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LSPR nanosensors with highly ordered gold nanoparticles fabricated on nanodimpled aluminium templates

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Abstract

The fabrication and characterization of a localized surface plasmon resonance (LSPR) based optical nanosensor, which utilizes highly ordered gold nanoparticles as transducers are presented in this work. The nanoparticles are synthetized using nanodimpled aluminium templates, which were prepared by a selective chemical etching of the porous anodic alumina grown over an aluminium sheet. The formed nanoparticles were directly transferred to PDMS (polydimethylsiloxane) based microfluidic cells, where their LSPR transmittance spectra were measured. The effect of the particle size and distribution on the LSPR bulk refractive index sensitivity is investigated.

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Keywords: Localized surface plasmon resonance; nanoparticles; plasmonics

1. Introduction

The phenomenon of localized surface plasmon resonance on nanostructures can be effectively utilized to measure changes in the refractive index of the surrounding media thus enabling its application in the fields of gas sensing, chemical sensing or biosensing. The sensitivity and limit of detection of LSPR sensor elements is strongly depending on the size, shape and distribution of the applied nanostructures and can vary a lot [1]. It is already proven that with the proper nanostructures the sensitivity of LSPR (considering molecular or biosensing applications) can reach the

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sensitivity of classic Kretschmann-configuration based SPR devices on the market [2,3], while offering the possible advantage of an easily integrable transmissive optical setup for smaller, even handheld devices.

In this work we present and characterize a fabrication technology which yields highly ordered nanoparticle systems on a large surface area for the preparation of cost-effective but sensitive LSPR sensor elements. For the nanoparticle synthesis (Fig. 1) a nanodimpled aluminium template is utilized which has the following advantages considering the application area: i) the process yields highly ordered distributions, where the nanoparticle size and spacing can be controlled with the dimple size and the deposited thin film thickness; ii) the synthesis is possible on a large surface area (in the cm2 range), which is required for SPR imaging applications; iii) the direct transfer of the nanoparticles to the wall of PDMS/PMMA based microfluidic elements is possible and iv) the fabrication technology is relatively cheap.

2. Experimental

An aluminium (Al) foil of 99.999 % purity and 250 µm thickness (Goodfellow) was used as the staring material. The Al foil was annealed in a vacuum (approx. $4 \cdot 10^{-4}$ Pa) at 550 °C for 10 h to allow material to relax and recrystallize. Afterwards, the foil was mechanically and electrochemically polished. The mechanical polishing was performed using ultra fine (P3000) sandpaper in ethanol. The electrochemical polishing was undertaken within simple two electrode setup, wherein the Al foil was set as the anode and a stainless steel mesh was used as the cathode. The polishing was performed for 1 minute at 20 V (approx. 100 mA/cm^2) in 70 % perchloric acid and ethanol (1:4, v/v) solution at 3 °C without solution stirring. After the preparation procedure, the Al foil was anodized in 0.3 M oxalic acid at 7 °C for 18 hours and applied voltage of 40 V (to obtain 100 nm dimples) or 1 M sulphuric acid at 3 °C for 12 hours at 20 V (50 nm dimples). Subsequently, the thick porous alumina layer was selectively removed, in 0.42 M phosphoric acid and 0.2 M chromium trioxide etching solution at 60 °C for 1 hour, revealing the patterned nano-dimpled aluminium template (schematically shown in Fig. 1A and in SEM images in Fig. 2:A and Fig. 2:B for 40V and 20V anodizing conditions, respectively).

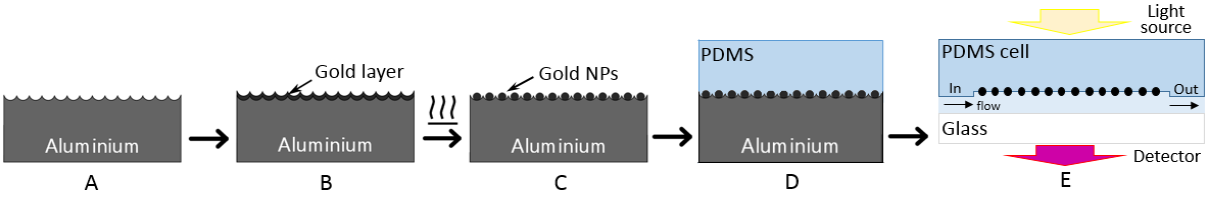

Fig. 1. Illustration of the synthesis and transfer of the gold nanoparticles. A) the nanodimpled Al substrate as a template; B) vacuum deposition of a gold thin film; C) synthesis of the nanoparticles through thermal annealing; D) transfer of the nanoparticles to a PDMS microfluidic cell during PDMS casting; E) illustration of the flow-through PDMS microfluidic cell with the integrated nanoparticles and the transmissive optical measurement setup.

The nanoparticles (NPs) fabrication is conducted by utilizing nanostructured aluminium substrate as a template for controlled dewetting of thin gold layer (schematically shown in Fig. 1). Firstly, a thin gold layer was deposited over the Al template by magnetron sputtering. Furthermore, the annealing in the ambient atmosphere at 300 °C leads to formation of NPs. The parameters such as NP size and spacing were controlled by combining and modifying deposition parameters and annealing procedures. SEM images of achieved NP films on corresponding Al substrate are shown in Fig. 2. Nanoparticle layer was transferred to a PDMS substrate by standard casting procedure within a specially design microfluidic cell mold. After solidification of PDMS the aluminium was dissolved in 5 M hydrochloric acid and 2 M copper(II) chloride solution. The final microfluidic cells with NP layers are shown in Fig. 3.

Scanning electron microscopy (SEM) measurements were done with a Tescan Mira II field emission scanning electron microscope equipped with in-lens detector of secondary electrons. Atomic force microscope (AFM) measurements were done with a Veeco (lately Bruker) diInnova type microscope in full contact and tapping mode with 512x512 sampling rate and 1 Hz scan rate. The PID values were optimized according to the user manual. We used Budget Sensors TAP 150-G probes for tapping mode imaging. For data evaluation the freeware Gwyddion 2.27

software was used. The optical spectroscopy measurements were performed with an Avantes Avaspec 2048-4DT spectrometer and an Avantes Avalight DHS halogen light source between 400 nm and 750 nm.

3. Results and Discussion

Fig. 2 presents SEM images of the nanodimpled aluminum templates, which were used for the nanoparticle synthesis. As can be seen, the dimples have a hexagonal arrangement on the whole template surface. The diameter of the dimples can be controlled trough the anodizing condition, especially anodizing potential, since it correspond to porous alumina cell size [4]. Together with layer thickness of the subsequently deposited gold thin film and the annealing parameters the resulting size of the nanoparticles, and also their spacing can be controlled as illustrated in Figures 2:A1-3 and B1-3. If the gap between the particles is sufficiently small the incited plasmons can tunnel through the gap which results in a type of coupled plasmon resonance between the particles [5]. This leads to a significant increase in the near field intensity in the gap and also to a significant increase in LSPR bulk refractive index sensitivity.

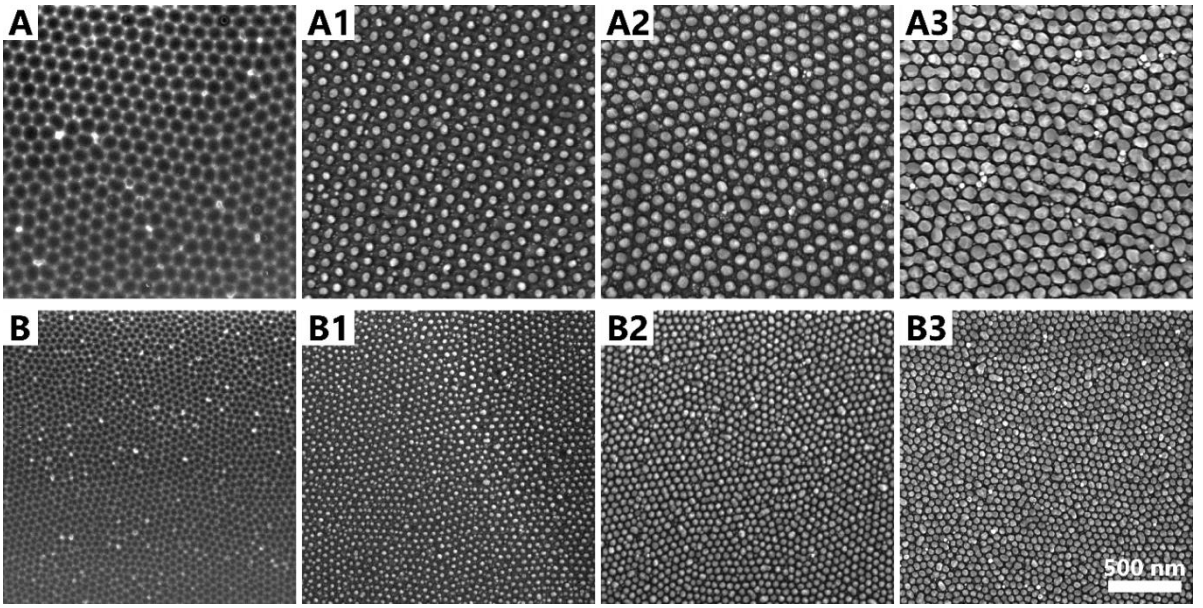

Fig. 2. SEM image of the nanodimpled aluminium substrate which serves as a template for the gold nanoparticle synthesis, prepared by anodic oxidation (A) in the oxalic acid at 40 V and (B) in the sulphuric acid at 20 V. In associate images are shown highly ordered gold nanoparticles with various sizes and spacing synthetized on such templates.

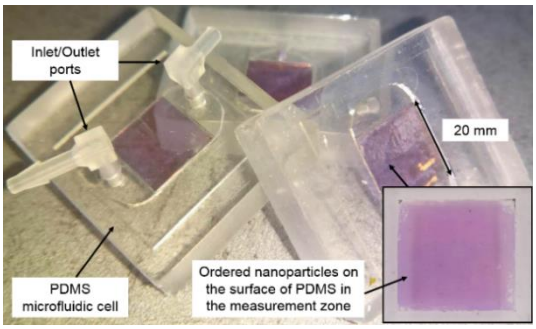

Fig. 3. The PDMS microfluidic cell with the highly ordered gold nanoparticles integrated onto the wall of the measurement chamber, which has an area of 20 mm x 20 mm.

Such tightly packed nanoparticles, synthetized by similar technique utilizing porous alumina templates were proved to be sufficiently sensitive for molecular scale sensing recently [6]. To increase the coupling effect between the

synthetized nanoparticles we managed to optimize the technological parameters to yield nanoparticles with diameters around 40 nm with average gap distances under 10 nm, as can be seen in Fig. 2:B3. Efforts to further decrease the gap resulted in the merging of the particles, which can already be observed in some cases in Fig. 2.

Fig. 3 presents the custom PDMS based microfluidic cells with the nanoparticles transferred to the wall of the reaction chamber. The cell was designed for flow-through microfluidic systems and transmissive optical LSPR measurements. A current challenge of the technological process is the proper transfer of the nanoparticles into the wall of the PDMS chamber. Fig. 4 presents AFM images from the transferred particles. In this particular case the template aluminum was not completely removed and the particles only partially protrude from the surface. In order to gain optimal sensitivity, the technology should be further optimized to ensure that maximal surface area of the nanoparticles is uncovered and accessible for sensing purposes.

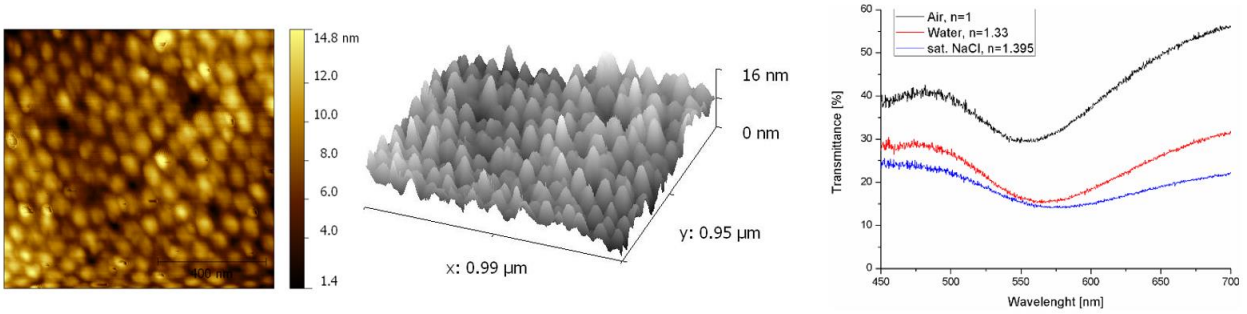

Fig. 4. Left: Tapping-mode topography AFM image of the nanoparticles transferred to the PDMS microfluidic cell. Middle: 3D representation of the same topography. Right: LSPR transmittance spectra of the transferred gold nanoparticles on a PMMA substrate in different media (air, water and saturated NaCl solution).

4. Conclusions

A complex technology to fabricate highly-ordered gold nanoparticle arrangements transferred to PDMS microfluidic devices to serve as transducer elements in LSPRS sensor devices is presented. The fabrication technology was optimized to yield nanoparticle distributions with minimized particle gap distances for enhanced sensitivity. The most challenging part of the technology is the transfer of the particles to the PDMS substrate, which still needs further optimization to obtain the highest possible sensitivity.

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