Plasmonic Nanopillar Structures for Surface-Enhanced Raman Scattering Applications

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ABSTRACT

Noble metal nanostructures support localized surface plasmon (LSPR) resonances that depend on their dimensions, shapes and compositions. Particle LSPR's can be used to spatially confine the incident light and produce enormous electromagnetic (EM) field enhancement spots, i.e. hot spots. Hot spots have been utilized in surfaceenhanced Raman spectroscopy (SERS) for biological and chemical sensing. We present Au nanopillar (NP) SERS structures that are excellent for molecular detection. The NP structures can be fabricated using a simple two-step process. We analyze NP optical properties experimentally and theoretically. Simulations show that that a single Agcoated NP supports two LSPR modes, i.e. the particle mode and the Ag cap resonant cavity mode. The Ag cap resonant cavity mode contributes most to the enhancement of the Raman scattering signal. The electric field distribution calculations show that the EM hot spots are located at the bottom of the Ag cap which is important observation for practical SERS sensing. Reproducible and repeatable SERS signal intensities can be obtained across large surface areas (>mm²). Application examples include detection of TAMRA-labeled vasopressin and cyanide (KCN).

Keywords: SERS, plasmonic nanopillars, Si RIE, SERS detection, SERS substrate

1 INTRODUCTION

Surface enhanced Raman scattering (SERS) technique is a well know spectroscopic tool suitable for biological and chemical sensing [1]. Noble metal nanostructures, e.g. nanosized silver or gold, support localized surface plasmon resonances (LSPRs) that can focus the incident light and produce very high electromagnetic field enhancement spots, i.e. hot spots [2]. Generally, a very good SERS substrate displays electric field enhancement factors (EFs) around 10^8 and even 10^{10} have recently been reported [1]. Although EFs are often used to describe the performance of a SERS substrate, it is also important that SERS substrate (for practical use) display (i) high and reproducible EFs over



Figure 1: Fabrication of Au-coated Si NP structures involves only Si reactive ion etching, (a), and Au metal deposition, (b). (c)-(d) Solvent drying induces Au NP leaning which creates micro sized Au NP clusters and electromagnetic hot spots suitable for SERS. Scanning Electron Microscope images before and after Au NP leaning are shown in (e) and (f), respectively.



Figure 2: (a) Optical properties of Au NP SERS substrates measured using the dark-field scattering set up (see the inset). Red dots indicate the two incident laser lines that were used in SERS experiments (633 and 780 nm). (b) Simulated extinction cross section of a single Au NP (see dimensions in section 2.1). The inset shows electric field distribution at 710 and 865 nm LSPR wavelengths.

large (>mm²) surface areas, (ii) a tunable LSPR wavelength and (iii) are easy and cheap to manufacture [1,3].

In this report, we present an excellent SERS platform which consists of vertically standing Au-capped Si nanopillar (NP) structures. The lithography-free nanofabrication process is cheap, quick and involves only two process steps, see schematic process summary in Fig. 1(a,b). First, we briefly investigate optical properties of Au NP SERS substrate experimentally and theoretically. Second, we present detection of TAMRA-labeled vasopressin (TVP) molecules in the pM regime. Detection and quantification of vasopressin in the pM regime is clinically important for identifying hemorrhagic shock [4]. Finally, we present progress towards quantitative detection of hydrogen cyanide (HCN) in the nM regime which is a potential biomarker for monitoring cystic fibrosis [10].

2 EXPERIMENTAL

2.1 Fabrication of Au NP structures

Au NP SERS substrates were fabricated on a 4" Si wafer following the procedure described in ref. [3,5]. The fabrication procedure essentially consists of two process steps: (i) Si reactive ion etching (a mixture of SF₆ and O₂ gases) and (ii) deposition of Au metal film (200 nm). Resulting Si NP structures (~18 Au NP/ μ m²) are ~635 nm in height and 40 nm in width. Deposition of 200 nm Au metal film produces ~124 nm in width and ~310 nm in height Au caps on top of Si NPs.

2.2 Dark-Field Microscopy Set-up

Optical properties of Au NP SERS substrates (dark-field scattering) were analyzed using a high-sensitivity microscopic and spectroscopic platform that combines an inverted Nikon Ti-U microscope and Andor SR-303i spectrometer equipped with an EMCCD (Andor Newton) camera. White light from the halogen lamp was focused on a sample using dark-field objective (Nikon NA0.8, 50X), see the inset in Fig. 2(a). The scattering spectra were then measured over the spectral range of 400-1000 nm.

2.3 FEM Simulations

In order to gain some insight into optical properties of Au NP structures, extinction cross section and electric field around single Au NP structure was calculated using the Finite Element Method (COMSOL), see Fig. 2(b). Au NP dimensions were obtained from SEM images, Fig. 1(e). The Au-coated Si substrate is not included into the calculations and the surrounding medium is vacuum [5].

2.4 Detection of TAMRA-labeled Vasopressin

First, Au NP SERS substrate was functionalized with an aptamer that can bind specifically to vasopressin molecules, as described in ref. [7]. Second, the aptamer functionalized Au SERS substrates were incubated with TVPs (1-100 pM concentrations) for ~1 hour at 37°C. Third, the substrates were immersed into vasopressin buffer solutions in order to remove all unbound molecules (15 min at 37°C). In the last step, the SERS substrates were rinsed using deionized water to prevent accumulation of salt on dried SERS substrates that can block the Au NP leaning and formation of electromagnetic hot spots.

All SERS maps (Fig. 3) were recorded using the 632.8 nm laser excitation light (He-Ne) and an inVia Raman microscope (Renishaw, UK) equipped with a standard backscattering configuration. The SERS signal was guided through a confocal pinhole (25 μ m in diameter) using a 50X (NA 0.75) magnification objective (Leica

Microsystems, Germany). An automated XY stage was employed to acquire 10087 SERS spectra (130 x 76 μ m area). The SERS signal acquisition step size in both dimensions was 1 μ m. The SERS signal collection time was 1 second, laser power before the 50X objective was 0.3 mW. All the SERS spectra from TAMRA were background corrected using the WiRE 3.2 software (Renishaw, UK) around the TAMRA label specific mode, i.e. 1350-1390 cm⁻¹.



Figure 3: SERS intensity distribution of 1370 cm⁻¹ TAMRA peak for three TAMRA-labeled vasopressin molecular concentrations. The SERS map area in all three cases is $130x76 \ \mu m^2$. A maximum measured SERS intensity is ~4x10³ counts. In order to enhance the difference between 1 and 10 pM SERS intensity maps, the maximum shown intensity value is set to 200.

2.5 Detection of Cyanide

Solutions of potassium cyanide (KCN) with concentrations varying from 10 nm to 1 mM were prepared [11]. The pH in all solutions was adjusted to pH=11 using NaOH. Prior to immersing the SERS substrates into



Figure 4: A comparison between theoretical Raman spectrum of HCN and SERS spectrum of KCN, (a). (b) Intensity of the ~2140 cm⁻¹ Raman mode as a function of KCN concentration (both axis log scales).

KCN solutions, the substrates were additionally kept in ethanol (absolute grade, CHROMASOLV, Sigma-Aldrich) for 3 min, and without de-wetting immediately immersed into water (Molecular Biology Reagent grade, Sigma-Aldrich) for 3 min. Next, without de-wetting the SERS substrates were immersed into KCN solutions for 3 min, removed and left for drying. A reference SERS signal was collected using the same procedure but without KCN, i.e. water with added NaOH to reach pH=11 was used instead.

The cyanide detection experiments shown in Fig.4 were performed using a Raman DXR microscope (Thermo Fisher Scientific) equipped with thermoelectric CCD cooling and a 780 nm laser excitation line. A microscope was connected to a single grating spectrometer (5 cm⁻¹ FWHM spectral resolution, \pm 2 cm⁻¹ accuracy). All SERS spectra were collected for 5 s (averaged twice) at a laser power of 5 mW before microscope objective (10X). Ten SERS spectra in total were recorded from the same SERS substrate for each KCN concentration. Each SERS spectrum was baseline

corrected and fitted using Voigt profile (~2130 cm^{-1} Raman mode).

Theoretical Raman scattering spectra of HCN were calculated using Gaussian 09W package [9], DFT/B3LYP/6-311G.

3 RESULTS AND DISCUSSION

3.1 Optical Properties of Au NP Structures

Optical properties of Au NP SERS substrate were explored experimentally and theoretically employing darkfield scattering microscopy and FEM simulations, respectively, see sections 2.2-2.3. The Au NP scattering spectrum was recorded using the backward scattering configuration [6], see the inset in Fig. 2(a). Au NP structures exhibit a very broad LSPR line-shape across ~600-900 nm range and the behavior is similar to the one observed for Ag NP structures fabricated using identical process [5]. The result indicates that the incident laser lines e.g. 632.8 nm and 780 nm are suitable for SERS based molecular detection because it coincides with the LSPR peak position. In order to understand the origin of the broad LSPR peak, we simulate theoretically extinction cross section of a single Au NP together with electric field enhancement maps that correspond to the observed LSPRs, see Fig. 2(b). For simplicity, the underlying Au metal film was not included into the calculation which is a plausible simplification based on similar calculations for single Ag NP structures [5], i.e. the LSPR peak positions remain almost unaltered in comparison to the case which includes the underlying metal film.

The two LSPR modes correspond to standard particle dipolar mode (~710 nm) and particle resonant cavity mode (~865 nm), see electric field distribution maps (insets in Fig. 2(b)). The recorded broad LSPR peak is likely due to variation in Au NP dimensions, e.g. the change in the Si NP width affects the peak position of the resonant cavity mode [3].

3.2 Detection of TVP and Cyanide

In order to experimentally verify the SERS performance of Au NP structures, we target pM concentrations of TAMRA-labeled vasopressin molecules down to pM concentration range [7,8]. A total of 10087 SERS spectra were collected across 130x76 μ m sample area. Results show that quantitative detection of TVP is possible down to 1 pM, which is clinically important concentration range [4], see SERS intensity maps in Fig. 3. The SERS intensity range was adjusted to 0-200 interval to clarify the difference between 1 and 10 pM concentration maps.

Solutions of potassium cyanide (KCN) were used as a model system for detection and quantification of cyanide in solution, see results in Fig. 4. The triple bond between C and N in cyanide (characteristic Raman mode at \sim 2130 cm⁻¹) is an excellent marker to identify presence on cyanide on

the Au SERS substrate, Fig. 4(a). By monitoring the SERS intensity of the characteristic cyanide peak the presence of cyanide can be identified down to the nM concentration range, Fig. 4(b). We estimate that cyanide detection limit is between 18 ppb (detected) and 1.8 ppb (not detected).

4 CONCLUSION

In the report we present a simple and cost-effective method to fabricate Au NP SERS substrates on the wafer scale (4 or 6 inch) that can be successfully used for detecting TAMRA-labeled vasopressin molecules and cyanide down to the pM and nM concentration range, respectively.

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