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A fully biocompatible poly(ethylene glycol)–gold plasmonic crystal for optical sensing

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ABSTRACT

A significant challenge in nano and biophotonics is to demonstrate fully biocompatible nano-optics devices that can perform biofunctions *in vivo*. Here we present a scalable, cost-effective, and large-area nanofabrication method for creating a quasi-3D plasmonic crystal using poly(ethylene glycol) (PEG) and gold (Au), both biocompatible materials. The plasmonic crystal was prepared by depositing an Au layer on the upper hemisphere of the replicated PEG nanospheres array. Additionally we demonstrated that the fabricated plasmonic crystal can behave as a label-free glucose sensor with sensitivity and figure-of-merit values comparable to other plasmonic crystal based sensors.

1. Introduction

The ability to control electromagnetic waves on the metallic surface, through the phenomenon of surface plasmon resonance (SPR), has proven to be attractive for direct optical sensing to probe refractive index (RI) changes [1–3]. The advantage of employing SPR in optical sensing lies in its ability to monitor light-analyte interaction without labeling, along with the real-time determination of individual analyte interaction. In particular, localized surface plasmon resonances (LSPRs) carried by metal nanostructures cause dramatically improved light-matter interaction and therefore are a means to measure local RI changes at the nanoscale, with only a simplified measurement system (not entailing prisms or gratings to couple incident light to metallic surfaces) [3]. Numerous LSPR based bio/chemical sensors have been demonstrated using nanoparticles, nanoshells, nanoslits, nanoholes, etc. [4–7]. More complex plasmonic sensors based on specific physical mechanisms (e.g. perfect absorption, electromagnetically induced transparency, and extraordinary transmission (EOT)) have also been reported [8–11]. Especially plasmonic crystals based on colloidal crystals can induce interesting optical phenomena such as the EOT and the absorption-enhancement, along with cost-effective fabrication methods [12–14].

An additional degree of utility that helps extend sensor applications to *in vivo* experimentation can be derived by the use of biocompatible materials [15]. Since noble metals used for plasmonic applications are basically biocompatible, it can open up an avenue to realizing a fully biocompatible plasmonic bio-device when used in conjunction with biopolymers [16]. To date, the conventional approach to demonstrating plasmonic devices is through the integration of metallic nanostructures onto silicon, glass, and polydimethylsiloxane (PDMS), which have poor biointerfaces and functional programmabilities [17]. This is because conventional fabrication methods have been developed to be suitable for semiconductors. Harsh processing conditions such as high temperatures, high-energy plasma treatments, and reactive wet chemicals restrict the adaptation of conventional methods to biopolymers. Therefore, newer ways to tackle these challenges are required for the successful demonstration of biopolymer-based plasmonic devices. And spontaneous adhesion of noble metals on all proteins and most other biopolymers can be a key feature to find new ways [18].

In this letter, we report a simple, scalable, cost-effective, and high throughput fabrication for a fully biocompatible plasmonic device. The close-packed monolayer of poly(ethylene glycol) (PEG) nanospheres is replicated from that of polystyrene (PS) nanospheres via an intermediate water-soluble silk template. To

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the best of our knowledge, no periodic and large area PEG nanostructure has been yet demonstrated. The following deposition of a thin gold (Au) layer allows for the demonstration of a quasi-3D plasmonic crystal bio-platform. The fabrication process is performed under mild conditions, *i.e.* at room temperature with water treatment. The Au–PEG biocompatible plasmonic crystal (BPC) exhibits an EOT, which originates from a strong plasmonic resonance. A finite-difference time-domain (FDTD) simulation is performed to analyze the resonance behavior. We characterize the sensing capabilities of our Au–PEG BPC using glucose as a model analyte.

2. Materials and methods

Fig. 1 presents a schematic of the process flow for the fabrication of the Au–PEG BPC. The monolayer of the close-packed PS nanospheres (5% concentration dispersed in water, Invitrogen), with a diameter of 420 nm, was assembled using the convective coating process on a glass substrate [19]. Aqueous silk solution was then cast onto the PS monolayer, yielding a removable template. Details for the silk solution are described in Ref. [20]. The PS nanospheres were subsequently removed by exposure to toluene. A poly(ethylene glycol) diacrylate (PEG-DA, Sigma–Aldrich, M_n = 250) precursor solution containing 5 wt% photoinitiator (2,2-dimethoxy-2-phenyl-acetophenone, Sigma Aldrich) was then poured onto the silk template and polymerized using a UV light box (8 min. and 78 μW/cm^2, Osram, Ultra-Vitalux). The silk template was thereafter selectively removed by immersion in water. A 50-nm-thick Au film was subsequently deposited on the free standing PEG film with the monolayer of the PEG nanospheres. This process creates the plasmonic crystal by forming a hexagonal array of nanoscale holes. This 50-nm thickness of the Au film was chosen because efficiency to sustain surface plasmon modes becomes very poor when the thickness is considerably thinner than the skin depth, ~33 nm at the wavelength of 650 nm, and the Au-deposition process targeting to over 50-nm thickness could block the nano-voids [11,13].

3. Results and discussion

Fig. 2(a) shows a photographic image of the fabricated Au–PEG BPC. The strong diffraction of visible light spanning the entire sample indicates complete coverage of the periodic plasmonic structures. Scanning electron microscopy (SEM) images at each process step depicting removal of the PS spheres, curing of the PEG-DA solution, and finally coating with an Au layer are shown in Fig. 2(b)–(d) respectively. These help confirm that the monolayer of the close packed PS nanospheres on the glass substrate has been successfully replicated with PEG as the replacement material. We note that the top view of the SEM images for the replicated PEG nanospheres shows a hexagonal pattern due to the overlapping outer covering of the nanospheres. The prolonged exposure of the inversed silk template to toluene, for the removal of the PS nanospheres, induces the shrinkage of the template, thus reducing the center-to-center distance of the PEG nanospheres [12].

The spectral responses of the transmission and the reflection measurements were examined to analyze the optical response of the fabricated Au–PEG BPC. For the transmission, white light was illuminated to the side of Au/air interface of the Au–PEG BPC. The transmitted signal was coupled to a fiber tip on the opposite side and went to the spectrometer (USB-2000, Ocean Optics). The reference signal was collected using an aluminum mirror. For the reflection, we used a 1 × 2 fiber coupler and white light was fed into its input port. Illumination and collection of the reflected signal were performed through the output port of the fiber coupler. Fig. 3(a) exhibits the measured transmission and reflection spectra. A notable phenomenon is the EOT peak at 550 nm that originates from the coupling of the surface plasmon (SP) modes to the Bragg resonances. Although the incident light penetrates the Au–PEG BPC through very tiny holes (~30 nm diameter), the intensity of the EOT peak is over two times higher than that at any other wavelength. The full width at half maximum (FWHM) value of ~150 nm is comparable with other reported results for the metal-coated monolayer of colloidal spheres. As a reference, we fabricated the Au–PS plasmonic crystal with a gold layer deposited on the monolayer of the PS nanospheres. The measured transmission spectrum is also shown in Fig. 3(a). Although the Au–PS plasmonic crystal exhibits a 50-nm red-shift of the EOT peak from that of the Au–PEG BPC due to a difference in its center-to-center distance and the higher RI of PS (n_{PS} = 1.59 and n_{PEG} = 1.48), the definite feature of the EOT displayed by both plasmonic crystals indicates that the colloidal crystal was successfully replicated as a biocompatible form.

Additionally, for further understanding of the optical responses, 3D numerical simulations were performed using the Lumerical software, which is based on the FDTD method. The simulated transmission is illustrated as the dotted black curve in Fig. 3(b), along with the measured transmission. All geometrical parameters in the simulation were taken from the SEM images shown in Fig. 2. The simulated and measured spectra are found to be highly consistent with each other in terms of the prediction of the EOT mode, although the bandwidth of the experimentally measured EOT

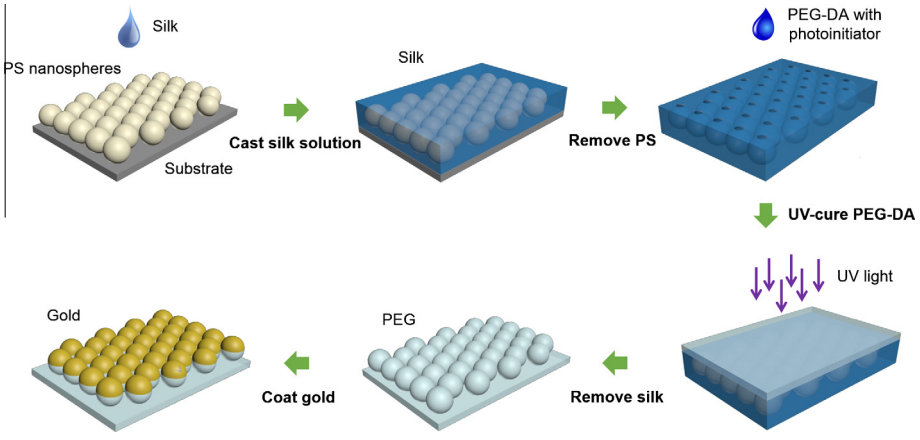

Fig. 1. Schematic of the fabrication process for a free-standing plasmonic template on the monolayer of PEG nanospheres.