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Electronic supporting information

Precise patterning of gold nanoparticle gratings on gelatin films

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1. General experimental details and methods

Materials

A dichromated version of the natural biopolymer gelatin, the so-called DCG has been used as support for the gold nanoparticles gratings (AuNPGs). To make a surface relief grating, a DCG film (prepared by spin-coating) is holographically exposed, and then it is dry-developed in an oxygen plasma.[1] This is in contrast with the traditional wet-development procedures used to make volume holograms.[2] The initial thickness of the gelatin film, which approximately determines the depth of the surface relief grating, depends on the gelatin concentration in the solvent (distilled water) used in the spin-coating process. Here, we have used the soft gelatin Rousselot (200 bloom) in a concentration of 2.2 wt% to obtain films of thickness 120 nm and final grating depths of about 100 nm. Sensitization was made with ammonium dichromate from Merck. The gold precursor in the doping step was chloroauric acid ($HAuCl_4$ $3H_2O$, Aldrich).

Methods for AuNPG fabrication

The DCG films were prepared by spin-coating over fused silica (FS) substrates (2.5 × 2.5 cm^2) by means of a LabSpin6 SÜSS Microtec machine.

(a) *Holographic exposure*. The HL exposure of the DCG films was performed with a Lloyd's interferometer illuminated with a spatially filtered, expanded, and collimated beam (diameter 50 mm) from an Ar laser (Coherent Innova 308C) emitting at 364 nm. In this interferometer, a mirror is rigidly attached perpendicularly to the DCG film to produce the second beam (experimental setup reported elsewhere). So, in this simple arrangement, the sensitivity to mechanical vibrations is quite low and the grating period, Λ, is easily changed by varying the angle of the mirror-DCG plate assembly according to the equation:

$$\Lambda = \lambda / 2 \sin(\theta / 2) \qquad (1)$$

where θ is the angle between the two beams that interfere in the DCG plate. The smallest period fabricated is 200 nm, which corresponds to an angle θ of 131.0 °. The laser is provided with an intracavity etalon to increase the coherence length and light is polarized perpendicular to the plane of incidence to have the maximum contrast of the interference fringes. The exposure was performed at saturation conditions (average exposure of approximately 65 mJ/cm^2).

(b) *Desensitization of ammonium dichromate from the DCG*. This is accomplished by first washing the sample with mild agitation in a cold bath (15 °C) of distilled water for 5 s; and then centrifuging it at 500 rpm for rapid drying.

c) *Doping with a gold precursor*. The sample is immersed in an aqueous solution of chloroauric acid ($HAuCl_4$), and agitated (mild) at 15 °C for 10 s. Then, it is centrifuged at 500 rpm for rapid drying. The explored range of gold precursor concentration was 10^{-4} M - 2 × 10^{-2} M. Importantly, steps b) and c) cannot be performed simultaneously because precipitates are formed. The temperature in both baths is maintained at 15 °C to avoid gelatin dissolution, and times were determined by considering the spectrophotometric signals corresponding to ammonium dichromate and chloroauric acid (see Figure 1f, main manuscript).

(d) *Oxygen plasma treatment* (80 W, 0.5 NL/h). This was was carried out in an oxygen plasma cleaner apparatus (Diener Zepto). The power supply was operated at 80 W. The chamber pressure was 0.4 mbar and the oxygen gas was introduced at a controlled flow rate, 0.5 NL/h.

(e) *Annealing treatment*. It was performed in a hot plate (JP Selecta™ Plactronic Hotplate).

Finally, we note that the whole process was carried out under red light to prevent the accidental effects due to parasite light of short wavelength.

Methods for AuNPG characterization

Absorption measurements were performed in a double-beam spectrophotometer (Jasco V-650, Jasco, Tokyo, Japan). Measurements were taken against air at normal incidence in the center of the sample over the area of the slit image of about 1 mm × 7 mm, between 300 and 850 nm, with light of a spectral bandwidth of 1 nm.

FESEM images were obtained with a Carl Zeiss apparatus (model Merlin VP compact) using the backscatter electron detector (BS-FESEM).

Transmission electron microscopy (TEM) images were obtained in a JEOL microscope (model JEM-1400 Plus).

2. Additional characterizations of AuNPGs

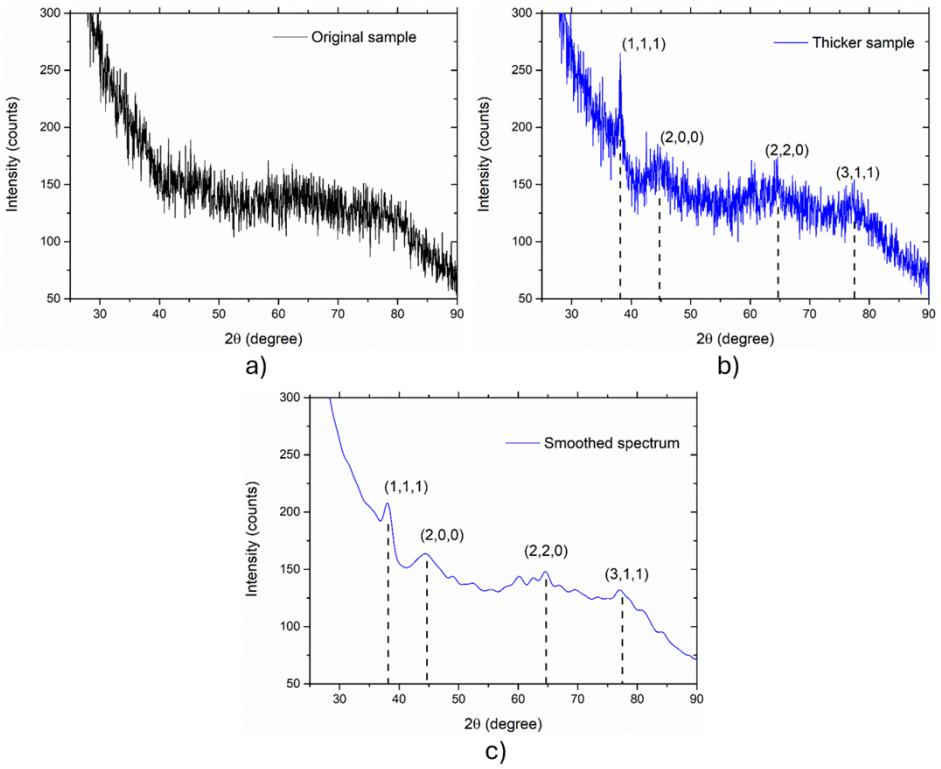


Figure S1. XRD analysis: (a) XRD spectrum of one of the original samples shown in the paper. b) XRD spectrum of a thicker sample. c) Smoothed spectrum of the thicker sample.

Figure S1 shows the XRD spectra obtained for two different samples. Fig. S1a illustrates the XRD measured with one of the samples shown in the main text of the paper. As it can be seen, the signal obtained is really weak making it very difficult to differentiate between the peaks corresponding to the Au NPs and the signal noise. For this reason, new thicker samples were prepared ($\sim 1\,\mu$m) and the Au NPs were evenly dispersed throughout the film, with no pattern on it. The objective was to increase the concentration of Au NPs to obtain a stronger signal were the peaks corresponding to the Au NPs could be seen. This spectrum is shown in Fig. S1b.

Although the signal is still very weak, the peak corresponding to the (111) gold plane can be seen at 38º. In addition, a slight peak is observed at 44º corresponding to the (200) plane. Despite the peak signals are weak and noisy, a smooth of the spectrum (Fig. S1c) clearly shows the first two peaks, as well as two additional peaks, at 64º and 78º, corresponding to the (220) and (311), respectively.

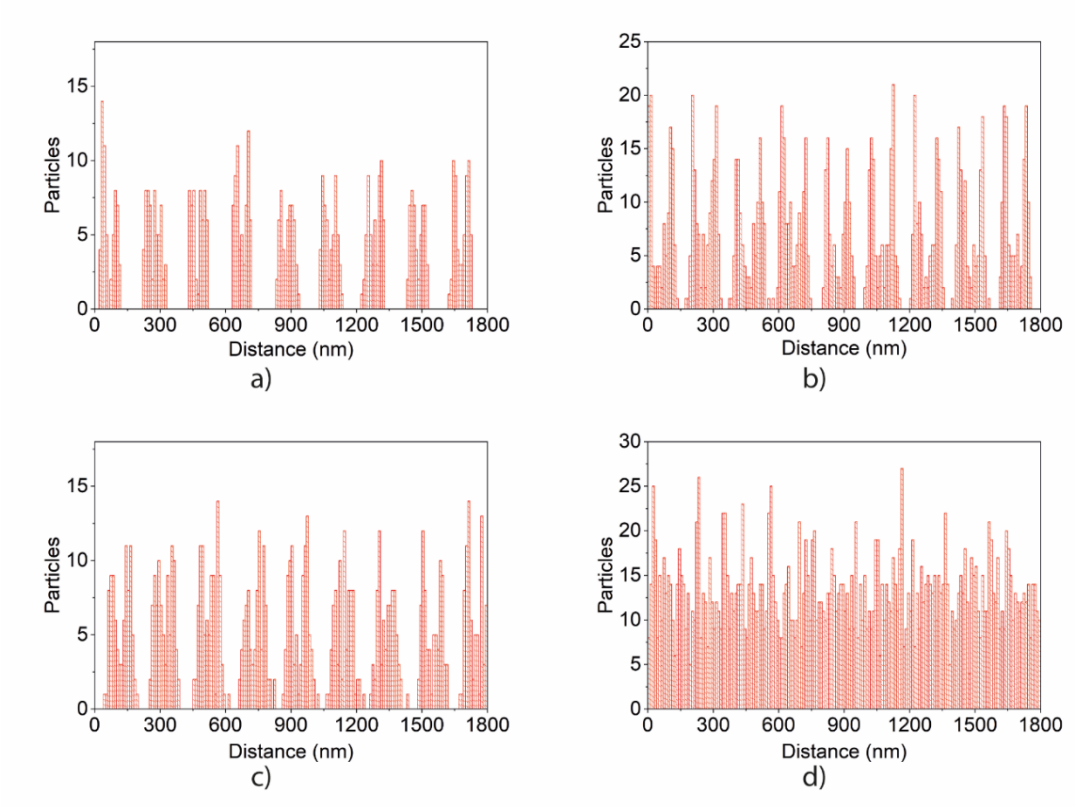
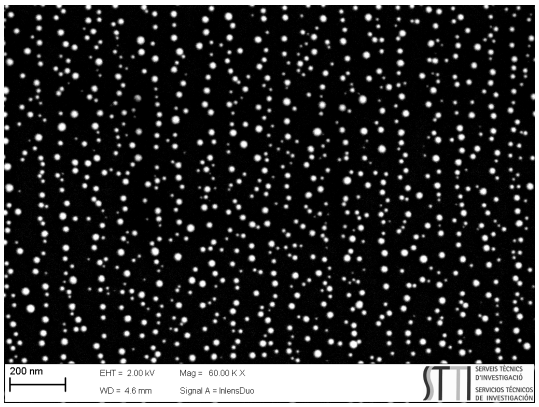
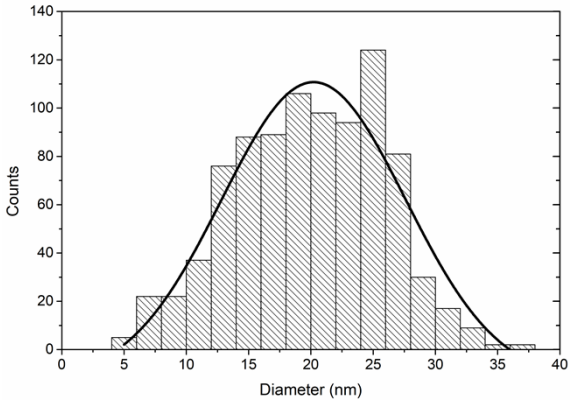


Figure S2 Histograms for size distribution analysis corresponding to the BS-FESEM images of AuNPGs shown in figure 2. Histograms (a) and (b) correspond to AuNPGs obtained both with the same annealing conditions (T = 120 ^{o}C, t_a = 8 h), and different plasma treatment times, t_d (3 and 6 min, respectively). Histograms (c) and (d) correspond to AuNPGs obtained under the same t_d = 6 min and different annealing conditions: T = 20 ^{o}C and t_a = 1 month (in c); and T = 180 ^{o}C and t_a = 20 min (in d).



(a)



(b)

Figure S3 (a) BS-FESEM image and b) Au NPs size distribution in a PNG (plasma treatment time of 6 min, annealing at 120 ^{o}C for 8 hours) after calcination of gelatin at 800 ^{o}C for 1 hour.

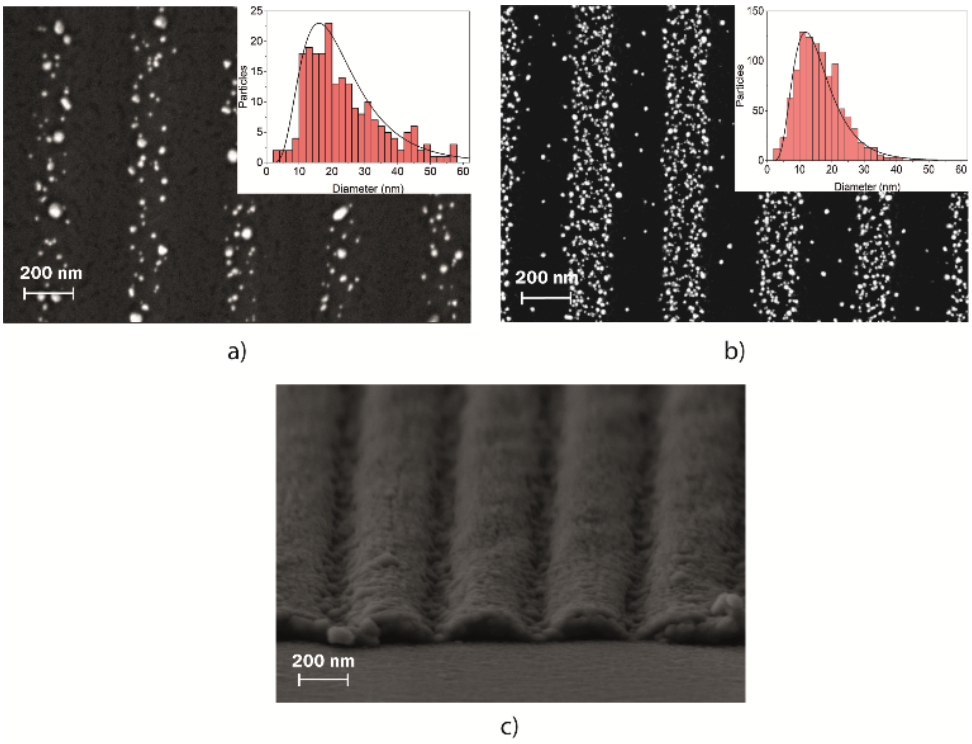


Figure S4 BS-FESEM images of AuNPGs with a period 400 nm, obtained with a gold precursor concentration of 5×10^{-3} M, t_d = 3 min, and annealing treatments of: (a) t_a = 1 month, T = 20 °C (room T); and (b) t_a = 8 h, T = 120 °C. Figure (c) shows a SE-FESEM image for sample shown in b), showing the sinusoidal profile.

References

1. J.M. Villalvilla, J. Crespo, J. A. Quintana, C. Santos and J. A. Valles-Abarca, *Thin Solid Films*, 1998, **317**, 340–342.
2. J.A. Quintana, P. G. Boj, J. Crespo, J. A. Vallés-Abarca and J. M. Villalvilla, *Thin Solid Films*, 1998, **317**, 343–346.