Evaluation of High-Density Arrays of Au Nanoparticles on Porous Anodic Aluminum Oxide for Refractometric Sensing

Uldis Malinovskis, Raimonds Popļausks, Aušrinė Jurkevičiūtė, Aleksandrs Dutovs, Donats Erts, Juris Prikulis

Institute of Chemical Physics, University of Latvia, 19 Raina Blvd., Riga LV-1586, Latvia
E-mail address: juris.prikulis@lu.lv

Exceptionally dense (~100 µm^{-2}) non-close-packed (NCP) arrays of Au nanoparticles (NP) were produced using capillary force assisted colloidal assembly on porous anodic aluminum oxide (PAAO) (Fig. 1a). The PAAO structure prevents particle aggregation [1] while the NPs have a large exposed surface area. Arrays of AuNP with 40 nm, 60 nm, and 80 nm diameter were evaluated for localized surface plasmon resonance (LSPR) refractometric sensing. The actual system consisted of a bulk aluminum substrate, a variable thickness porous PAAO layer, and an NCP array of Au nanoparticles (Fig. 1b) with different diameters [2]. Production of such structures relies on self-organizing physical and chemical processes and can be done in a wet chemistry lab without use of lithography tools.

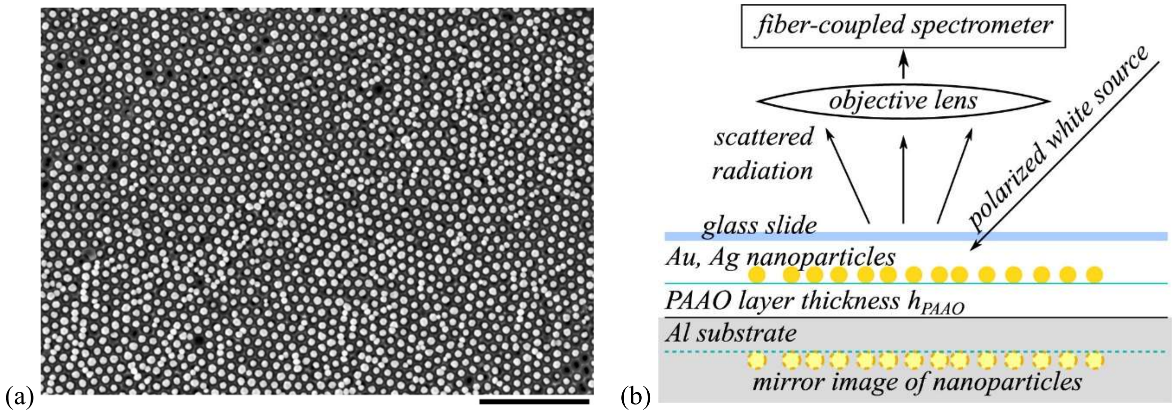

Fig. 1 (a) Scanning electron microscope image of 60 nm diameter Au nanoparticle NCP array on PAAO (scale bar 1 µm). (b) Schematic of the optical setup.

For specific combinations of NP size and PAAO layer thickness, the scattering signal with well resolvable spectral peaks was observed upon angled illumination with S-polarized incandescent source. The samples with 60 nm and 80 nm Au NP had the strongest scattering at PAAO thickness ~350 nm, whereas 40 nm diameter Au NP showed a relatively weak scattering with resolvable peaks found only in a comparatively narrow PAAO thickness range between 350 nm and 550 nm. The scattering intensity variations with PAAO thickness can be understood by considering the particle - mirror image pairs (Fig.1b), which at certain distances and wavelengths form a directional antenna with radiation pattern that fits within the aperture of the objective lens. When the wavelength matches the LSPR, this leads to increased recorded signal intensity. The bright and colorful scattering could easily be observed even by the naked eye.

The RI sensitivity $\Delta\lambda/\Delta n$ was tested by immersing the NP arrays in different liquids contained between a glass slide and PAAO surface (Fig. 1b). The key observation was that for 60 nm diameter Au NP the sensitivity was maximized at PAAO thickness ~500 nm and exceeded 200 nm/RIU, while for other thickness and diameter combinations typical sensitivity values were in 75-100 nm/RIU range.

Based on the above observations a good compromise between signal intensity and RI sensitivity can be achieved using 60 nm diameter AuNP on PAAO with ~350-500 nm thickness. Considering the production tolerances of NP diameters, the PAAO thickness may require adjustment for each batch of AuNP colloid solution. In order to circumvent this problem, a continuous thickness gradient PAAO [3] can be used to find the optimal PAAO thickness. The RI sensitivity of Al-PAAO-AuNP arrays is similar to that of individual NP LSPR sensors, however the high brightness, tunability and ease of production of PAAO based substrates can be very useful for sensor device design.

References

[1] Malinovskis, U. *et al*., 2019, *Nanomaterials* **9**: 531.
[2] Malinovskis, U. *et al*., 2022, *ACS Omega* **7**: 40324–32.
[3] Poplausks, R. *et al*., 2018, *ACS Omega* **3**: 5783–88.