Excitation of plasmons in self-ordered arrays of aluminum and silver nanoconcaves within UV–IR spectral range

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Abstract. Large-scale hexagonally aluminum nanoconcave arrays were synthesized by electrochemical anodization of aluminum using oxalic acid and mixtures of phosphoric acid and citric acid; which, in turn, were used as nanostructured substrates to control the plasmonic resonances of silver. Plasmonic properties of both systems were investigated based on specular reflectivity in the ultraviolet–visible–infrared range. We found that their optical reflectance was dramatically reduced as compared with unstructured films deposited by thermal evaporation that were used as references. At the same time pronounced reflectance dips were detectable in the 262–1077 nm wavelength range, which were ascribed to plasmonic resonances of first and higher orders. We propose that the use of nanostructured aluminum as a substrate can be extended for the control of plasmonic properties of other metals.

1. Introduction
The growing interest for the study of plasmonic nanostructures has increased due to their interesting physical properties[1-3] and multiple applications[4-6]. Various metals such as aluminum (Al), gold (Au), silver (Ag) and copper (Cu) are potential candidates for low-loss plasmonic materials in the ultraviolet-infrared (UV-IR) spectral range[7]. In general, Al, Au and Ag are most often used because they are air stable materials, while Cu is more reactive.

Although Al presents an interband transition around 826 nm (1.5 eV) [8] it offers the possibility of the fabrication of plasmonic structures to access the ultraviolet–visible–infrared (UV–Vis–IR) region of the electromagnetic spectrum [9]. Besides, Al offers additional advantages such as its relatively low cost, high natural abundance and high stability because the formation of native layer of aluminum oxide (Al₂O₃) (∼2.5-3 nm) [10] on its surface which acts as a passivation layer preventing further oxidation. Al has been used in plasmonics for Localized Surface Plasmon Resonance Spectroscopy (LSPR) [11], Surface Plasmon Polariton (SPP) propagation [12], Surface-Enhanced Fluorescence (SEF) [13], and Surface Enhanced Raman Scattering (SERS)[9,14].

On the other hand, Ag is one the predominantly preferred material for plasmonic applications [15-17] due to its high electrical conductivity and its relatively low loss in the visible and Near Infrared (NIR) ranges.
In this work we present an easy electrochemical method to fabricate regular and hexagonally aluminum nanoconcave arrays, which by themselves are plasmonic structures, but now we use them as a nanostructured substrate to control the plasmonic resonances of silver operating in Vis–IR region of the electromagnetic spectrum. This method allowed the preparation of nanoconcave arrays with well-controlled geometrical parameters such as nanoconcave diameter ($D_p$), interconcave distance ($D_c$), and therefore, well-controllable plasmonic resonances. The optical properties of the nanoconcave arrays were investigated through specular reflectance measurements. We found that plasmon are excited both in Al and Ag nanoconcave arrays, and those plasmonic resonances in nanoconcave arrays with Ag film show shifts to higher wavelengths respect to Al nanoconcave arrays with same interconcave distance.

2. Experimental details

High-purity aluminum foil (Sigma-Aldrich 0.25 mm thick, 99.999% purity) were cut in 1 cm X 2 cm samples. Before the anodization process the Al foils were annealed at 600 °C for 6 h in an atmosphere of H$_2$ at ambient pressure. Subsequently they were cleaned in solutions of 0.25M Na$_2$CO$_3$ at 80 °C for 3 min and 35% wt HNO$_3$ for 30 s (Figure 1. a)). The samples were electropolished in a mixture of perchloric acid (70%) and ethanol (1:5 vol.) under constant voltage of 18 V for 2 min at 3 ºC (Figure 1. b)).

For the anodization of the samples oxalic acid (C$_2$H$_2$O$_4$) and mixtures of phosphoric acid (H$_3$PO$_4$) and citric acid (C$_6$H$_8$O$_7$) as electrolytes at ambient temperature for 24 h were used (Figure 1. c)). The anodizing voltage and the corresponding electrolyte are in Table 1. The solutions were continuously stirred to homogenize both the electrolyte and its temperature. Ethylene glycol (EG) acts as a heat exchanger in the electrochemical cell an also to reduce the breakdown effect.

After anodization, the samples were immersed in a mixture of 1.8 wt% CrO$_3$ and 6 wt% H$_3$PO$_4$ at 60 °C for 12 h to selectively dissolve the porous anodic alumina (PAA), with this procedure an array of nanoconcaves is observed in the remaining Al surface corresponding to the negative shape of the bottom of the PAA (Figure 1. d)).

Finally, Ag (Electronic Space Products International shot 3-6 mm, 99.9% purity) film of 50 nm thickness was deposited by thermal evaporation on top of Al nanoconcave arrays (Figure 1. e)).

The morphology of nanoconcave arrays was evidenced by using field-emission scanning electron microscope (SEM) JEOL 7600F equipped with energy dispersive X-ray spectrometer (EDS). The structural features and geometric parameters of nanoconcave arrays were evaluated directly from SEM images by using WSxM[18] and Image J[19] software.
The optical properties of the nanoconcave arrays were investigated based on specular reflectivity. Reflectivity measurement was performed using UV–vis spectrophotometer (UV–2600 Shimadzu Corporation). The probe was set at normal angle and reflectance spectra were collected using integrating sphere in the 190–1400 nm wavelength range. For comparison purposes, Al and Ag films on glass substrates obtained by thermal evaporation were also measured.

3. Results and discussion
After anodization and thorough removal of the resulting AAP, an array of nanoconcaves appears on the Al sample, which is an exact replica of the morphology of the AAP pore bottoms. In Figure 2 representative top view SEM images of Al and Ag nanoconcave arrays synthesized at different voltages are shown.

The geometric parameters such as nanoconcave diameter (Dp) and pore interconcave distance (Dc) of these nanostructures were estimated from SEM micrographs for each sample using Image J software. The values for Dp were within 260-1140 nm, while for Dc were in 298-1395 nm, as shown in Figure 3. a) and b) respectively. An FFT analysis was also performed from SEM micrographs, shown six distinct points in the corners of a hexagon, confirming good hexagonal arrangement of the nanoconcave arrays (see lower inset of figure 2).

Reflectance spectrums as a function of light wavelength of Al and Ag nanoconcave arrays are shown in Figure 4. Significant dips in the reflectance intensity in all samples at 826 nm (~1.5 eV) for the case of Al and at 318 nm (~3.9 eV) for the case of Ag are observed. This features are respectively related with interband transitions (IT) of electrons in the crystalline aluminum and silver [20,21].

| Voltage (V) | Electrolyte |
|------------|-------------|
| 100        | 30 ml of 0.3M H2C2O4+60 ml of EG |
| 200        | 90 ml of 0.01M H3PO4+10 ml of 1M C6H5O7 |
| 300        | 20 ml of 0.01M H3PO4+80 ml of 1M C6H5O7 |
| 400        | 15 ml of 0.01M H3PO4+40 ml of 1M C6H5O7+50 ml of EG |
| 500        | 3 ml of 0.01M H3PO4+45 ml of 0.5M C6H5O7+45 ml of EG |
| 550        | 1 ml of 0.01M H3PO4+50 ml of 0.1M C6H5O7+50 ml of EG |

Table 1. Anodizing conditions used for the fabrication of nanoconcave arrays.

Figure 2. Some SEM micrographs of a)-d) Al and e)-h) Ag nanoconcave arrays. The value of the shown voltage is the one used for anodization, with their respective FFT images (insets).
Apart of the interband transition, other minima in the reflectance appear (vertical green arrow). In the samples with Al nanoconcave arrays, dips in the reflectance in the 263nm -1028 nm wavelength range appear, while in samples with Ag nanoconcave arrays, the dips appear in the range of 343nm – 1077 nm depending on the nanoconcave dimensions.

The dips are related with surface plasmons resonance (SPR) of first order and higher orders\cite{9,22}. The SPR manifest themselves as minima in reflectance spectrum in UV–visible region, which means that the incident light couples with SPR located at nanoconcave arrays.

The SPR are directly associated with the periodicity of the nanoconcave arrays (in this case $D_c$) and to the optical properties of metals (Al and Ag). Using as a first approximation for SPR an ideal model, coupling of photons with 2-dimensional hexagonal periodic array gives at normal incidence SPR or minimum of the reflectance at the wavelength given by\cite{9}:

$$\lambda_{SPR} = \frac{D_c}{\sqrt{\frac{4}{3} (i^2 + ij + j^2)}} \sqrt{\frac{\epsilon_m(\lambda_{SPR}) \epsilon_d}{\epsilon_m(\lambda_{SPR}) + \epsilon_d}}$$

Figure 3. The relation between the a) nanoconcave diameter ($D_p$) and b) interconcave distance ($D_c$) of nanoconcave arrays and the applied anodization voltage.

Figure 4. Reflectance spectrums of Al and Ag nanoconcave arrays with their respective anodization voltages. Results for electropolished Al foil, Al and Ag films obtained by thermal evaporation are shown for comparison.

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where \( D_c \) is the period of the array, \( \varepsilon_m \) and \( \varepsilon_d \) are respectively the dielectric constants of the metal and the dielectric material in contact with the metal and \( i, j \) are the scattering orders of the array.

The most pronounced dips in the reflectance spectra can be ascribed to the \((i,j)=(1,0)\) or first order \(\lambda_{(1,0)}\) according to eq. (1). A second dip present in some spectra of nanoconcave arrays synthesized with different voltages may be attributed to a higher order SPR mode \((i,j)=(1,1)\) or second order \(\lambda_{(1,1)}\).

Figure 5 shows experimental data of the observed reflectance dips and theoretical curve for the SPR model with periodicity described by Eq. (1).

For calculations, the real part of eq. (1) was solved using experimental values for the complex dielectric function of Al and Ag [23] \(\varepsilon_m(\lambda) = \varepsilon_1 + i\varepsilon_2\) and taking \(\varepsilon_d = 1\) for air. It is observed in Figure 5 that the analytical curves for the \(\lambda_{(1,0)}\) and \(\lambda_{(1,1)}\) modes fit acceptably to the experimental reflectance dips within the 298-1395 nm range of \(D_c\).

Because plasmonic applications require materials with negative real permittivity, metals have traditionally been the materials of choice for plasmonics due to their large plasma frequencies and high electrical conductivity. Silver is probably one the most important material in plasmonics. On the other hand, aluminum also has attracted a lot of attention due to recent potential applications in plasmonic materials. In terms of plasmonics, it is important to choose a metal that can support surface plasmons (SP) at the desired resonance wavelength. Silver is able to do so across the spectrum within Vis-IR, while aluminum does it within UV-IR.

4. Conclusion
In summary, the reported nanoconcave arrays are simple to fabricate compared to other expensive techniques such as lithography and their plasmonic properties can easily be tuned by changing their size through the appropriate electrolyte and anodization voltage. The plasmonic properties of Al nanocave arrays are excluded in wavelength regions within 650-980 nm (around 826nm), while for Ag nanocave arrays are excluded for wavelength regions smaller than 318 nm, both because of interband transitions, where electrons jump to higher empty energy levels caused by absorption of incident
photons; which is a significant loss mechanism in materials at optical frequencies. These systems can be useful in the ultraviolet-infrared (aluminum) and visible-infrared (silver) wavelength ranges. Our proposal is that taking advantage of the easy process of electrochemical anodization, nanostructured aluminium substrates can be used to control the plasmonic properties of other metals.

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