Nanopyramid surface plasmon resonance sensors

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We report the achievement of sensitive chemical and biological sensing using periodic gold nanopyramids with nanoscale sharp tips created by a simple and scalable colloidal templating approach. The sharp tips and the long-range periodic structure of the nanopyramid arrays enable the excitement of both localized and propagating surface plasmons. The optical reflection and the detection sensitivity of the templated nanopyramid surface plasmon resonance sensors agree reasonably well with the theoretical predictions using a finite-difference time-domain model. We have also demonstrated that specific antigen-antibody binding can be detected by using nanopyramid arrays in a real-time and label-free manner. © 2010 American Institute of Physics. [doi:10.1063/1.3460273]

Surface plasmon resonance (SPR) technique is of great importance for monitoring binding events in biological systems because it offers a direct and label-free platform for rapid screening test.^{1–7} Surface plasmons (SPs) are electromagnetic waves that propagate along a metal/dielectric interface and can be pictured as a traveling charge density wave on the surface of a metal.^{8,9} The coupling of incident light with free electrons in metal forms SP waves that are essentially confined to the metal/dielectric interface, leading to a strong concentration of electromagnetic field. The adsorption of molecules to a metal surface significantly changes the oscillation of SPs, resulting in the modulation of light output. The modulation could be monitored by the angular distributions of reflection and transmission, wavelength, intensity, phase, and polarization changes.^{1,10} Compared to other immunoassays, such as enzyme-linked immunosorbent assay and radioimmunoassay,¹¹ the SPR technique is highly promising for rapid and sensitive biosensing because the label-free and real-time characteristics of SPR sensors shorten the sample preparation time, minimize the interference of conjugating radioactive or enzyme labels, and enable direct analyte detection without a sandwich format.^{1,2,12}

To generate SPs, the difference in the momentum of incident light and SP must be compensated.⁹ In the traditional Kretschmann configuration of the attenuated total reflection method, a prism is used to couple the incident light to SPs.¹⁰ However, the bulky experimental setup impedes miniaturization and integration in microfluidic systems.¹³ The exploitation of localized SPR (LSPR) around metal nanoparticles is favorable for developing planar on-chip-based sensors.^{14–16} However, the stochastic separation between neighboring nanoparticles that significantly affects LSPR impedes the sensing reproducibility. Periodically patterned nanostructures, which support both localized and propagating SPR, therefore draw great attention due to their high reproducibility.^{17–21} We have developed a scalable bottom-up technique for generating wafer-sized periodic gold nanopyramids with nanoscale tips as an efficient surface-enhanced

Raman scattering substrate.^{22–24} Here we demonstrate that the templated nanopyramids can also be utilized as sensitive SPR sensors for chemical and biological sensing. Finite-difference time-domain (FDTD) simulation has been conducted to complement the optical measurements.

Periodic Au nanopyramids were fabricated by a simple templating technology using spin-coated monolayer colloidal crystals as structural templates.²² Fig. 1 shows tilted scanning electron microscope (SEM) images of an array of gold nanopyramids templated from 320 nm silica spheres. The long-range hexagonal ordering of nanopyramids can be

FIG. 1. (a) Tilted-view (35°) SEM images of a templated Au nanopyramid array. (b) Magnified image of (a). 320 nm silica spheres were used as template.

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FIG. 2. (Color online) Optical reflection of white light (incident angle of 45°) from an Au nanopyramid array immersed in glycerol solutions of different refractive indices.

clearly seen from Fig. 1(a). A magnified SEM image in Fig. 1(b) reveals the sharp tips and the smoothness of the nanopyramids. As demonstrated earlier, a similar templating technology produced ultrasmooth pure metal films with SP propagation lengths approaching theoretical values for perfectly flat films.²⁰

A sandwich cell, consisting of a gold nanopyramid array, a 2 mm thick polydimethylsiloxane (Sylgard 184) spacer, and a glass microslide, was used to evaluate the reflection from the nanopyramids when the cell was filled with glycerol solutions of different refractive indices. A high-resolution spectrometer (HR4000, Ocean Optics) with a tungsten halogen light source (LS-1) and a reflection probe (R600-7) was used for the optical measurements. The angle of incidence was controlled at 45° by using a RPH-1 probe holder. Figure 2 shows the reflection spectra obtained from glycerol solutions of different refractive indices. A redshift in the maximum reflection wavelength is observed as the solution refractive index increases. The sensitivity of the nanopyramid array was evaluated to be 239 nm per refractive index unit (nm/RIU) (see Fig. 4) and is favorably comparable to other grating coupler-based SPR sensors.¹

The experimental measurements were complemented by FDTD simulation under a Lumerical Solutions platform. The base length, nanopyramid height, lattice spacing, and tip radius of curvature were obtained from the SEM image in Fig. 1(b) as 300 nm, 200 nm, 420 nm, and 50 nm, respectively. Bloch boundary conditions were used in both x - and y -axis because of the periodic structure. The metal boundary condition was set at the bottom for providing a radiation boundary and the perfect matched layers approach was used at the top for providing an absorption boundary condition.²⁵ Plane waves with wavelength from 500 to 700 nm were used for the modeling. To simplify the simulation, the real incident angle at a gold nanopyramid array was calculated using Snell's law by considering the incident angle in air (45°) and the refractive indices of air, glass, and liquid as follows: $n_{\text{air}} \times \sin(\theta_{\text{air}}) = n_{\text{glass}} \times \sin(\theta_{\text{glass}}) = n_{\text{liquid}} \times \sin(\theta_{\text{liquid}})$, where n is the refractive index and θ is the angle of incidence. Only the zero-order signals were simulated due to the narrow acceptance angle (24.8° in air) of the reflection probe.

Figure 3(a) shows FDTD-simulated reflection spectra from a gold nanopyramid array immersed in glycerol solutions of different refractive indices. A redshift in the maxi-

FIG. 3. (Color online) (a) FDTD-simulated optical reflection of plane wave from an Au nanopyramid array immersed in liquids of different refractive indices. (b) Comparison between normalized experimental (black solid line) and FDTD-simulated optical reflection from nanopyramids with 10 nm (red dotted line) and 50 nm (blue dashed line) tips.

um reflection is observed as the refractive index increases, showing the same trend as the experimental result in Fig. 2. However, the calculated reflectivity is nearly 1 order of magnitude smaller than the experimental result. This is caused by the short pulse length (7 femtosecond) which was chosen to simplify the FDTD simulation. In addition, the simulated reflectivity increases in the higher refractive index environment, contradicting with the experimental results. This contradiction can be explained by using the above Snell's law. For the same θ_{liquid} , a higher solution refractive index leads to a larger θ_{air} , thus a more divergent beam coming out of the sandwich cell. For simulation, we consider the far-field distribution of the reflected light and all 0th order signals will be collected. Figure 3(b) shows a comparison between experimental and theoretical reflection from Au nanopyramids with different tip sharpness. The peak position of the experimental spectrum is closer to the simulation with 10 nm tips while peak shape is more similar to the simulation with 50 nm tips. The difference in the maximum reflection may result from the discrepancy between the real and ideal arrays of Au nanopyramids, such as defects and the sharpness of edges and tips. The apparent broadening of the peak could be caused by defects. It is well-known that polycrystalline domains and point and line defects can significantly broaden optical spectra.²⁶ The maximum reflection wavelength of both simulated and experimental spectra obtained from solutions of different refractive indices is summarized in Fig. 4. It is apparent that the simulated reflection peaks are redshifted by ~ 20 to 30 nm than the experimental results. The sensitivity

FIG. 4. (Color online) Comparison of detection sensitivity between the experimental result and FDTD simulation.

of the simulated reflection is calculated to be 314 nm/RIU, larger than that of the experimental value (239 nm/RIU). The difference in sensitivity could also result from the defects and the nonideal sharpness of tips and edges of the templated nanopylramids.

We further investigated the biosensing performance of the nanopylramid arrays by using Rabbit IgG antibody to alcohol dehydrogenase. The Au nanopylramid array was treated with Protein A to enhance the conjugation of rabbit IgG on Au nanopylramids. 5 $\mu\text{g}/\mu\text{l}$ of Protein A (MP Bio-medicals) was put on a clean Au nanopylramid array sample and incubated overnight at 4 $^{\circ}\text{C}$. After incubation, the nanopylramid array was rinsed three times with phosphate buffered saline (PBS) buffer to wash away unadsorbed Protein A and then incubated with 10 $\mu\text{g}/\text{ml}$ of rabbit polyclonal to alcohol dehydrogenase (abcam) overnight at 4 $^{\circ}\text{C}$. The corresponding normalized reflection spectrum due to the adsorption of anti-alcohol dehydrogenase is shown in Fig. 5 with a peak wavelength of 595.9 nm. 40 ng/mL of alcohol dehydrogenase (MP Biomedicals) in PBS was then added on the array and incubated for 1 h at room temperature, followed by three times rinsing with PBS buffer for removing unbound residue. A redshift in peak wavelength from 595.9 to 602.3 nm was observed when alcohol dehydrogenase was added. We have also tested the detection selectivity by using casein,

FIG. 5. (Color online) Normalized reflection spectra obtained from a gold nanopylramid array with adsorbed anti-alcohol dehydrogenase shown as the first spectrum from the left, followed by the addition of specific alcohol dehydrogenase, and nonspecific protein casein. The spectrum shows a red shift after the alcohol dehydrogenase addition, and a slightly blue shift is observed after the nonspecific protein binding.

a protein commonly used as a blocking reagent. After the conjugation of alcohol dehydrogenase, the same array was exposed to 1% casein in PBS (Thermo). As expected, no obvious peak shift was noticed due to the negligible binding of nonspecific protein casein on the sample, even though the blocking protein concentration is $\sim 250\,000$ higher than the enzyme concentration. The purpose of adding casein after the enzyme adsorption is to prevent false signal caused by the binding of this blocking protein on Au nanopylramids not covered by the antibody.²⁷

In summary, we have demonstrated that templated nanopylramid arrays with sharp nanotips exhibit strong SPR due to the efficient localization of electromagnetic field. The templating technology is scalable and compatible with standard microfabrication, promising for developing sensitive chemical and biological sensors for real-time and label-free detection.

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