Complex Nanoporous Anodic Alumina Photonic Structures for Sensing: Design, Fabrication and Application

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Nanoporous anodic alumina (NAA) is a promising material formed by the electrochemical anodization of aluminum, a cost-effective and fully scalable process compatible with conventional micro and nanofabrication approaches that allow the precise control over the geometry and distribution of the pores [1-2]. NAA has high chemical and physical stability, provides stable optical signals without further passivation; and its surface chemistry can be easily modified with a broad range of molecules.[3] Moreover, the optical properties of NAA rely intrinsically upon its nanoporous architecture. Therefore, to engineer the nanoporous structure of NAA provides novel means of modulating its refractive index in a multidimensional fashion to fabricate advanced materials with unique optical properties to guide, reflect, transmit, emit incident light [4]. Furthermore, the pore geometry can be varied by different methods to obtain different functionalities such as funnels [5], branched pores and even structures with remarkable optical properties such as Distributed Bragg Reflectors, Rugate filters, etc [6-7]

Photonic structures (PS) can be obtained by NAA pore engineering. NAA-PSs are obtained by applying a sinusoidal anodization current, which results in a continuous modulation of the pore diameter along its length. The application of this modulation results in a one-dimensional photonic crystal with a periodic variation of the refractive index along the pore direction and a photonic stop band.[8]. Previous studies have also developed NAA-PSs with different anodization current profiles such as sawtooth-like pulse anodization [9], and square wave [10] to achieve better control over the oxide growth rate and porosity of NAA.

In this work, we propose novel methods to obtain NAA-PSs applying different current profiles. Our study establishes a better understanding of the effect that the different anodization parameters have on the optical properties of NAA-PSs such as their characteristic reflection bands across UV-visible-NIR spectrum. We present a comprehensive study of different NAA-PSs based on single and multiple structures with sinusoidal profiles in an overlapped

and stacked configuration. The stacked configuration consists of multiple currents are applied sequentially and the overlapped configuration consists of the average sum of multiple sinusoidal waves into a single complex waveform. Each sinusoidal wave determines the position and the reflectance amplitude of a forbidden band. In this case, the different periodic structures are stacked or overlapped on the same structure. The effective medium of the resulting photonic structures (PSs) is demonstrated to be optimal for the development of optical bio-sensing platforms.

All these photonic structures were prepared by anodization of a high-purity aluminum foils in 0.3 M oxalic acid electrolyte at 5 °C. Figure 1 shows ESEM top view (a) and cross-section (b) picture in a stacked configuration. The straight pores can be recognized in the cross-section, Figure 2 shows the reflectance spectrum of the sample after removing the remaining aluminum. Figure 2a shows the reflection spectrum of a sample in overlapped configuration with $I_0 = 4 \text{ mA}, I_1 = 2 \text{ mA}, T1 = 100 \text{ s},$ T2= 150 s and T3= 200 s. In figure 2b we can observed the reflectance spectrum in stacked configuration wit $I_0 = 4 \text{ mA}$, $I_1 = 2 \text{ mA}$, T1 = 125 s, T2 = 125 s150 s and T3= 175 s. The application of stacked sinusoidal current profile gives rise to the formation the three photonic stopbands. The height of these stop bands reaches 18-37 % while its width was 10-23 nm and the position of the photonic band corresponding central wavelength, $\lambda = 330-500$ nm.

In order to evaluate the suitability of these complex NAA-PSs, we assessed shifts in the position of the reflectance band filling the nanopores with different concentrations of aqueous solutions of D-Glucose.

We analyzed changes in the refractive index of the medium filling the pores by real-time spectroscopy. To this end, the sample is mounted in an acrylic cell with a transparent window that permits the measurement of the reflectance spectrum by a fiber mini spectrometer while different fluids are injected to cell and fill the NAA-PSs pores. Figure 3 illustrates the sensing principle of these photonic structures. The position of the reflectance band shifts to longer wavelengths when the nanopores are filled with different concentrations of D-Glucose.

In this work, we demonstrate the possibility to fabricate NAA-PSs by the application of different types current profiles. We also demonstrate the ability of structures to detect a change in the refractive index of the fluid filling the pores by means of real-time spectroscopy. With this method, it is possible to sense glucose in low concentrations. These results open up the possibility of using these complex NAA-PSs for detection of many other molecules for bio-sensing applications. Acknowledgments: This work was supported by the Spanish Ministerio de Ciencia, Innovación y Universidades (MICINN/FEDER) RTI2018-094040-B-I00, by the Agency for Management of University and Research Grants (AGAUR) ref. 2017-SGR-1527 and by the Catalan Institution for Research and Advanced Studies (ICREA) under the ICREA Academia Award.

References

[1] J. Ferre-Borrull, J. Pallares, Macías G, L.F. Marsal, Materials. 7 (2014). 5225-5253

[2] G. Macias, L.P. Hernández-Eguía, J. Ferré-Borrull, J. Pallares, L.F. Marsal, ACS Appl. Mater. Interfaces, 5 (2013) 8093.

[3] A. Santos, P. Formentín, J.Pallarés, J. Ferré-Borrull, L.F. Marsal. Journal of Electroanalytical Chemistry (2011) 73-78.

[4] A. Santos, T. Kumeria, Y. Wang, D. Losic, Nanoscale, 6 (2014) 9991.

[5] M. Porta i Batalla, E. Xifre-Perez, C, Eckstein, J. Ferre-Borrull, L.F. Marsal. Nanomaterials.(8) 2017.2-12

[6] M. Mahbubur Rahman, L.F. Marsal, J. Pallarès, J. Ferré-Borrull, Applied Materials and Interfaces, 5 (2013) 13375-13381.

[7] G. Macias, J. Ferré-Borrull, J. Pallarès, L.F. Marsal, Nanoscale Research Letters, 9 (2014) 315

[8] Laura K. Acosta, Francesc Bertó-Roselló, E. Xifre-Perez, Abel Santos, J. Ferre-Borrull, L.F. Marsal. ACS Appl. Mater. Interfaces, 11, (2019). 3360-3371

[9], C. Suwen Law, A. Santos, Mahdieh Nemat, D.Losic ACS Appl. Mater. Interfaces, 8 (2016) 13542-13554.

[10] A.L Sadykov, S.E Kushnir,IV Roslyakov,A.E. Baranchicov, K.S. Napolskii. Electrochemistry Communications. (100) 2019. 104-107.

Figures



Figure 1. (a) Top view (scale bar $1\mu m$) and (b) Cross-section (scale bar $1\mu m$) of NAA-PSs (stacked configuration)



Figure 2. Reflectance spectrum of NAA-PSs (a) Overlapped configuration and (b) stacked configuration



Figure 3. Sensing Principle of stacked NAA-PSs with Water and D-Glucose showing the red-shift in the position of de bands.