On-chip Photonic-Plasmonic Integration for Surface-enhanced Raman Spectroscopy for Water Contaminants and Heavy Metal Ions Detection

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Abstract: An on-chip ultrasensitive Surface-Enhanced Raman Spectroscopy platform employs hybrid photonic-plasmonic devices to detect water contaminants and heavy metal ions, with analytical calculations of a strong SERS enhancement factor via a 2D hexagonal photonic crystal slab.

1. *Introduction*

Monitoring water quality has become crucial for protecting the environment, biodiversity, and human health, necessitating advanced sensing technologies for rapid and highly sensitive detection of environmental toxins, including heavy metal ions such as arsenic, mercury, lead, and water contaminants at trace levels. Surface-enhanced Raman spectroscopy (SERS) has demonstrated its capability for single-molecule detection, making it attractive for various environmental monitoring, chemistry, and medicine applications. SERS is the spectroscopic analytical tool that utilizes nanostructured plasmonic nanoparticles or materials to create "hot spots" near target molecules, significantly enhancing their Raman signals [1]. The shape, size, and the arrangement of nanostructures rule the frequency and magnitude of the localized surface plasmons (LSPs). SERS uses the large local field enhancements on metallic surfaces to boost Raman signals of molecules at or close to the surface. The SERS single-molecule enhancement factor (SMEF) can be estimated by the $|E_{LOC}|^4$ of the local electric field at the resonance frequency (ω_L) divided by the $E_0{}^4$ of the incident electric filed as: $SMEF \approx \frac{|E_{LOC}(\omega_L)|^4}{E_0{}^4}$ [1].

A key challenge in SERS research is the inefficiency of single-molecule detection caused by the low density of random "hot spots," despite their high enhancement factors (EF) of up to ~10^{14}. Guided mode resonances (GMRs) in photonic crystal (PC) slabs address this issue by efficiently trapping light, amplifying localized electric fields, and enhancing Raman signals. Recent advancements have combined GMR with localized surface plasmon resonance (LSPR) effects from metallic nanoparticles [2-4]. Plasmonic-photonic hybrid nanosensors exploiting GMRs in 1D grating photonic structures and LSPR generated from SiO_2 nanopillars have achieved a combined SERS enhancement of 1.8×10^9 [5]. However, these systems require expensive fabrication techniques, like e-beam lithography, to precisely place metallic nanoentities on dielectric gratings. Alternatively, Fano resonances, which arise from the interaction between guided mode resonances and radiative modes of the incident field in photonic crystals (PCs), enhance the local electromagnetic field in uniform dielectric PC slabs, eliminating the need for precise nanoentity placement. Our group previously demonstrated SERS enhancement factor up to ~10^9 using a 2D square lattice PC slab to localize and enhance the electromagnetic field.

In this study, we investigated 2D hexagonal photonic crystal slabs, which offer larger band gaps for efficient light confinement, symmetry for predictable and uniform optical behavior, tunability to adapt properties for specific wavelengths, and compatibility with natural structures, including water environments for bio-chemical inspired designs. Using the Lumerical Finite Difference Time Domain (FDTD) method, we optimized the silicon nitride (Si_3N_4) rod-on-silica (SiO_2) photonic crystal slab parameters (radius *r* and lattice constant *a*) to achieve efficient guided mode resonances at the excitation frequency of 532 nm, guided by band structures from the RSoft plane wave expansion method. Integrating this optimized design with silver nanoparticle dimers achieved a significant SERS enhancement $|E|^4$ of ~1.13×10^{10}. When paired with plasmonic nanotubes we anticipate achieving SERS enhancement of ~10^{14}. These findings highlight the potential of 2D hexagonal PC slabs as cost-effective, highly efficient platforms for single-molecule detection by the proposed on-chip SERS spectroscopy.

2. *Device Design and Numerical Simulation*

The device employs a 2D hexagonal PC slab with a silicon nitride (Si_3N_4) rod layer (n ≈ 1.98, 100 nm thick) suspended in air on a silica (SiO_2) substrate (200 nm height). Designed as a guided mode resonance platform, the PC consists of Si_3N_4 rods with a radius of 77 nm, a lattice constant of 158 nm, giving the normalized radius (r/a) of 0.48. Using Lumerical FDTD, we investigated interactions between PC resonance modes and localized surface plasmons (LSPs) of silver nanoparticles, optimizing for 532 nm normal-incidence excitation light. Figs. 1a show a schematic of PC slab with Si_3N_4 rods. Fig. 1b shows the simulated Fano resonance/reflectance (or) guided mode resonance peak (red solid line) at the excitation wavelength of 532 nm, absent in Si_3N_4 flat substrates.

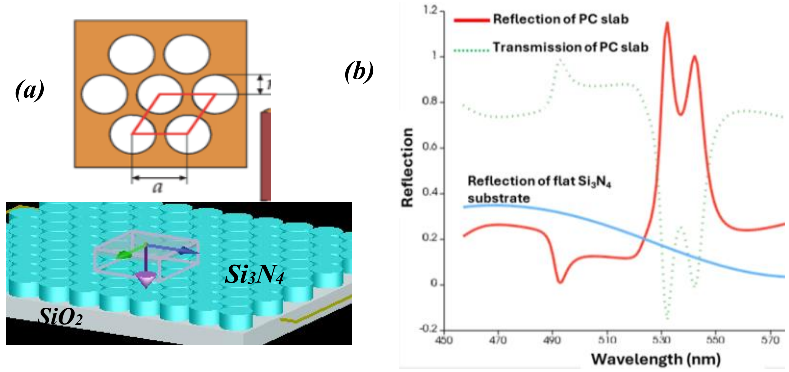

Fig. 1: (a) Schematic of a 2D hexagonal Si_3N_4 rods in air *photonic crystal (b) Guided mode resonance (or) Fano resonance peaks of 2D PC slab at the 532 nm excitation wavelength.*

For hybrid photonic-plasmonic SERS substrates, Fig. 2a depicts the hybrid device configuration, by placing Ag dimer (radius = 40 nm) nanoparticles on a flat Si_3N_4 substrate – achieving a peak SERS enhancement factor (EF) of only 28.2. In contrast, Fig. 2b illustrates the enhanced electric field distributions when Ag dimers are positioned on a 2D hexagonal PC slab with Si_3N_4 rods, resulting in a significantly higher EF value of 1.13×10^{10}. As expected, the maximum electric field is concentrated within the gap of the Ag dimer. Increasing the number of nanoparticles generate additional "hot spots," further enhancing the SERS effect [6]. The EF ($|E|^4$) values were calculated using a Lumerical script that evaluates the distributed electric fields along the XY, XZ, and YZ planes.

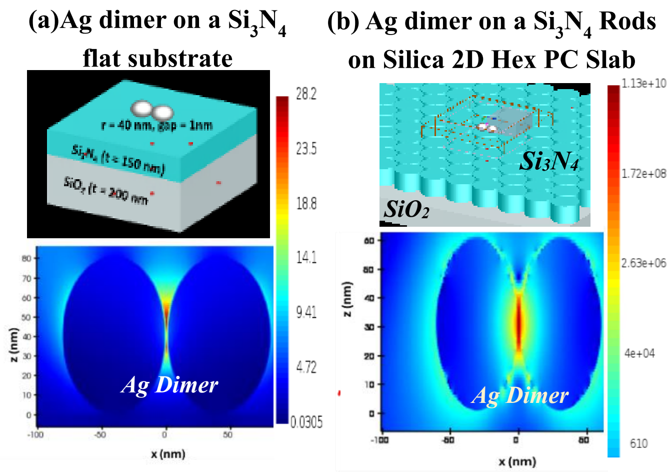

Fig. 2: Electric field distributions (side views) of Si_3N_4 SERS substrates (a) Ag dimer on Si_3N_4 flat substrate, (b) Ag dimer on 2D hexagonal photonic crystal slab with Si_3N_4 rods on top of the SiO_2layer at 532-nm excitation.

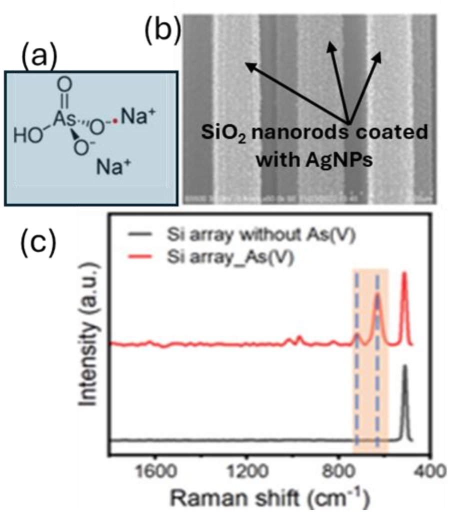

Fig. 3: SERS detection of Sodium Arsenate (V) ($Na_3AsO_4{\cdot}7H_2O$). (a) Chemical formula of Na_3AsO_4. (b) SERS-active substrate with AgNP on SiO_2 nanorods. (c) Raman spectra indicate peaks at 690 cm^{-1} and 780 cm^{-1} to identify the presence of As (V) ions at a concentration of 75 nM.

The proposed 2D hexagonal photonic crystal slab design, featuring Si_3N_4 rods, demonstrates robust guided mode resonances/reflections that effectively enhance and couple the localized electric field (E-field) generated by localized surface plasmon resonances. This significantly contributes to the SERS detection enhancement, with a calculated enhancement factor (EF) of approximately 10^{10} achieved using a simple Ag dimer structure. Detected Raman signals for Arsenic ions are shown in Fig. 3c, applying a 0.1 µL drop of sodium arsenate ($Na_3AsO_4{\cdot}7H_2O$) at 75 nM to an AgNPs@Si substrate. Our ongoing efforts aim to integrate this photonic PC device with Ag nanoporous structures and SiO_2 nanorods coated with dense Ag nanoparticles (as shown in Fig. 3b) with anticipated EF values of 10^{14}, enabling highly sensitive detection of heavy metal ions in water. The authors thank and acknowledge DOE for supporting this work under contract number DE-SC0024015.

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