PLASMONIC NANOPARTICLE DEPOSITION ON A MICROPILLAR ARRAY AS A 3D NANOSENSOR

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ABSTRACT

A sensitive and compact 3D plasmonic nanosensor was developed by deposition of gold nanoparticles (AuNPs) on a silicon micropillar array for label-free biosensing. This silicon micropillar array also worked as an autonomous capillary pump, capable of transporting a specific amount of bio-samples into the sensing area without external pumping requirement. The developed device greatly decreased system complexity and sample consumption. Both the extinction spectra peak position and the maximum extinction exhibited good linear relationships with the surrounding refractive index of the environment.

KEYWORDS: Capillary flow, Micropillars, Localized Surface Plasmon Resonance (LSPR), Nano-(bio)sensor

INTRODUCTION

Noble metal nanoparticles such as gold or silver nanoparticles, reveal an intense color that can be explained by the phenomenon known as Localized Surface Plasmon Resonance (LSPR), which are collective oscillations of conduction electrons induced by visible light. These light-absorption and scattering properties of the nanoparticle are very sensitive to changes in the local environment around it and have been used for label-free biosensing. Previous work reported the AuNPs-based biosensors for the detection of various biomarkers in suspensions and on substrates [1]. Recently, the AuNPs have also been integrated with a microfluidic chip, thus taking advantages from both technologies [2]. However, the main drawback of this configuration was that the affinity-based bio-reaction (e.g., antibody-antigen interaction) could only take place at the vicinity of the 2D biosensor surface (vicinity of the LSPR AuNPs). The analytes far away from the sensor surface (e.g., analytes in the middle or top area of the channel) were just flushed away. Therefore, the efficiency of the 2D biosensor was relatively low. Meanwhile, given the low surface area to volume ratio (S/V) of the AuNPs coated 2D substrates, the diffusion-based immunoassay kinetics was also rather slow.

In this study, the concept of microfluidic integrated nanosensor was extended to a capillary-driven device as a 3D nanosensor. AuNPs were deposited on a microfabricated 3D Si micropillar array, both on the top surfaces and side walls for LSPR biosensing. The micropillar array also worked as a capillary pump for loading aqueous sample. This configuration takes the advantages of LSPR biosensing on a 3D structure and allows autonomous detection without external pump or valve.

WORKING PRINCIPLE

As shown schematically in Figure 1, AuNPs exhibited unique LSPR effect, which could be used as an optical nanosensor for the detection of immunoassays. By measuring the extinction spectra shift, the analyte concentration could be quantitatively determined. In this study, unlike the conventional LSPR nanosensor on a flat substrate, we proposed a 3D plasmonic nanosensor by deposition of AuNPs on microscale pillars inside a channel. As schematically shown in Figure 2, the Si micropillar array is prepared by microfabrication and the AuNPs are deposited both on the top and the side wall of the micropillars. For detection of biomolecules (e.g., Immunoassay), the antibody is pre-immobilized on the AuNPs’ surface. When the aqueous sample containing antigen is added into the device, the sample will propagate along the micropillar array and interact with the antibody. By using the optical detection approach shown in Figure 1, the antibody-antigen interaction can be detected. The micropillar array not only provides large surface area for AuNPs deposition for facilitating the biosensing, but also simultaneously works as a capillary pump, generating autonomous capillary flow to load aqueous sample into the device. By controlling the dimensions of the pillar and inter-pillar distance, as well as the surface properties, the capillary flow can be precisely controlled.

EXPERIMENTAL

The 3D nanosensor contains a 7.2×80 mm channel, which is filled in with highly ordered cylindrical micropillars with a diameter of 5 μm [3]. The device was fabricated using standard lithography and deep reactive ion etch (DRIE) of Si wafer. Afterwards, a SiO2 layer was thermally grown on the device to obtain a hydrophilic surface. AuNPs in suspension with a diameter of 43 nm were prepared by sodium citrate reduction of hydrogen tetrachloroaurate (HAuCl4), as described elsewhere [1, 2]. The prepared AuNPs in suspension were further deposited on the silicon micropillar array by a protocol of self-assembled monolayer (SAM) of 3-mercaptopropyltrimethoxysilane [2].

To characterize the capillary flow behavior, one dimensional liquid propagation was studied by adding a 20 μL droplet of water on one end of the 3D nanosensor and measuring the water penetration along the channel. To assess the sensitivity of the device to the environmental refractive index (RI) change, droplets of different glycerol solutions with different RIs were added into the nanosensor and the UV-vis spectra were measured. Another same Si micropillar device but without coated AuNPs was used as a reference.
RESULTS AND DISCUSSION

Figure 3 shows the SEM images of the fabricated 3D nanosensor. The pillars are approximately 5 µm in diameter and 50 µm in height with excellent uniformity. A closer observation of the pillars shows that both the top and sidewall surfaces are fully covered with a monolayer of AuNPs with an averaged diameter of 43 nm. The SEM images also shows that the most of the AuNPs are not touching but they are isolated with an interval of the same magnitude as the AuNP’s diameter.

Figure 4 shows water meniscus propagation along the device driven by capillary force when 20 µL of deionized water was added on the sample loading port. It was observed that the entire device (80 mm long) was completed filled in by water within 3 min with a decreasing flow rate (Figure 5).

Figure 6a shows the optical extinction spectra of the 3D nanosensor when different glycerol solutions with different RIs were penetrated into the device by using a micropillar array without AuNPs as a reference. When changing the surrounding RI of the AuNPs, a red-shift of peak position and an increase of the maximum extinction occurred. Both the peak position and the maximum extinction exhibited linear relationships with the surrounding RIs (Figure 6b). The variation trends of the 3D nanosensor agreed well with reported 2D nanosensor on planar substrates [1, 2]. Moreover, the surface to volume ratio (S/V) of the 3D nanosensor was increased up to 1000, which was 30 times higher than a 2D LSPR nanosensor. This greatly increased S/V ratio indicated greater accessibility of the sensors to biomolecules, thus a higher sensitivity and faster detection for the developed 3D nanosensor was expected.
CONCLUSION

In this research, we have successfully deposited plasmonic AuNPs on a 3D micropillar array, which simultaneously worked as a capillary flow device and a LSPR nanosensor. Our approach provided a direct way to couple highly sensitive, label-free nano-biosensors with a compact 3D capillary flow device, thus taking advantages from both technologies.

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REFERENCES


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