a strong enhancement of 3.1 times on the photonic crystal device compared to that of the flat Si₃N₄ substrate, which validates the enhancement function from the designed photonic crystal device compared to a blank sample. The result is further confirmed by multiple measurements as shown in Fig. 2(d), where an enhancement of 3-6 times is observed on the photonic crystal device compared to that from the blank Si₃N₄ substrate.

In conclusion, we design and fabricate a Si₃N₄ 2D photonic crystal slab SERS substrate with coupled plasmonic nanocapsules which can readily offer a 3-6 times Raman signal enhancement comparing to the un-coupled nanocapsules. Such highly sensitive SERS substrate could have significant potentials in early disease diagnostics, chemical detection and environmental protection.

References:

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