

Nanoporous Gold Nanoleaf as Tunable Metamaterial

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Abstract: We have studied optical properties of single and multi-fold nanoporous gold leaf metamaterials and demonstrated that they can be controlled with applied voltage and dielectric environment.

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Complex metal-dielectric environments, including metamaterials, plasmonic structures, and Fabry-Perot cavities, have been demonstrated to control scores of phenomena including spontaneous and stimulated emission, Förster energy transfer, van der Waals interactions, and chemical reactions. At this time, we report studies and real-time control of optical properties of nanoporous gold leaves (NPGLs) – unique centimeter-size and ~100 nm thick multilayered (meta) materials.

The NPGL samples have been prepared from one layer of 12 K gold leaf through dealloying in 10 ml of concentrated HNO₃ (68%, ACS, VWR) solution at room temperature for one hour. Different thicknesses of the fabricated samples, ranging from 84 nm to 943 nm, were achieved by folding one layer of the gold leaf once (two layers), twice (four layers), and three times (eight layers). The dealloying parameters for all samples studied were nominally the same, resulting in pore diameters (in different samples) ranging from 20±3 nm to 27±3 nm. The NPG leaf was rinsed thoroughly in DI water for at least three times after the dealloying process before being transferred onto glass substrates. Finally, the fabricated samples were dried in air before taking any measurements. The scanning electron microscope (SEM) image of a single-layer Au nanoleaf sample is depicted in Fig. 1a.

The results of the transmittance measurements are summarized in Fig. 1b. The reference sample, 90 nm thick gold film deposited on glass, had the transmission maximum at 505 nm, near to epsilon-near-zero (ENZ) point for Au. At the same time, Au nanoleaf samples had two transmission peaks. The first had its maximum almost at the same wavelength as the transmission peak in a smooth Au film, while the second was shifted to longer wavelengths (up to 605 nm). The characteristic “wiggles” could be seen in the reflection spectra of the nanoleaf samples at the wavelengths corresponding to both transmission maxima. (Note that qualitatively similar double peak transmission spectra were obtained when Au films were deposited on nanoporous alumina membranes. However, the effect was not universal and the spectra of gold-coated polymers with micro-bubbles were quite different.)

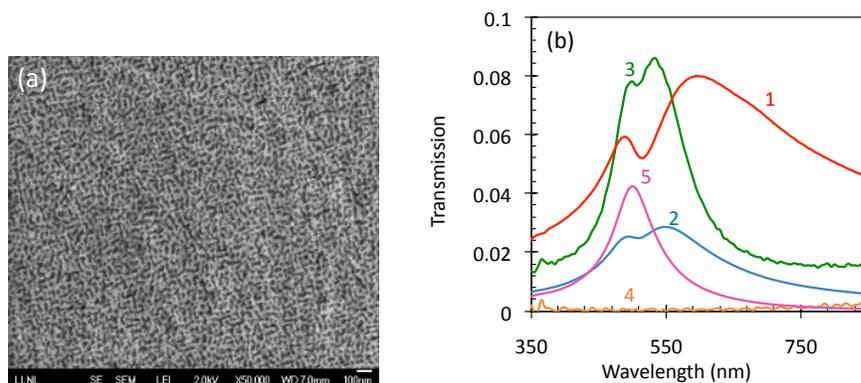


Fig. 1. (a) SEM image of the single-layer Au nanoleaf sample. (b) Transmission spectra of a single-layer (trace 1), two-layers (trace 2), four-layers (multiplied by 100, trace 3) and eight-layers (multiplied by 100, trace 4) NPGLs. Control sample: 90 nm Au film (trace 5).

With increase of the number of layers, the width of the long-wavelength transmission peak got reduced and its spectral position was shifted to shorter wavelengths. This could be the effect of (i) the overall thickness of NPGL layers or (ii) the (coincidental) effect of the sizes of voids or ligaments, which were slightly different in different samples. (More studies are needed to differentiate between the two possible causes of the spectral shifts.) The absorbance [$A = -\log(T)$] calculated for both transmission maxima, grew almost linear with the thickness of (single-layer or multi-layer) nanoleaf samples, in a good agreement with the Beer's law. This result is not trivial, since strong diffusion (and deviation from the Beer's law) could be expected in the highly scattering samples.

When Au nanoleaf was placed in water, its long-wavelength absorption peak moved slightly (by ~ 10 nm) to shorter wavelengths, while the short-wavelength peak practically did not change its spectral position. This result is in qualitative agreement with Ref. [1]. However, the spectral shift in our studies is smaller than that reported in [1]. Different behavior of the short-wavelength and long-wavelength transmission peaks suggests that they have different nature.

To tune the optical properties of NPGL, we placed the sample in a two-electrode electrochemical cell. Gold nanoleaf, with attached copper tape conduit, served as a working electrode, while the a platinum wire played a role of a counter electrode. Following [2], the electrolyte was 0.7 M solution of NaF in water. The applied voltage, varied between -2V and +2V, caused changes in both strength ($\sim 10\%$) and the wavelength position ($\Delta\lambda \sim 20$ nm) of the long-wavelength transmission peak. These changes in the optical spectra were, presumably, due to change in the charge density [2]. However, in contrast to [2], larger spectral changes in our experiment were observed when negative (rather than positive) voltage was applied to the gold leaf.

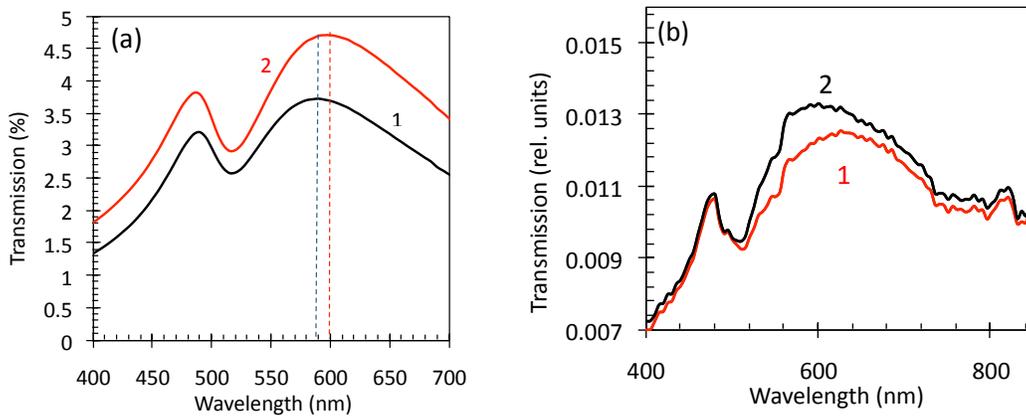


Fig. 2. (a) Transmission spectra of the Au nanoleaf in air (trace 1) and water (trace 2). (b) Transmission spectra of Au nanoleaf in electrochemical cell at applied positive voltage (+1.5V, trace 1) and negative voltage (-2V, trace 2).

In Ref. [3], it has been shown that the vicinity of metallic (Ag) films or lamellar metal/dielectric structures helps to reduce the rate of concentration quenching of the HITC laser dye. In our preliminary studies, we have found that Au nanoleafs inhibit concentration quenching even stronger than smooth gold films do. Real-time control of the dye emission with active and tunable Au nanoleaf metamaterials is the subject of future studies.

To summarize, we have studied optical properties of single and multi-fold nanoporous gold leaves and demonstrated that they can be controlled with applied voltage as well as dielectric environment. The experimental results, their analytical modeling and tentative explanation will be discussed in more detail at the conference.

This work was supported by the NSF RISE grant 1646789, NSF EiR grants 1830886 and 1856515, DoD grant W911NF1810472, and AFOSR grant FA9550-18-1-0417.

[1] X. Lang, L. Qian, P. Guan, J. Zi, and M Chen, "Localized surface plasmon resonance of nanoporous gold", *Appl. Phys. Lett.*, 98, 093701 (2011).

[2] D. J alas, L. Shao, R. Canchi, et al. "Electrochemical tuning of the optical properties of nanoporous gold", *Sci Rep* 7, 44139 (2017).

[3] S. Prayakarao, S. R. Koutsares, C. E. Bonner, and M. A. Noginov, "Effect of nonlocal metal–dielectric environments on concentration quenching of HITC dye", *JOSA B*, 36, 3579-3587 (2019).