Nanobowled Aluminum Platforms Based on Nanoporous Anodic Alumina for SERS Applications

Gohar Ijaz Dar, Elisabet Xifre-Perez, Lluis F. Marsal

Department of Electronic, Electric and Automatic Engineering, Rovira i Virgili University, Avda. Països Catalans 26, 43007, Tarragona,Spain

E-mail: lluis.marsal@urv.cat

In recent years, surface-enhanced Raman scattering (SERS) has garnered a lot of attention due to its high potential to be utilized in chemical and biological sensing as well as biomedical diagnostics.

In this work, the development of nanobowled aluminium (Al) platforms for SERS applications is presented, recreating the interesting honeycomb configuration on an Al substrate and its adaptable functionalization [1,2]. The initial formation of a nanoporous anodic alumina (NAA) sacrificial layer allows the tuning of the self-ordered nanobowls distribution on the Al surface. Using phosphoric acid and oxalic acid electrolytes, an anodization technique that consisted of two steps was utilized in order to create the NAA initial layer. Al nanobowls with diameter of ~500 nm were obtained with phosphoric acid electrolyte. In this case, a self-ordered pore structure of NAA was created by hard anodization with phosphoric acid of the Al templates at a voltage of 195 V [3]. The second step of the anodization process was carried out for a period of three hours while maintaining the same temperature and voltage parameters. Al nanobowls with diameter of ~100 nm were obtained with oxalic acid electrolyte, by applying 40 V for both anodization steps.

In order to obtain the nanobowls morphology at the surface of the Al template, the NAA substrates were submerged in a stirred aggressive combination of chromium trioxide (0.2 M) and phosphoric acid (0.42 M) for two hours while the temperature was maintained at 70 ºC. The resultant Al nanoconcavities are presented in Figure 1. For further functionalization, the resultant Al substrates were sputtered with gold for 120 s followed by thermal annealing at 400 °C for 1 h (Figure 2). The sputtering time and thickness of the gold film, followed by the shape of the aluminium template, are the factors that determine the size of the resultant nanoparticles, as the gold layer interacts with the topography of the Al nanoconcavities [4].

The findings of this study demonstrate an effective and robust process for assembling gold nanoparticles onto dense nanoarrays that were manufactured by electrochemical means. These nanoarrays have a shape similar to honeycombs and have a high spatial resolution. Experiments have been conducted to assess their plasmonic characteristics across a broad spectrum, ranging from the visible to the near-infrared area. These results have demonstrated that they are effective substrates for very sensitive applications, particularly for SERS [5,6]. Hypothetically, these interstitial spots were caused by concentrated electromagnetic fields that were coupled with intense localized surface plasmon resonance [7,8]. It is necessary for the nanoparticles to have a shorter separation distance in order for interparticle plasmon coupling to take place. This will result in a large rise in the near field intensity as well as SERS or an increase in the sensitivity of the LSPR refractive index [8,]. These fascinating substrates are highly helpful for SERS studies to detect various probe molecules, such as 4-Mpy, and antibiotics as well, owing to their high enhancement factor for low concentration. These prepared substrates have the potential to be functionalized and control morphological parameters that could be employed in various further applications in the sense of detection and sensing platforms.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 945413 and from the Universitat Rovira i Virgili (URV). This work was supported by the Spanish Ministerio de Ciencia e Innovación (MICINN/FEDER) PDI2021-128342OB-I00, by the Agency for Management of University and Research Grants (AGAUR) ref. 2021-SGR-00739, COST Action 20126-NETPORE and by the Catalan Institution for Research and Advanced.

References

[1] Josep Ferré-Borrull, Josep Pallarès, Gerard Macías, and Lluis F. Marsal, *Materials*, 7 (2014): 5225-5253.

[2] Gayathri Rajeev, Elisabet Xifre-Perez, Beatriz Prieto Simon, Allison J. Cowin, Lluis F. Marsal, and Nicolas H. Voelcker, *Sensors and Actuators B: Chemical,* 257 (2018): 116-123.

[3] Abel Santos, Lukáš Vojkuvka, Josep Pallarés, Josep Ferré-Borrull, and Llius F. Marsal. *Journal of Electroanalytical Chemistry,* 632(2009): 139-142.

[4] Santos, L. Vojkuvka, M. Alba, V. S. Balderrama, J. Ferre-Borrull, J. Pallares, L. F. Marsal, Physica Status Solidi (A) Applications and Materials Science, 209 (2012), 2045.

[5] Gohar Ijaz Dar, Elisabet Xifre-Perez, Lluis F. Marsal, *J. Materials Chemistry C*, (2024).

[6] Gohar Ijaz Dar, Elisabet Xifre-Perez, Lluis F. Marsal, *Advanced Materials Interfaces*, 10 (2023): 2300560.

[7] L. K. Acosta, F. Bertó-Rosello, E. Xifre-Perez, A. Santos, J. Ferre-Borrull, L. F. Marsal, ACS Applied Materials and Interfaces, 11, (2019), 3360.

[8] G. Macias, J. Ferré-Borrull, J. Pallares, L.F. Marsal, Nanoscale Research Letters, 9, (2014), 314.

Figures

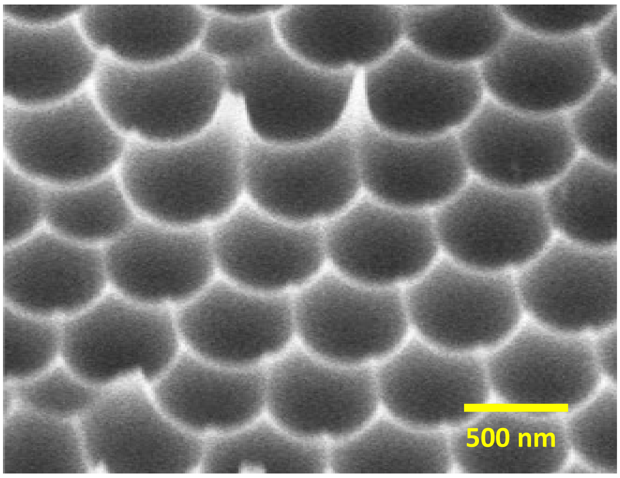

Figure 1. Top view FESEM image of Al nanobowls with diameter ~500 nm, obtained with phosphoric acid electrolyte.

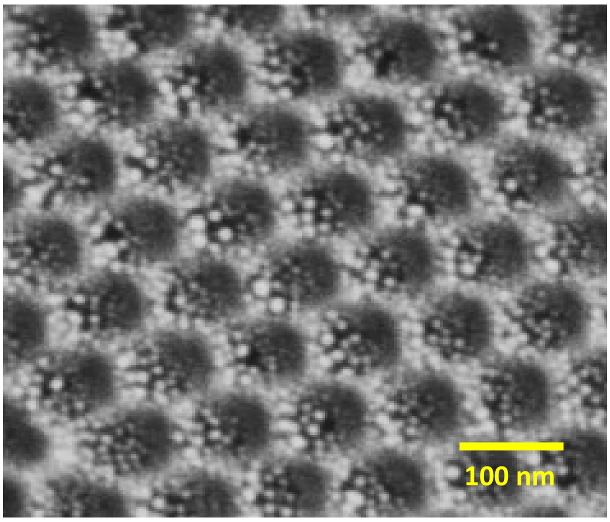

Figure 2. Top view FESEM image of Au nanoparticles formed in the Al nanobowls after thermal annealing. The diameter of the nanobowls is ~100 nm.