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Colorimetric imaging of layer-by-layer molecular deposition on nanoplasmonic lycurgus cup array

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ABSTRACT

A quantitative label-free colorimetric imaging of biochemical molecular thin film deposition at a single molecule layer (2 nm thickness) resolution was demonstrated on a nanoplasmonic sensor substrate known as nano Lycurgus Cup array (nanoLCA) and the penetration depth of the nanoplasmonic sensor was accordingly determined. Colorimetric nanoplasmonic imaging technique provides significant advantages in direct visualization and quick identification of surface deposited molecules. We implement layer by layer deposition of alternating polyelectrolyte layers with controlled thickness on the nanoLCA device to show surface color changes and determine the decay length of the device derived from the sensor spectral response to the molecular layer thickness. The calculated decay length of the nanoLCA device is 193 nanometers which corresponds well with the decay length of other known surface plasmon sensors. In addition micro contact molecular printing and transferring on the nanoLCA surface is used to selectively deposit poly-L-lysine and different alkanethiol molecules to demonstrate direct colorful visualization of surface patterned unlabeled molecules.

1. Introduction

In many biochemical sensing methods, labeling molecules are incorporated with the target molecule for detection such as fluorescent or chromatic dyes used in enzyme-linked immunosorbent assays (ELISAs)) [1]. Sometimes, the addition of labels may hinder the innate functionality of the target biomolecule, or lead to the interaction with background biomolecules altering the detection efficacy. While in the case of label-free sensing, the target molecule is directly detected without additional labels attached [2]. Label-free optical sensors based on surface plasmon resonance (SPR) has gained prominence because of the high-sensitivity to the optical refractive index of the biomolecules on sensor surface. Surface plasmon is a collective oscillation of surface-bound free electrons at the interface of a dielectric and a metal layer [3]. Surface plasmon polaritons (SPP) are generated when the free electrons oscillate in resonance ("couple") with the incoming light wave in the form of photons. The generated SPP then propagates along the interface of the dielectric layer and the metal layer, while at the same time penetrating both layers in the form of an evanescent field with exponentially decaying intensity away from the interface. The wave-vector of the SPP is given as, $k_{sp} = k_o\sqrt{\frac{\varepsilon_m\varepsilon_d}{\varepsilon_m+\varepsilon_d}}$ where ε_m and ε_d are the permittivity of the metal and the dielectric material respectively and k_0 (=ω/c) is the wave-vector of the incident light. The generation of SPP is not trivial due to a mismatch between the k_{SP} and k_0, therefore, further instrumentation is required to provide the additional momentum in order to generate SPP at the interface. The diffracted or scattered light from a grating structure, with increased momentum, can be used to couple light to generate SPP's. The grating coupling can be achieved by nanohole array structure shows extraordinary transmission (EOT) with optically thick metal deposited on the pattern [4,5]. The physical dimensions of the nanohole arrays (e.g. periodicity, depth, and diameter) have significant influence on the optical properties (e.g. the position of peak wavelength λ_{max}, full-width half-maximum (FWHM, sensitivity) of the extraordinary transmission, for a given noble metal (e.g. gold and silver) [6]. A large number of experimental studies have elucidated the relationship between the periodicity of the nanohole array, defined as the center-to-center distance between neighboring nanoholes, p, and the sensitivity, defined as change in the peak wavelength for a given change in refractive index.

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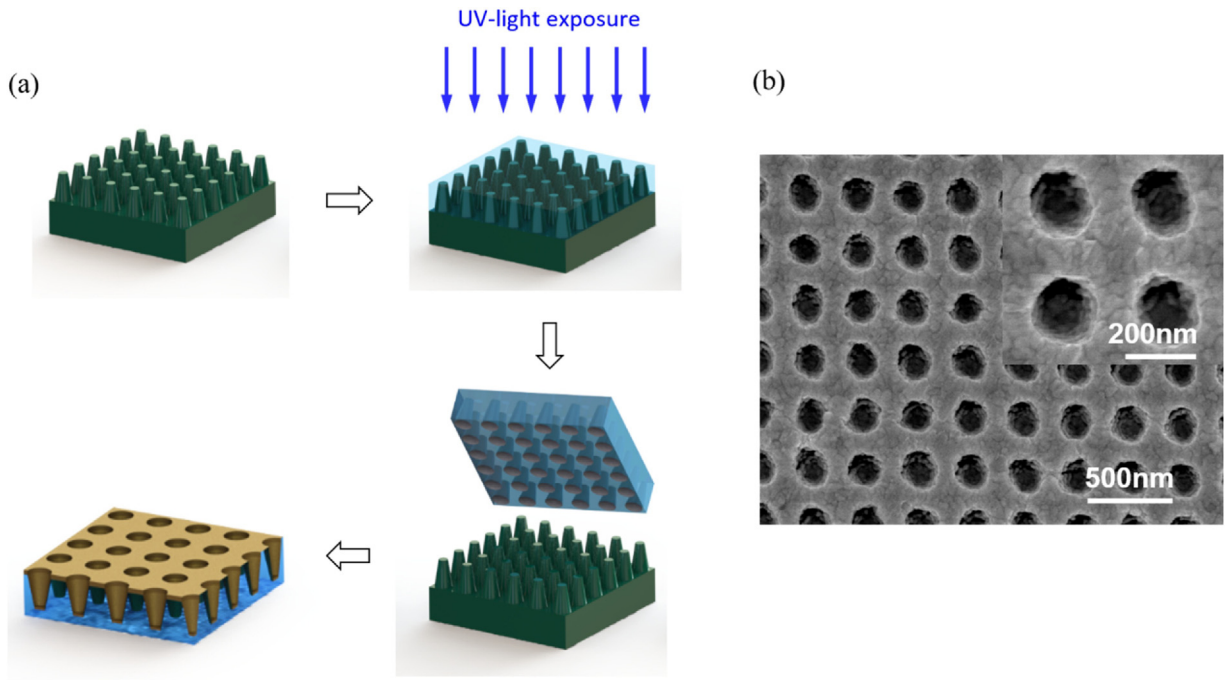

Fig. 1. (a) Schematic overview of the replica molding fabrication process. The nanocone master made on glass substrate is first cleaned and silanized followed by evenly spread of UV-curable polymer (UVcP) (NOA-61) on the top of it. Then, PET sheet is carefully put on top of the polymer, to avoid the bubble formation and exposed to UV-light. The PET substrate with nanohole arrays was peeled off carefully from the master mold and thin metal layer is deposited. (b) Scanning electron microscope (SEM) image of top view of nanohole array and inset is showing the nanoparticles inside the nanohole structure.

Recently, a plasmonic nanostructure known as nanoscale Lycurgus cup array (nanoLCA) has been demonstrated for highly sensitive refractive index sensing. [7,8] A master nanocone array pattern is fabricated on a glass substrate using laser interference lithography technique [9,10]. The two-dimensional square lattice on the master mold (pitch, $p = 350$ nm) is transferred to a flexible and optically transparent polyethylene terephthalate (PET) film using a nanoreplica molding process. The schematic of the replica molding fabrication process is shown in Fig. 1(a) with the SEM image shown in Fig. 1(b). It is quite clear that nanoscale features can be transferred to the polymer substrate from the original master mold with a high fidelity. The large-area replica molding process is deployed to make a low-cost, wafer-scale nanoplasmonic device, which opens up the opportunity for various biosensing applications. [11] This nanoLCA substrate achieves a single prominent resonance in the visible wavelength range from 1 refractive index unit (RIU) to 1.5 RIU, unlike previous EOT substrates that show multiple resonance wavelengths [12]. The resonance wavelength red-shifts with increasing the surrounding refractive index and resulting changes in transmitting colors. The nanoLCA device enables not only determination of the refractive index of an unknown fluids but also colorimetric sensing of target analytes [10].

Surface plasmon polaritons (SPPs) propagate along a metal-dielectric interface with an electric field that decays exponentially normal to the surface of the sensor. The evanescent field range is referred as the decay length or penetration depth typically in tens to hundreds of nanometer range, and it defines the sensing region of the device. One popular method of decay length characterization for SPR sensing is to deposit surface molecule films with controlled thicknesses and known refractive index and measure the optical response of the sensor to the deposited film. An analytical function can be derived to approximate the electric field decay characteristics on the sensor surface. Typically, the materials used in the layer by layer (LbL) deposition are two different polymers which are cationic and anionic under different conditions and mutually attracted to each other through electrostatic interactions. Although the growth rate of the polymer film is not self-limiting, the thickness of the deposited film can be controlled through the duration of the immersion (or exposure) to the polymer solution. In this paper, we demonstrated layer by layer deposition of polyelectrolyte films on the nanoLCA device to determine the decay length with the help of spectrum and colorimetric analysis. Furthermore, we have introduced micro contact printing to selectively deposit poly-L-lysine and different alkanethiol for surface functionalization on nanoLCA devices.

2. Materials and methods

2.1. NanoLCA device fabrication

On the master (mold) nanocone array pattern is fabricated on a glass substrate using the laser interference lithography technique is first cleaned and silanized followed by evenly spread of UV-curable polymer (UVcP) (NOA-61, Sigma Aldrich) on the top of it. Then, PET sheet is carefully put on top of the polymer, to avoid the bubble formation and to act as a substrate, and exposed to UV-light ($105\ \text{mW cm}^{-2}$). The PET substrate with nanohole arrays was peeled off carefully from the master mold and then a 90 nm thick metal layer of gold is deposited.

2.2. Layer-by-layer deposition

All of the reagents for the layer-by-layer deposition were purchased from Sigma Aldrich (Milwaukee, WI). The NanoLCA device was immersed in 33 mM of dithiodibutyric acid (DTBA) in ethanolic solution for 24 h to form a self-assembled monolayer with a carboxyl terminal. After the immersion, the sample was rinsed with ethanol and dried with Nitrogen gun. For layer-by-layer deposition, the sample was immersed alternately in two polymer solutions,

Poly(allylamine) (PAH) and Poly(sodium 4-styrenesulfonate) (PSS). PAH solution was prepared at a concentration of $3\ \text{mg mL}^{-1}$ (pH 8.0) in Millipore water and PSS solution was prepared at a