

Supplementary Information

Selective MOdification of NAnoparticle Arrays by Laser-Induced Self Assembly

(MONA-LISA): putting control into bottom-up plasmonic nanostructuring

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Summary: This supplementary information contains extensive experimental results that corroborate the results and conclusions presented in the manuscript, but due to their extent cannot fit in the manuscript. The manuscript refers to specific sections here, but in its entirety this document presents the complete results of our *MONA-LISA* work.

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1. *LISA* and *MONA-LISA* by UV lasers (ArF: 193 nm and KrF: 248 nm)

The Table below summarizes the materials (metals) used in the present work, the deposition techniques used and the laser annealing processes that followed. These samples were then characterized by Optical Reflectivity Spectroscopy (ORS), Atomic Force microscopy (AFM) and Scanning Electron Microscopy (SEM). The experimental setup of the aforementioned techniques is adequately described in the experimental session of the manuscript.

Table i. Seed materials developed for the present work.

Metallic Layer ¹	Film Structure	Deposition Technique	Laser Annealing
Ag	Ag (5nm) / SiO ₂ (2 nm) / Si Ag (10nm) / SiO ₂ (2 nm) / Si	MS, EBE, Chemical	UV LA: 1. 193 nm (ArF) 2. 248 nm (KrF) VIS LA: 1. 532 nm (SHG, Nd:YAG) 2. 620 nm (OPO, Nd:YAG)
Au	Au (5nm) / SiO ₂ (2 nm) / Si Au (10nm) / SiO ₂ (2 nm) / Si	MS	UV LA: 1. 193 nm (ArF) 2. 248 nm (KrF) VIS LA: 1. 532 nm (SHG, Nd:YAG)
Cu	Cu (5nm) / SiO ₂ (2 nm) / Si Cu (10nm) / SiO ₂ (2 nm) / Si	MS	UV LA: 1. 193 nm (ArF) 2. 248 nm (KrF)

MS: magnetron sputtering, EBE: e-beam evaporation, Chemical: Referring to chemical reduction of AgNO₃,
UV: ultraviolet, VIS: Visible, SHG: second harmonic generator, OPO: optical parametric oscillator

Fig. S1 shows digital photos of Ag samples (10 nm of effective thickness), on 4" Si wafers, after laser processing with 193 nm (Fig. S1a) and 248 nm (Fig. S1b), respectively. The spots reveal palettes of various colours, depicting the variation of plasmonic responses at each set of LA conditions, spanning from red to blue.

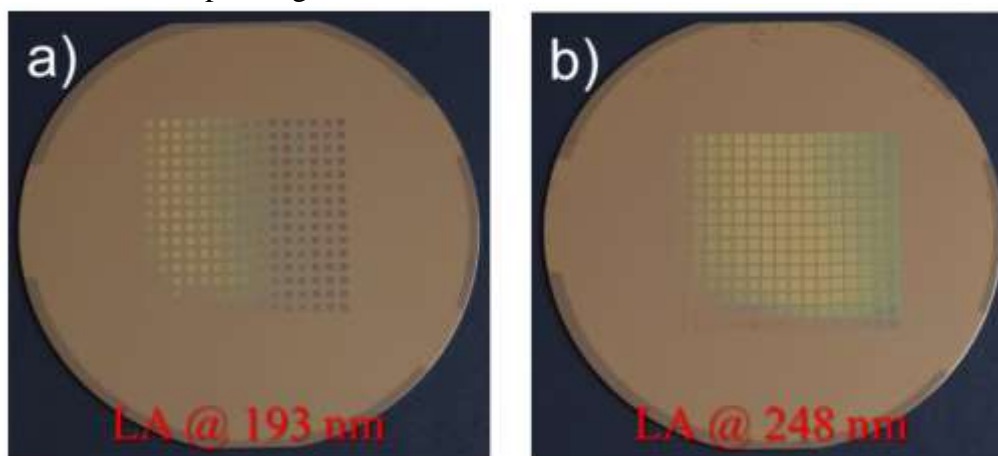


Figure S1. Digital photos of a Ag thin film (effective thickness of 10 nm) laser processed with (a) an ArF laser source emitting light at 193 nm and (b) a KrF source emitting light at 248 nm.

The laser spot delivered onto the samples was set, by an appropriate mask, to be a 2.0×2.0 mm² spot, for the case of 193 nm and 2.5×2.5 mm² spot, for the case of 248 nm. The variation in the spot sizes arises from the fact that the two laser sources have slightly different raw beam spot sizes and different beam delivery systems are used (see below for details of the LA experimental set up, section 5). The fluence varied from 200 mJ/cm² to 1000 mJ/cm² (left-to-right columns), using a step of 50 mJ/cm² and applying 1 to 15 (bottom-to-top) pulses (repetition rate was set at 1Hz). Single pulse UV LA is referred to as *LISA* process whereas successive UV laser pulses are referred to as UV *MONA-LISA*.

1.1. Contour plots vs fluence and number of pulses for each wavelength.

- **Ag (10nm) – LA@193 nm:** Fig. S2a and S2b present a map of the localised surface plasmon resonance (LSPR) spectral position and the reflectivity percentage at the LSPR, respectively. The results derived from the ORS spectra of each one of the LA spots. This map can provide a recipe that allows the design of plasmonic templates by UV LA. A green – yellowish response (530 – 570 nm) is observed by the spots that were produced under applied fluence between 200 and 500 mJ/cm². Above 450 mJ/cm² a gradual decrease in % reflectivity (%R) values is observed after the 4th pulse (where the maximum %R is reached), an indication of some loss of material due to ablation, concomitantly with a blueshift of the LSPR peak (due to larger empty space between particles). Above 650 mJ/cm² the laser process is ablating most of the material and as a consequence no LSPR peaks are apparent in the spectra; thus in Fig. S2 we present the contour plots only up to 650 mJ/cm². Note that at 250 mJ/cm² we can achieve the greatest variation of LSPR wavelengths and %R, where the saturation appears in high number of pulses contrary to all the other fluences applied.

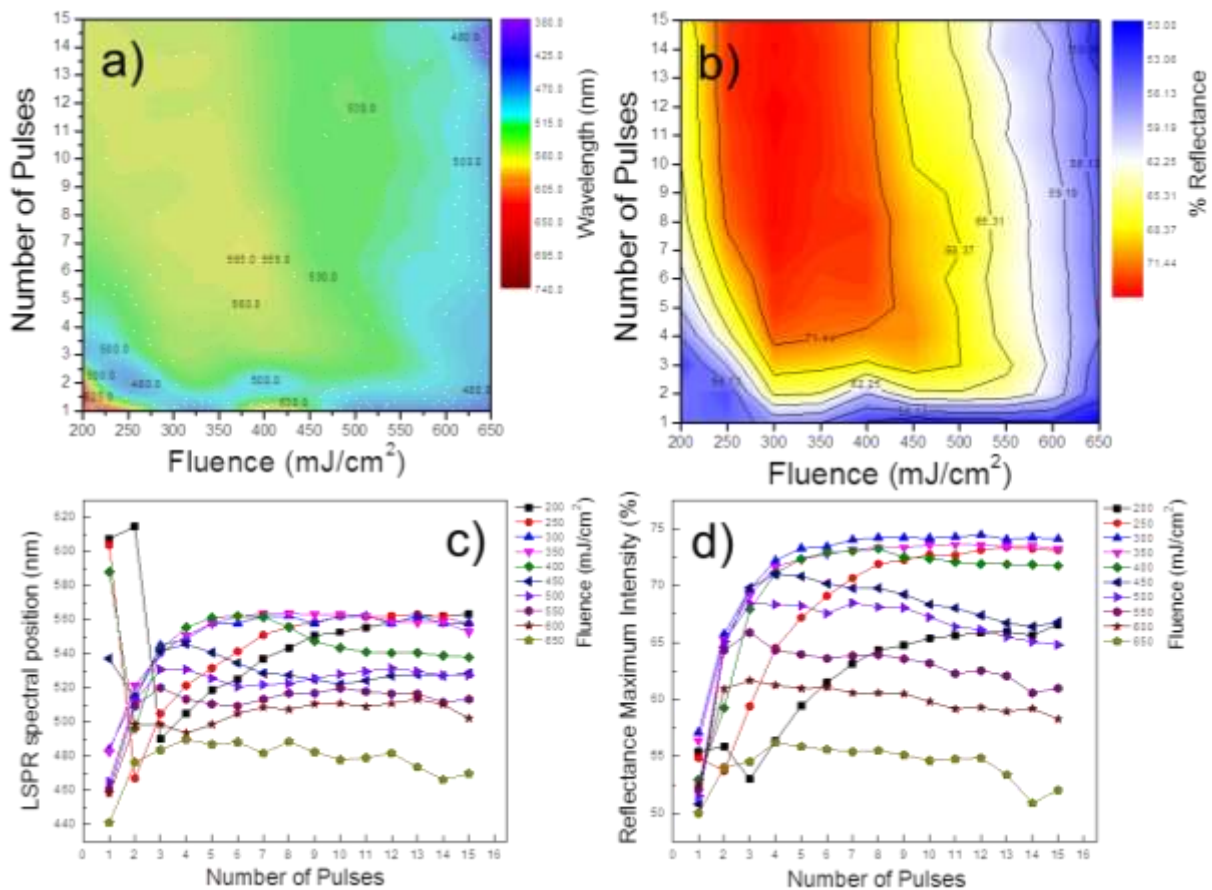


Figure S2. *LISA / UV MONA-LISA* (193 nm) of a Ag thin film with an effective thickness of 10 nm: (a) a contour plot of the dominant LSPR spectral position for the various number of pulses and applied fluence during LA, (b) a contour plot of the maximum reflectivity of the dominant LSPR for the various number of pulses and fluence applied during LA, (c) dominant LSPR spectral position for the various number of pulses under different applied fluence and (d) maximum reflectivity of the dominant LSPR for the various number of pulses under different applied fluence.

- **Ag (10nm) – LA@248 nm**: The overall behaviour of the sample under 248 nm exposure is the same as under the 193 nm. However, in this case, the optical response of the vast majority of the selected LA conditions is positioned in the green – yellowish range, between 530 and 575 nm. At the same time, for the same conditions, the maximum reflectivity percentage (%R) is achieved, varying from 70 – 75 %. However, it is remarkable that we manage to get a broad variation in plasmonic response, from 465 nm to as high as the limit of the VIS spectral range (735 nm for low fluence and low number of pulses).

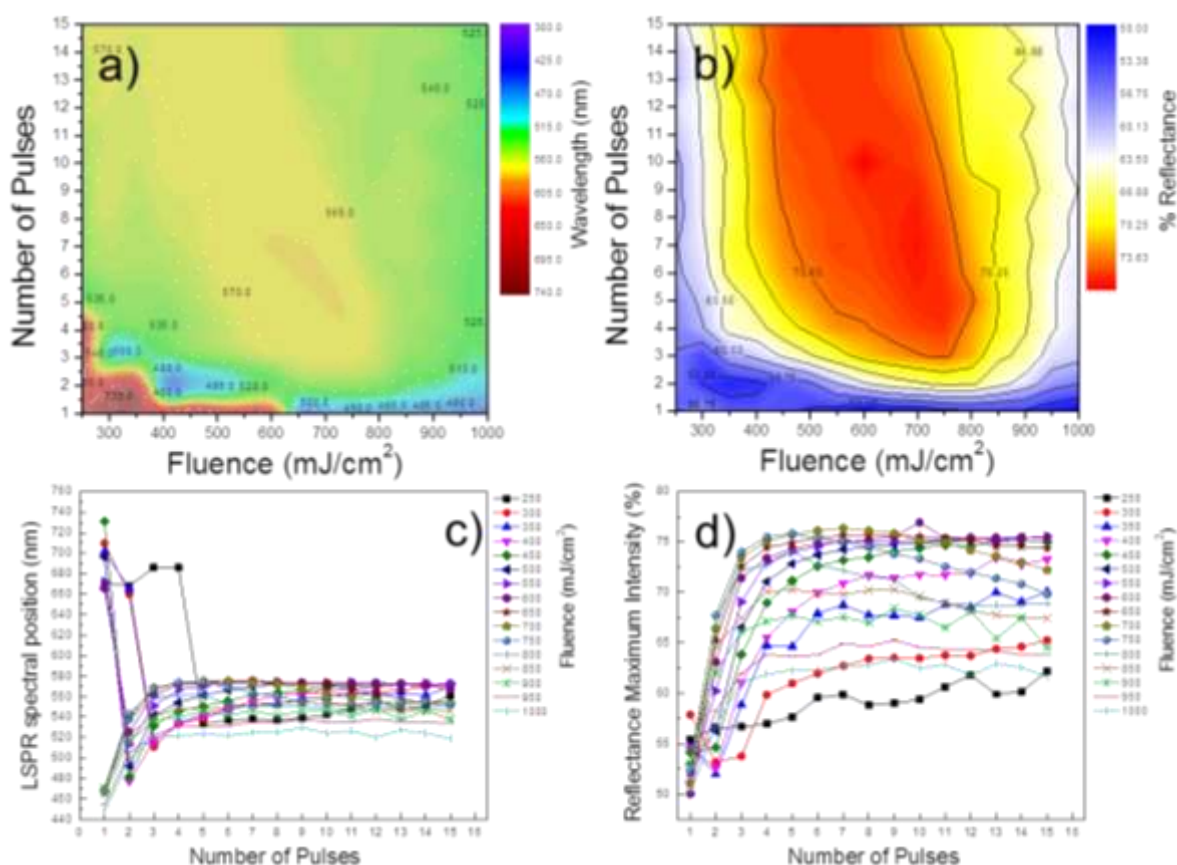


Figure S3. *LISA / UV MONA-LISA* (248 nm) of a Ag thin film with an effective thickness of 10 nm: (a) a contour plot of the dominant LSPR spectral position for the various number of pulses and applied fluence during LA, (b) a contour plot of the maximum reflectivity of the dominant LSPR for the various number of pulses and fluence applied during LA, (c) dominant LSPR spectral position for the various number of pulses under different applied fluence and (d) maximum reflectivity of the dominant LSPR for the various number of pulses under different applied fluence.

1.2 Optical Reflectivity Spectra (ORS) of Ag thin films

The number of samples that have been processed in the framework of this work is in the order of several thousands. That makes it practically impossible to present all those spectra (from which the previous colour maps derived). Alternatively, we chose to present results of some selective, representative conditions. These representative conditions were chosen for the experimental part of VIS *MONA-LISA*, comprising the UV LA (*LISA* / UV *MONA-LISA*) template to which the VIS LA (either 532 nm or 620 nm) applied.

The following figure (Fig. S4) presents ORS spectra of selective conditions of Ag samples (5 and 10 nm of effective thickness) processed by 193 nm and 248 nm LA.

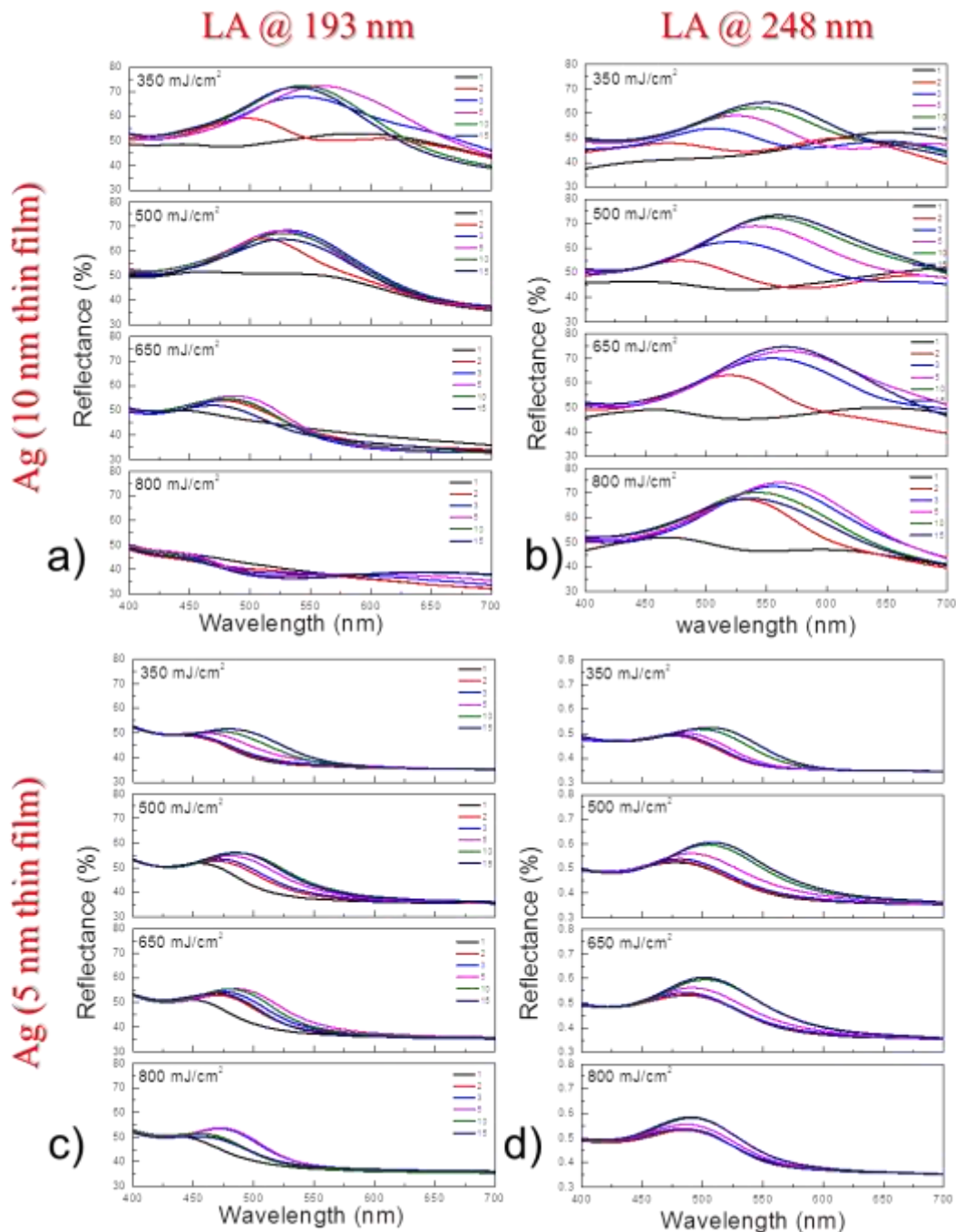


Figure S4. Optical reflectivity spectra of (a) *LISA* / UV *MONA-LISA* (193 nm) of a 10 nm Ag thin film, (b) *LISA* / UV *MONA-LISA* (248 nm) of a 10 nm Ag thin film, (c) *LISA* / UV *MONA-LISA* (193 nm) of a 5 nm Ag thin film and (d) *LISA* / UV *MONA-LISA* (248 nm) of a 5 nm Ag thin film.

1.3. ORS of Au thin Films

The following figure (Fig. S5) presents ORS spectra of selective conditions of Au samples (5 and 10 nm of effective thickness) processed by 248 nm LA.

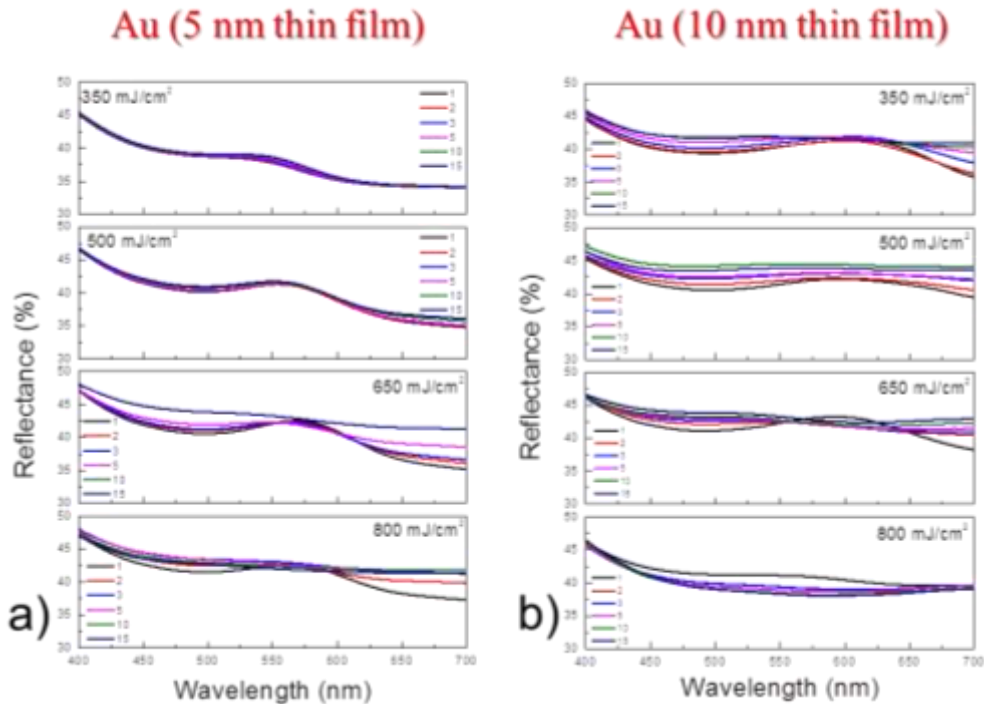


Figure S5. Optical reflectivity spectra of (a) *LISA* / *UV MONA-LISA* (248 nm) of 5 nm Au thin film and (b) *LISA* / *UV MONA-LISA* (248 nm) of 10 nm Au thin film.

1.4. ORS of Cu thin Films

The following figure (Fig. S6) presents ORS spectra of selective conditions of Cu samples (5 and 10 nm of effective thickness) processed by 248 nm LA.

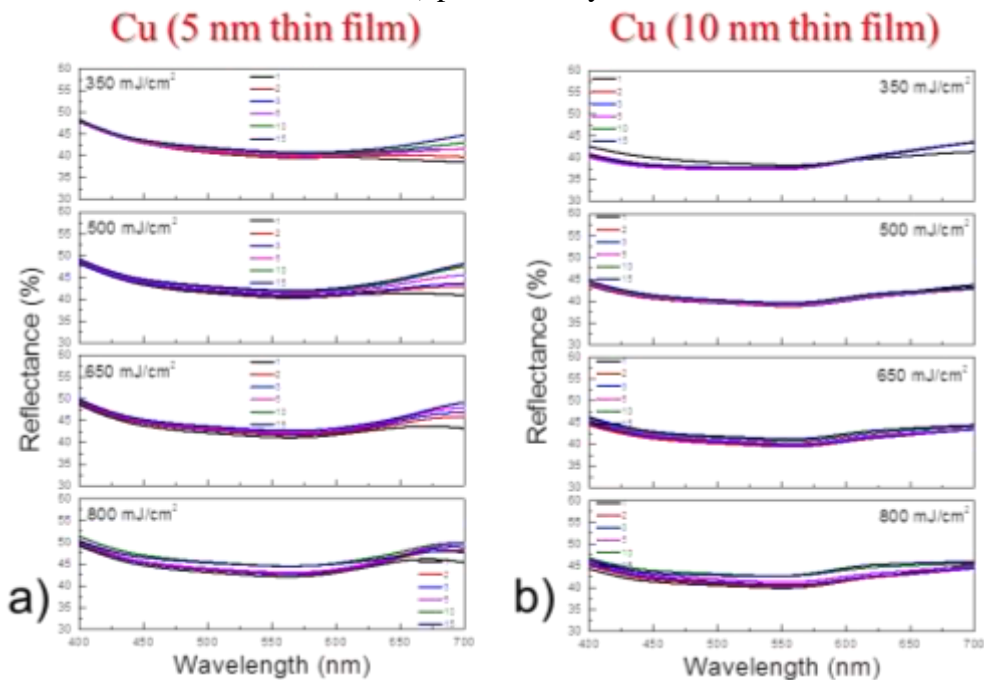


Figure S6. Optical reflectivity spectra of (a) *LISA* / *UV MONA-LISA* (248 nm) of 5 nm Cu thin film and (b) *LISA* / *UV MONA-LISA* (248 nm) of 10 nm Cu thin film.

2. VIS MONA-LISA of thin films

In this part of the supplementary information we describe the combined processes of UV LA (at 248 nm) and subsequent exposure to a Nd:YAG laser set with the second harmonic generator (SHG) to emit light at 532 nm or set with an optical parametric oscillator (OPO) unit to emit light at 620 nm (OPO is pumped with the third harmonic of Nd:YAG – 355 nm). We present the optical reflectivity spectra along side the scanning electron microscopy imaging, and in direct comparison between the initial UV LA and the UV LA followed by the VIS LA processes (the process which we call VIS MONA-LISA). The beam delivery path for the Nd:YAG laser comprised three mirrors, a variable attenuator to control the energy density of each pulse (6 ns in duration) and a round aperture allowing a 2 mm diameter round spot to reach the samples' surface. The repetition rate was set at 10 Hz.

2.1 Combined irradiations of UV (248 nm) and VIS (532 nm) on Ag thin films

i. Ag thin films deposited by magnetron sputtering

As mentioned above, under UV exposure the plasmonic response of the samples saturated after the first 4-5 pulses. Further tailoring of the plasmonic response can be achieved by delivering extra nanosecond pulses at a wavelength matching their LSPR.

To establish an initial processing window for the VIS LA treatment on the UV LA samples, we investigated the effect of fluence and number of pulses over a specific UV LA condition; 10 pulses (248 nm) at 650 mJ/cm², which gives a good plasmonic response close to 532 nm. As a starting point we began with very low fluence (25 mJ/cm²). Up to 75 mJ/cm² and for thousands of pulses the sample's optical response was not altered. Above 75 mJ/cm² the sample changed its optical properties; a slight blueshift occurred concomitantly with a reduction of the spectral width. At 100 mJ/cm² similar observations were made. We found that the optimum condition was the application of 500 pulses at 125 mJ/cm² (Fig. S7c). We treated the whole UV LA sample grid of Fig. S8 (right) with the VIS (532 nm) LA applying 500 pulses at 125 mJ/cm² with a repetition rate of 10 Hz.

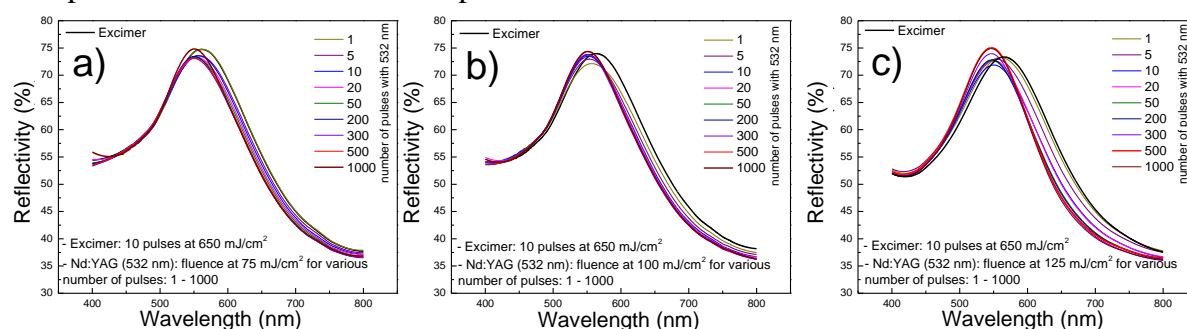


Figure S7. VIS LA (532 nm) of a sample previously processed with UV (248 nm) LA with 10 pulses at 650 mJ/cm². The choice of this particular condition of UV LA was made due to the optical response of the sample, showing a high plasmonic response close to 532 nm. Three fluences were tested for various number of pulses in order to find the optimum condition for the VIS LA: (a) 75 mJ/cm², (b) 100 mJ/cm² and (c) 125 mJ/cm².

Figure S8 shows digital photos of the sample grids used for the LISA / UV MONA-LISA, shown on the right, and of the same UV LA produced grid that subsequently was processed with the VIS MONA-LISA, shown on the left. Note that the VIS spot is round (2 mm in diameter) and is well placed at the centre of the square UV LA spot (2.5x2.5mm²). Also note the colour variations in the spots of the LISA / UV MONA-LISA process in comparison to the VIS MONA-LISA process, especially those with visual appearance far away from the green. Processing with the VIS LA shifts the colour to the green, an observation that is accompanied by shift of the plasmon peak towards wavelengths close to 532 nm.

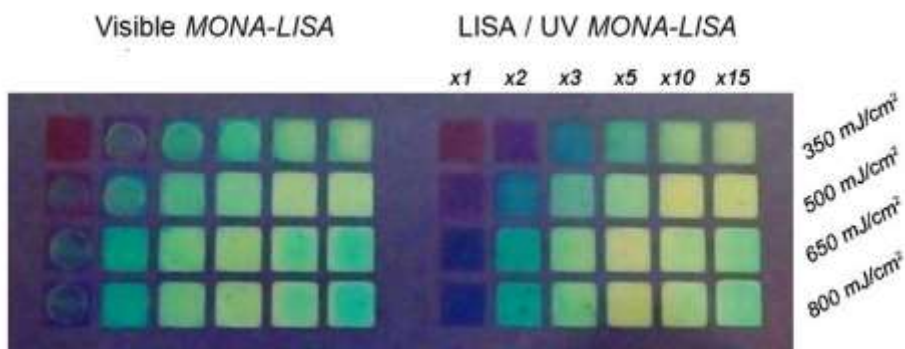


Figure S8. Digital photos of the sample grids used for irradiation with the UV laser (248 nm), shown on the right (*LISA / UV MONA-LISA*), and a combined irradiation with UV and VIS (532nm), shown on the left (*VIS MONA-LISA*). Note that the VIS spot is circular (2 mm in diameter). Also note the colour variation in the spots with visual appearance far away from the green.

The following figure (Fig. S9) presents a collage of SEM images in direct reference to the above-mentioned sample grids. The SEM snapshots of the spots corresponding to the *VIS MONA-LISA* processes are on the left, while on the right side are snapshots of the *LISA / UV MONA-LISA* template. Size distributions and shape variations can be observed.

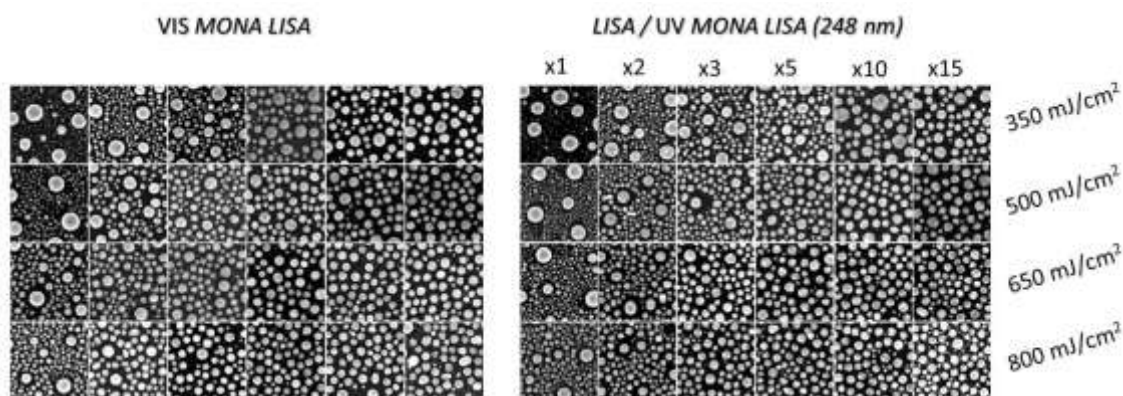


Figure S9. SEM snapshots of the corresponding sample grids shown in Fig. S8: *LISA / UV MONA-LISA* (248 nm) is shown on the right, and *VIS MONA-LISA* is shown on the left.

In the following paragraphs we present analytically the ORS graphs, SEM imaging and the statistical analysis of the *MONA-LISA* process. Since the *LISA / UV MONA-LISA* grid was used as a template for the *VIS MONA-LISA* process we entitle each case with the fluence used during the UV exposure. For the reader's convenience the black coloured lines, bars and SEM figure borders refer to the *LISA / UV MONA-LISA* process whereas the red coloured lines, bars and SEM figure borders refer to the *VIS MONA-LISA* (combined UV & VIS LA) process. Finally, in all the ORS graphs the green dashed line sets the wavelength used for the VIS LA experiment (532 nm).

LISA / UV MONA-LISA (248 nm, 350 mJ/cm²)

1 pulse of UV & 1 pulse of UV plus VIS treatment

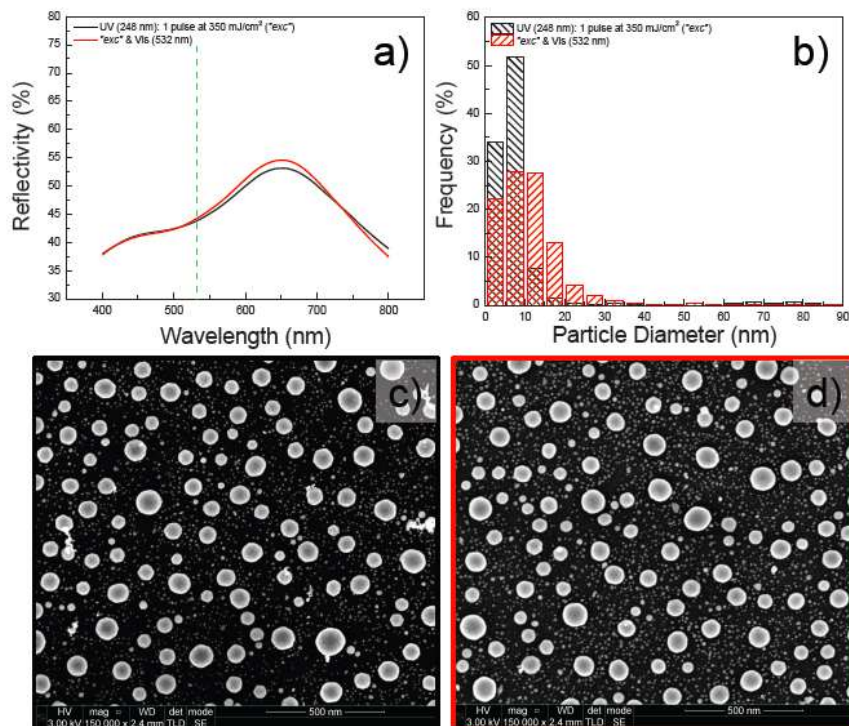


Figure S10. (a) ORS of the UV LA, 1 pulse at 350 mJ/cm² (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm² (red line), (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

2 pulses of UV & 2 pulses of UV plus VIS treatment

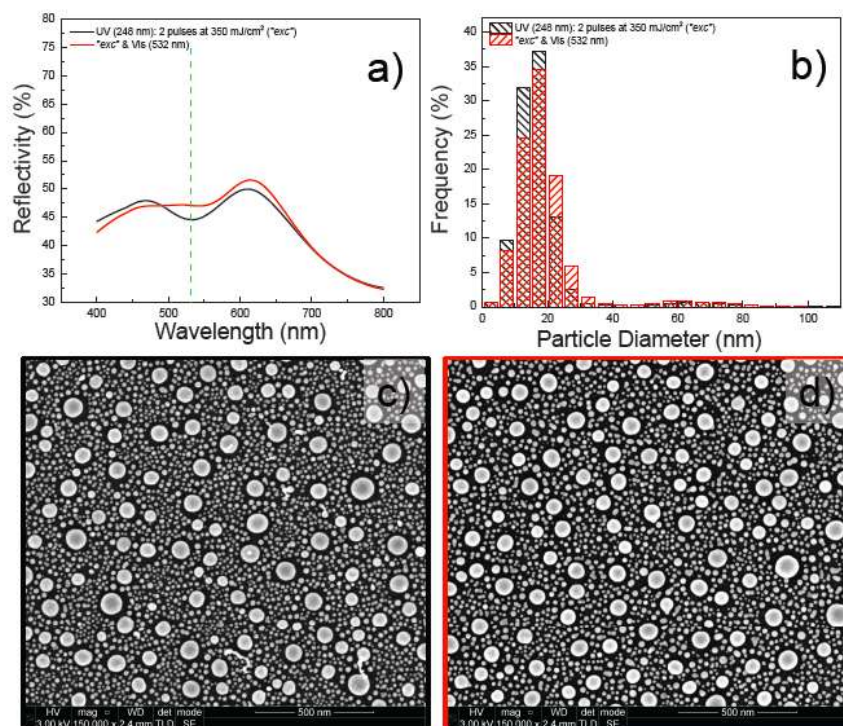


Figure S11. (a) ORS of the UV LA, 2 pulses at 350 mJ/cm^2 (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm^2 (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

For this particular sample we further investigated an increased number of pulses and we present results for VIS LA at 2000 and 4000 pulses. The results are shown in Fig. S12: The underlying template produced via UV LA shows a bimodal response with two clear bands, one close to 450 nm and another one close to 600 nm (black line). At 500 pulses of VIS LA a new plasmonic band, makes its appearance close to the 532 nm (red line). This band evolves as we further treat the sample with 2000 pulses (blue line) and can be now more clearly seen. In this case a clear triple plasmonic peak is observed. As we continue to treat the sample with more pulses (4000) the two peaks at higher wavelengths begin to overlap. This process could be seen as a “plasmonic evolution” process, which resembles the evolution by natural selection: only the particles with LSPR at 532 nm will eventually “survive”.

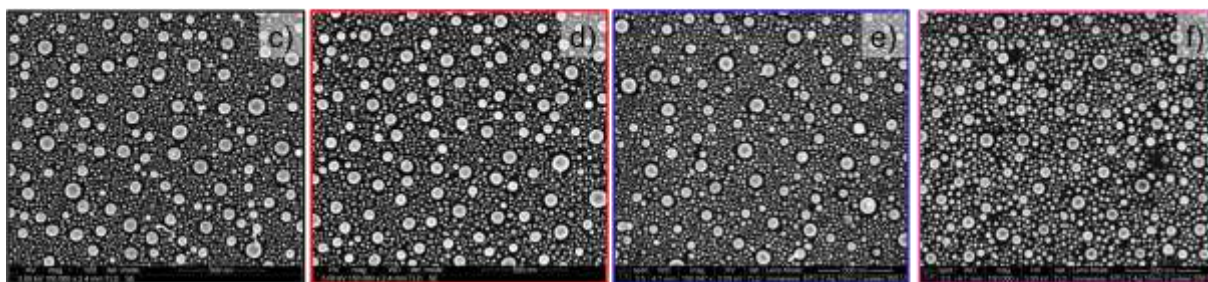
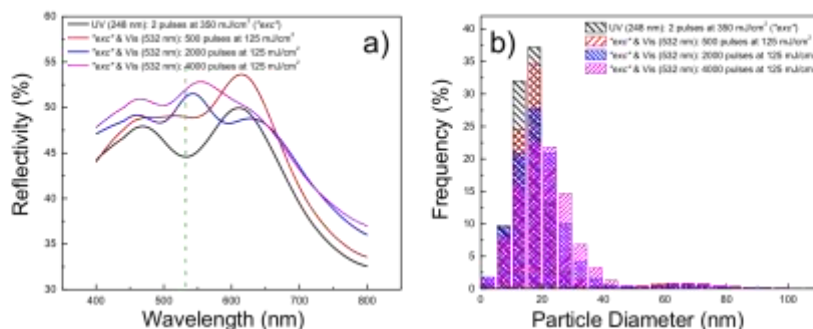


Figure S12. (a) ORS of the UV LA, 2 pulse at 350 mJ/cm^2 (black line), used as a template for the subsequent VIS LA process, 500 pulses (red line), 2000 pulses (blue line) and 4000 pulses (magenta line) at 125 mJ/cm^2 . The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black bars) and the sample treated with the UV LA and the VIS LA at 500 pulses (red bars), 2000 pulses (blue bars) and 4000 pulses (magenta bars), (c) SEM image of the UV LA processed sample, (d) SEM image of the UV LA and VIS LA processed sample at 500 pulses, (e) SEM image of the UV LA and VIS LA processed sample at 2000 pulses and (f) SEM image of the UV LA and VIS LA processed sample at 4000 pulses.

However, treatment at 4000 pulses produces “hot spots” in the film’s surface as shown in Fig. S13, where low magnification SEM images are presented. Up to 2000 pulses the sample’s surface is homogeneous and the VIS LA process is uniform throughout the surface. On the contrary, treatment at 4000 pulses produces irregularities on the surface morphology.

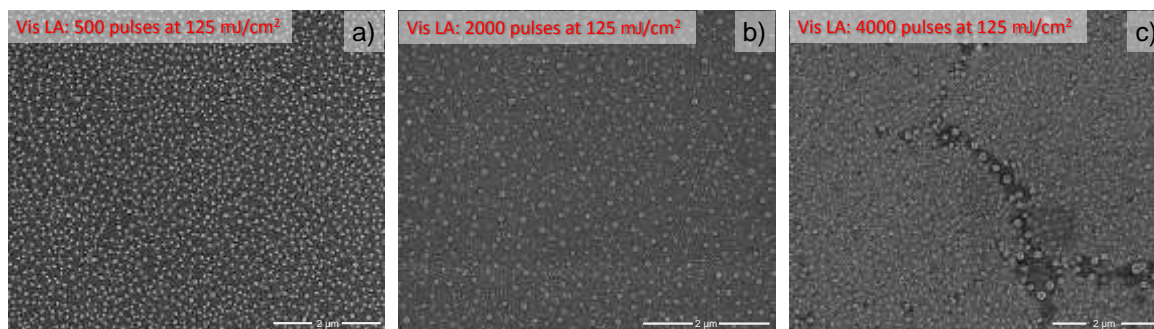


Figure S13. Lower magnification SEM images to show the uniformity of the samples produced with the VIS LA process. All samples were initially prepared with UV LA (2 pulses at 350 mJ/cm^2) and subsequently with VIS LA (532nm): (a) 500 pulses at 125 mJ/cm^2 , (b) 2000 pulses at 125 mJ/cm^2 and (c) 4000 pulses at 125 mJ/cm^2 processed sample.

3 pulses of UV & 3 pulses of UV plus VIS treatment

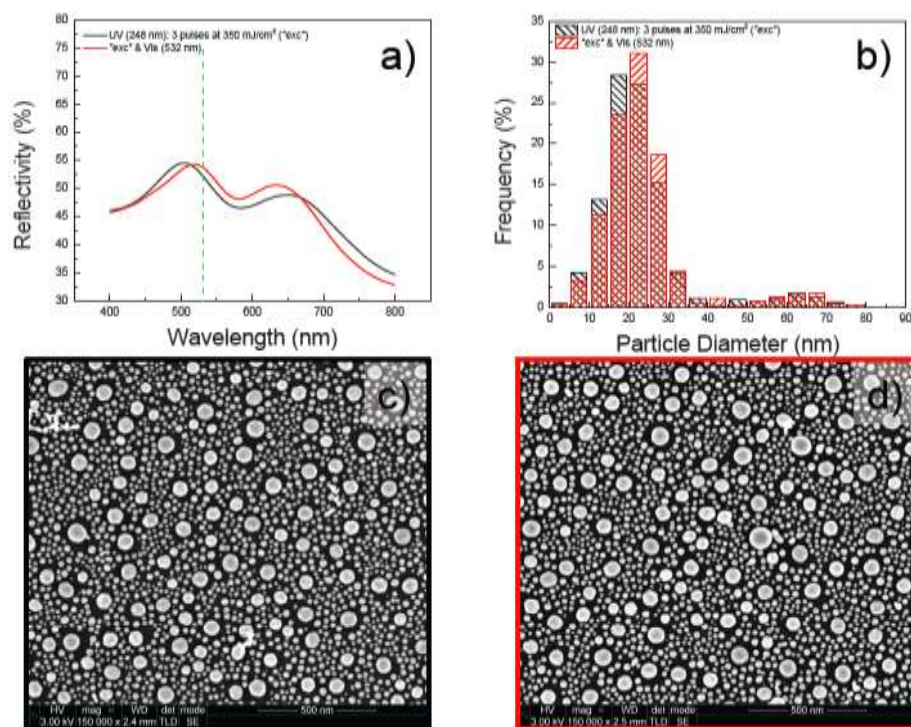


Figure S14. (a) ORS of the UV LA, 3 pulses at 350 mJ/cm^2 (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm^2 (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

5 pulses of UV & 5 pulses of UV plus VIS treatment

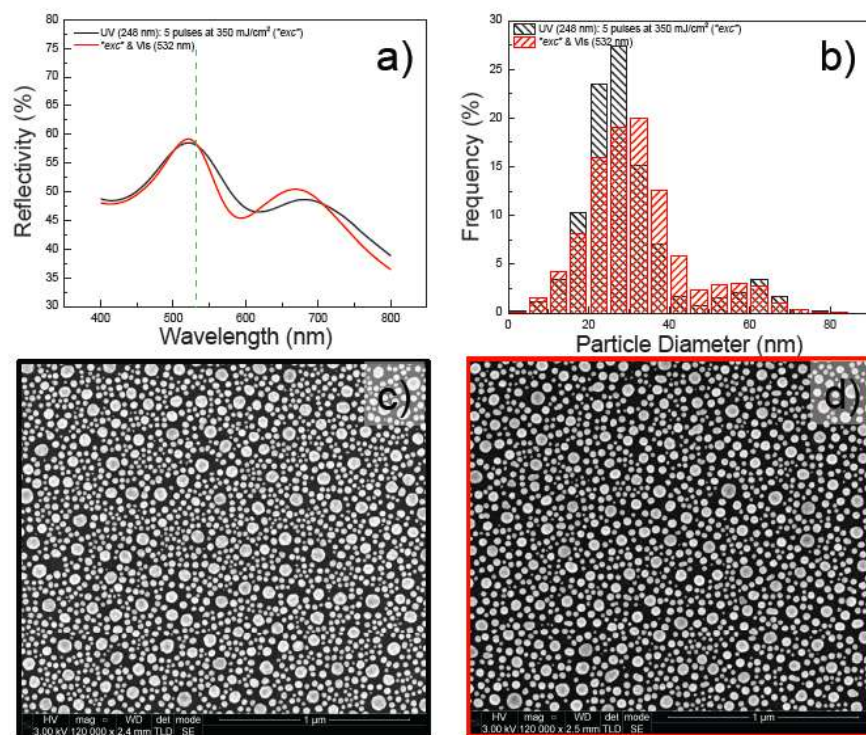


Figure S15. (a) ORS of the UV LA, 5 pulses at 350 mJ/cm² (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm² (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

10 pulses of UV & 10 pulses of UV plus VIS treatment

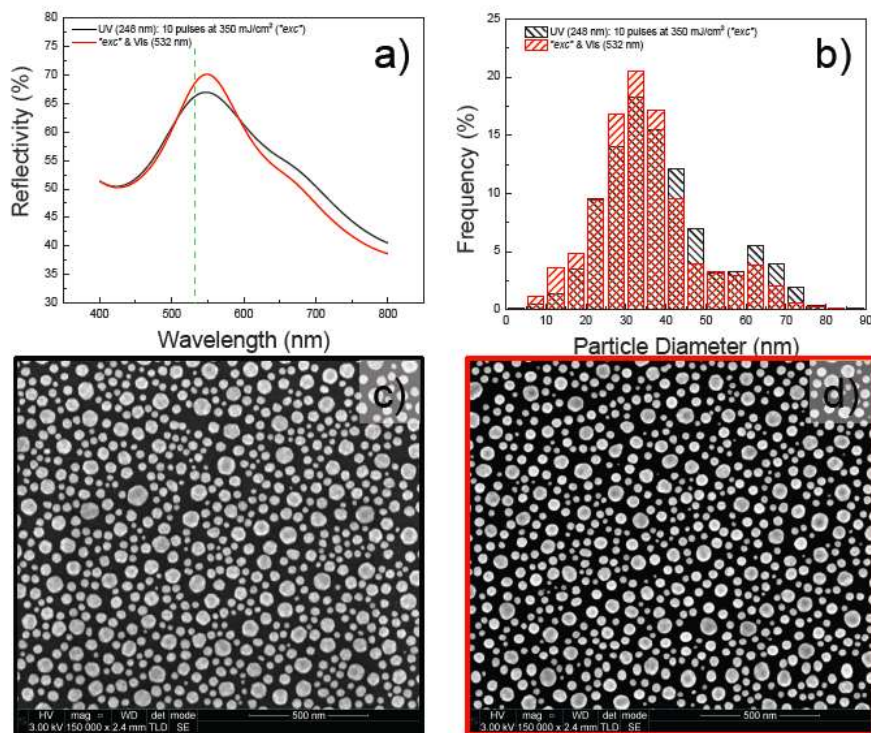


Figure S16. (a) ORS of the UV LA, 10 pulses at 350 mJ/cm² (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm² (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

15 pulses of UV & 15 pulses of UV plus VIS treatment

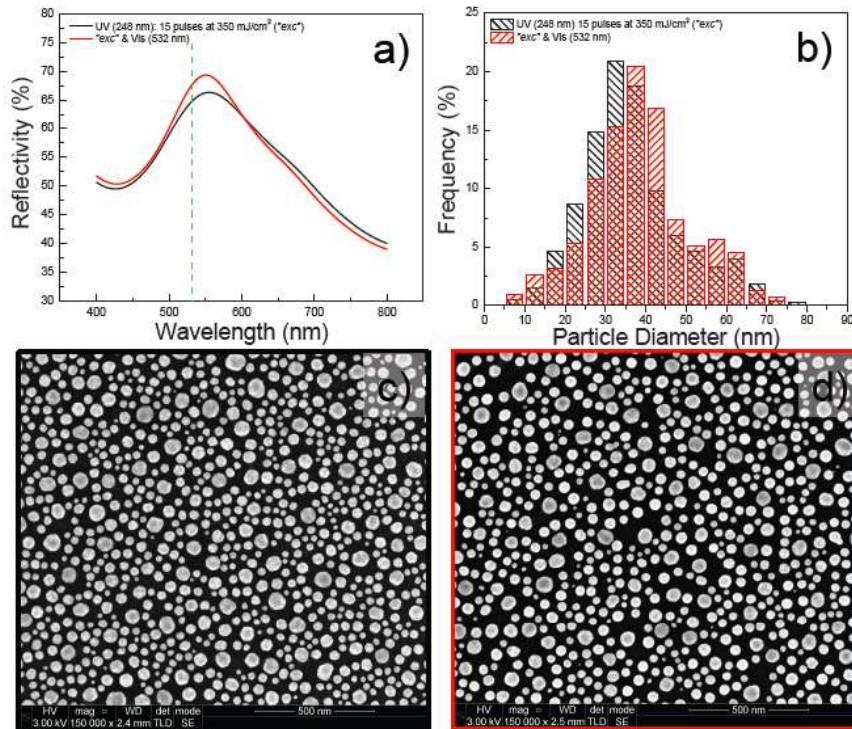


Figure S17. (a) ORS of the UV LA, 15 pulses at 350 mJ/cm² (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm² (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

LISA / UV MONA-LISA (248 nm, 500 mJ/cm²)

1 pulse of UV & 1 pulse of UV plus VIS treatment

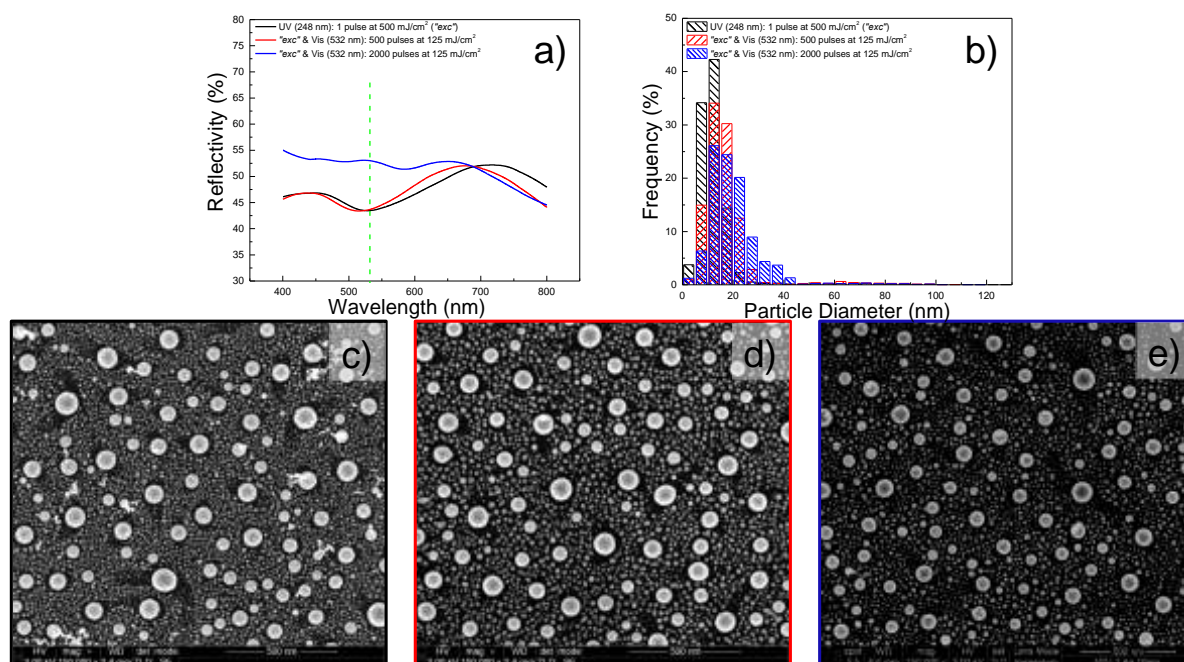


Figure S18. (a) ORS of the UV LA, 1 pulse at 500 mJ/cm² (black line), used as a template for the subsequent VIS LA process, 500 pulses (red line) and 2000 pulses (blue line) at 125 mJ/cm². The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black bars) and the sample treated with the UV LA and the VIS LA at 500 pulses (red bars) and 2000 pulses (blue bars) all at 125 mJ/cm², (c) SEM image of the UV LA processed sample, (d) SEM image of the UV LA and VIS LA processed sample at 500 pulses, (e) SEM image of the UV LA and VIS LA processed sample at 2000 pulses.

2 pulses of UV & 2 pulses of UV plus VIS treatment

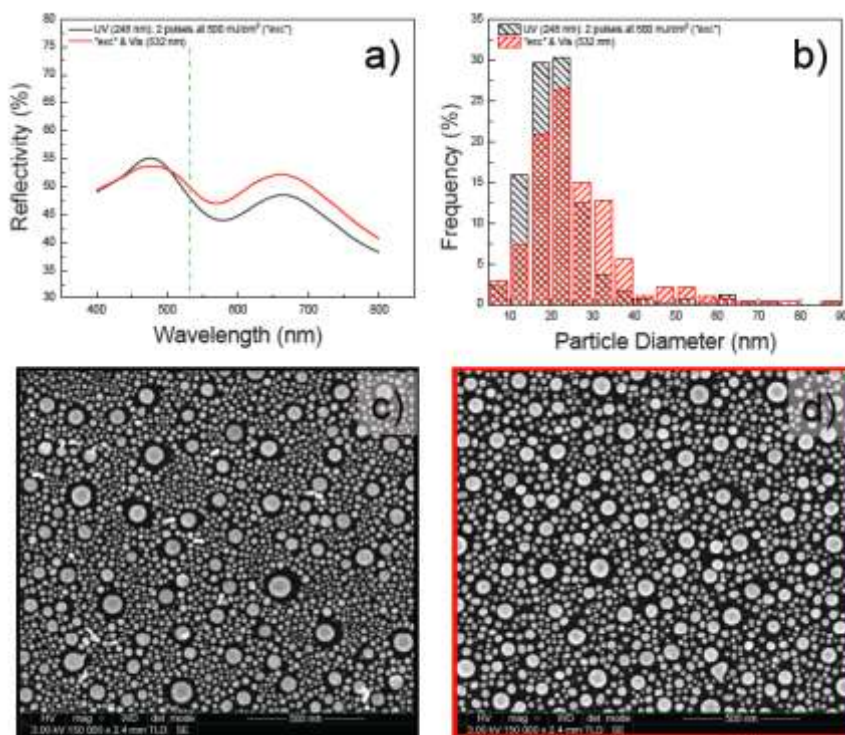


Figure S19. (a) ORS of the UV LA, 2 pulses at 500 mJ/cm^2 (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm^2 (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

3 pulses of UV & 3 pulses of UV plus VIS treatment

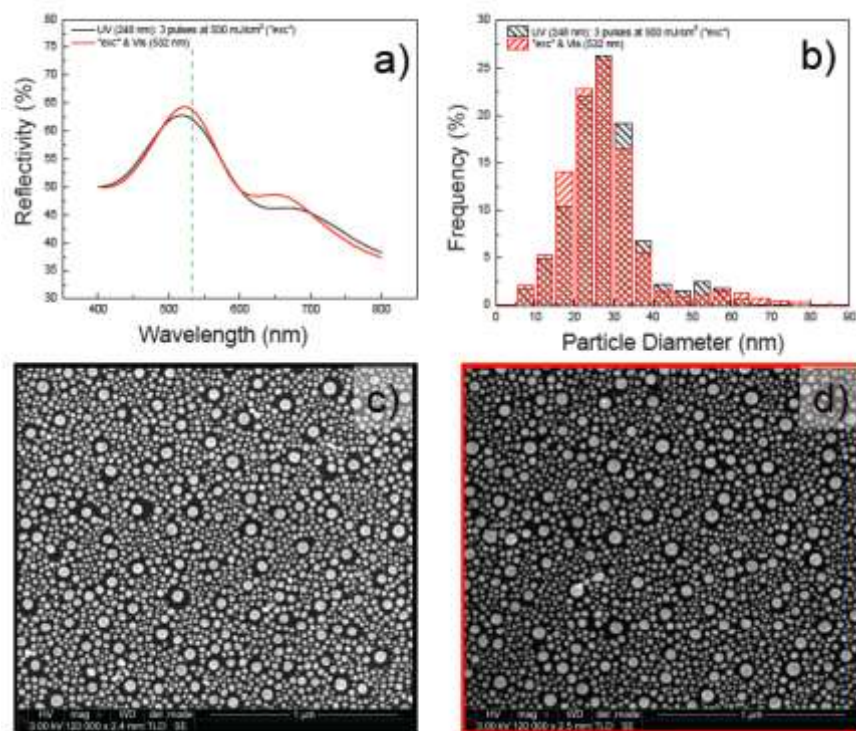


Figure S20. (a) ORS of the UV LA, 3 pulses at 500 mJ/cm^2 (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm^2 (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

5 pulses of UV & 5 pulses of UV plus VIS treatment

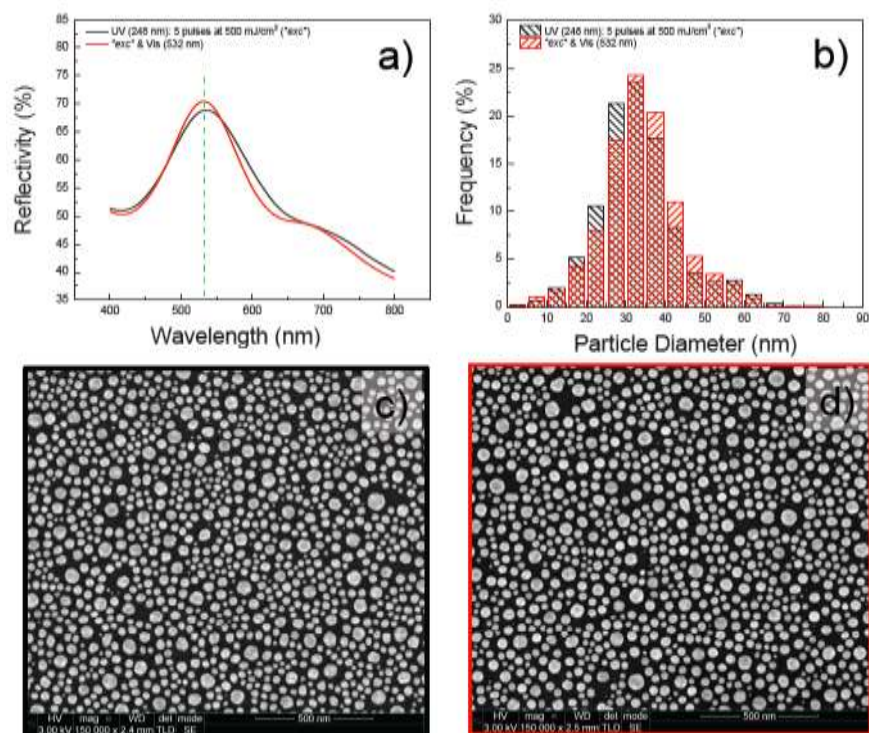


Figure S21. (a) ORS of the UV LA, 5 pulses at 500 mJ/cm² (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm² (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

10 pulses of UV & 10 pulses of UV plus VIS treatment

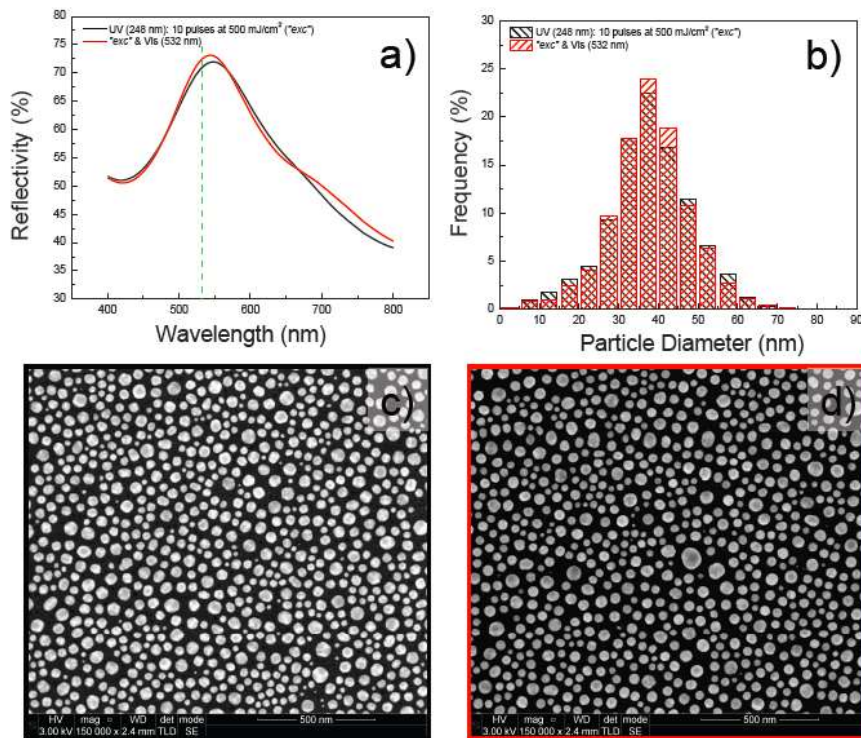


Figure S21. (a) ORS of the UV LA, 10 pulses at 500 mJ/cm² (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm² (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

15 pulses of UV & 15 pulses of UV plus VIS treatment

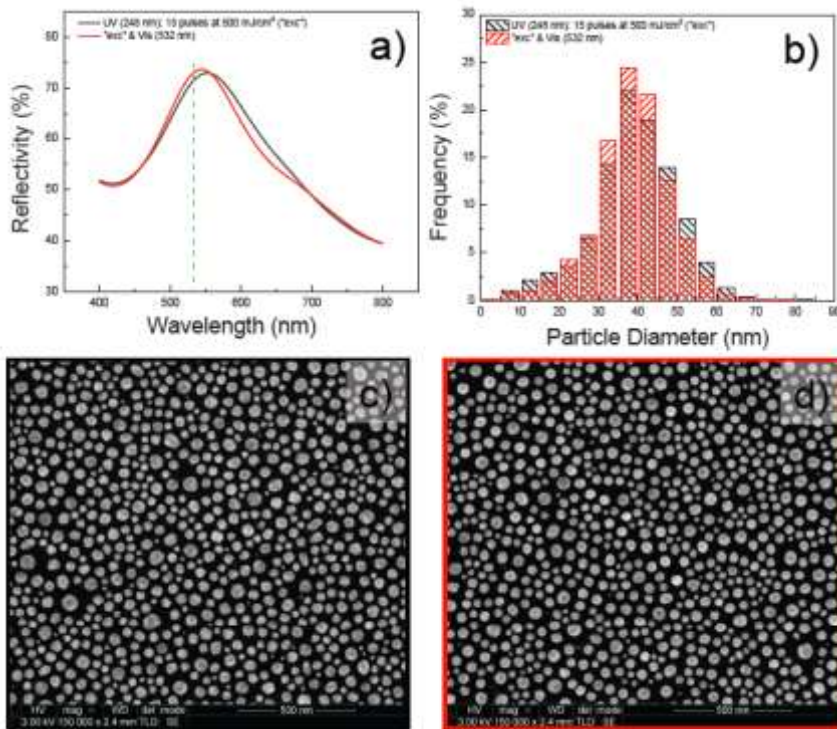


Figure S22. (a) ORS of the UV LA, 15 pulses at 500 mJ/cm^2 (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm^2 (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

LISA / UV MONA-LISA (248 nm, 650 mJ/cm²)

1 pulse of UV & 1 pulse of UV plus VIS treatment

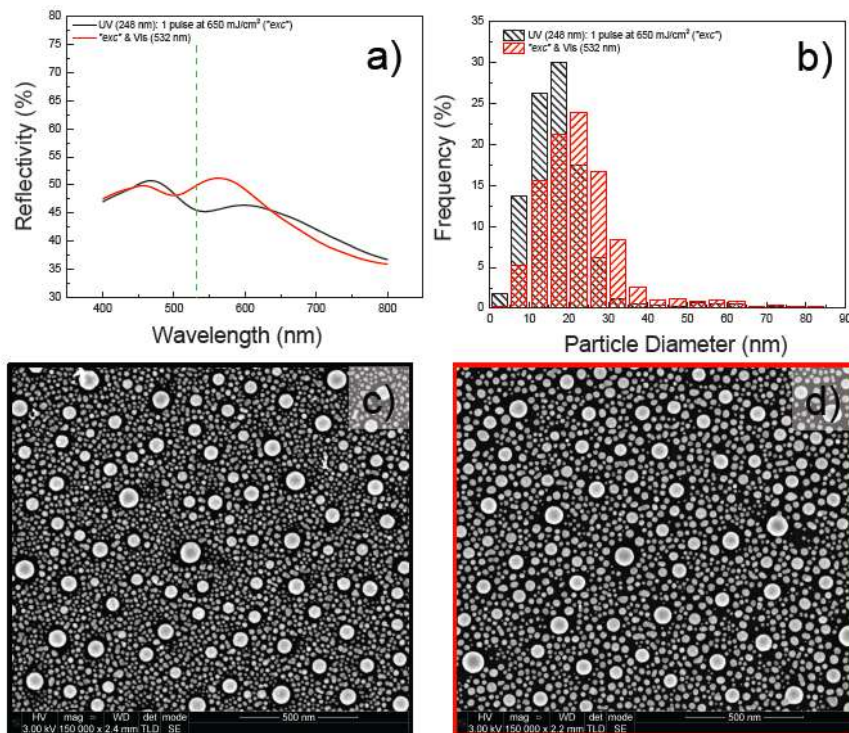


Figure S23. (a) ORS of the UV LA, 1 pulse at 650 mJ/cm² (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm² (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

2 pulses of UV & 2 pulses of UV plus VIS treatment

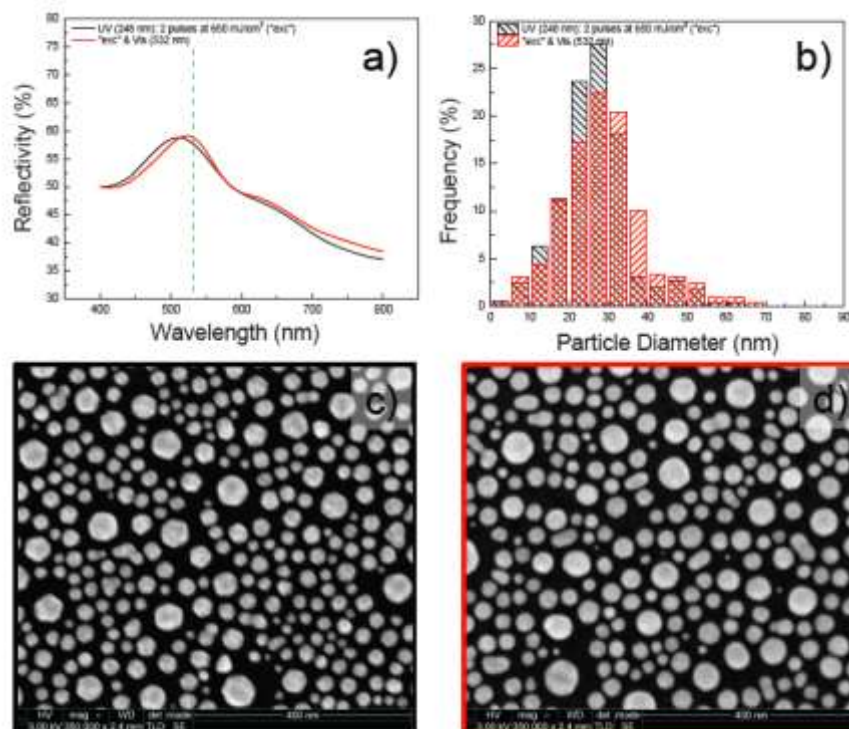


Figure S24. (a) ORS of the UV LA, 2 pulses at 650 mJ/cm^2 (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm^2 (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

3 pulses of UV & 3 pulses of UV plus VIS treatment

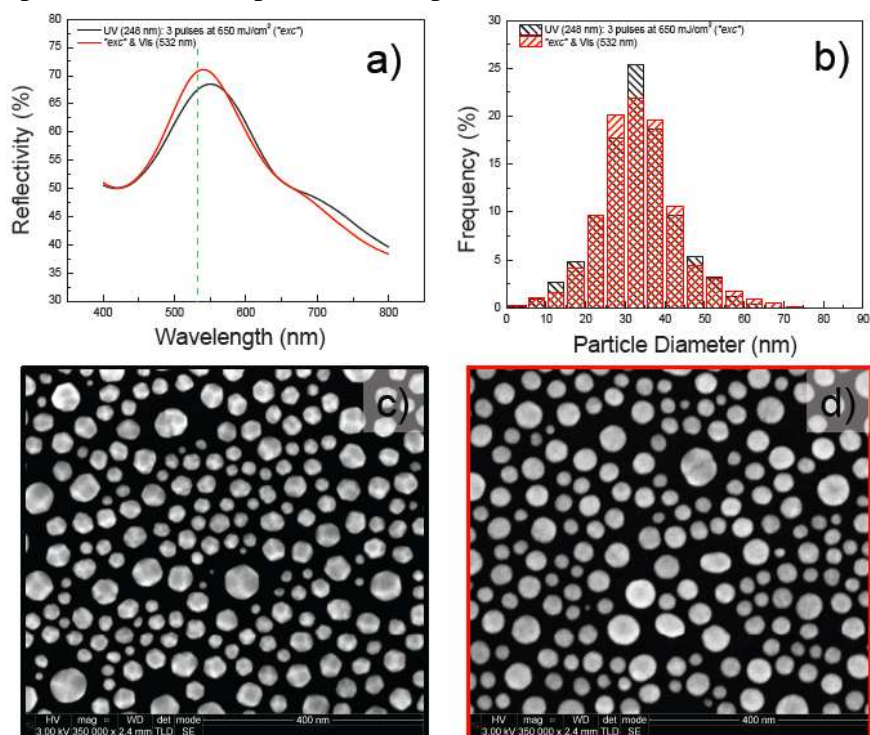


Figure S25. (a) ORS of the UV LA, 3 pulses at 650 mJ/cm² (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm² (red line). The green dashed line sets the 532 nm mark (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

5 pulses of UV & 5 pulses of UV plus VIS treatment

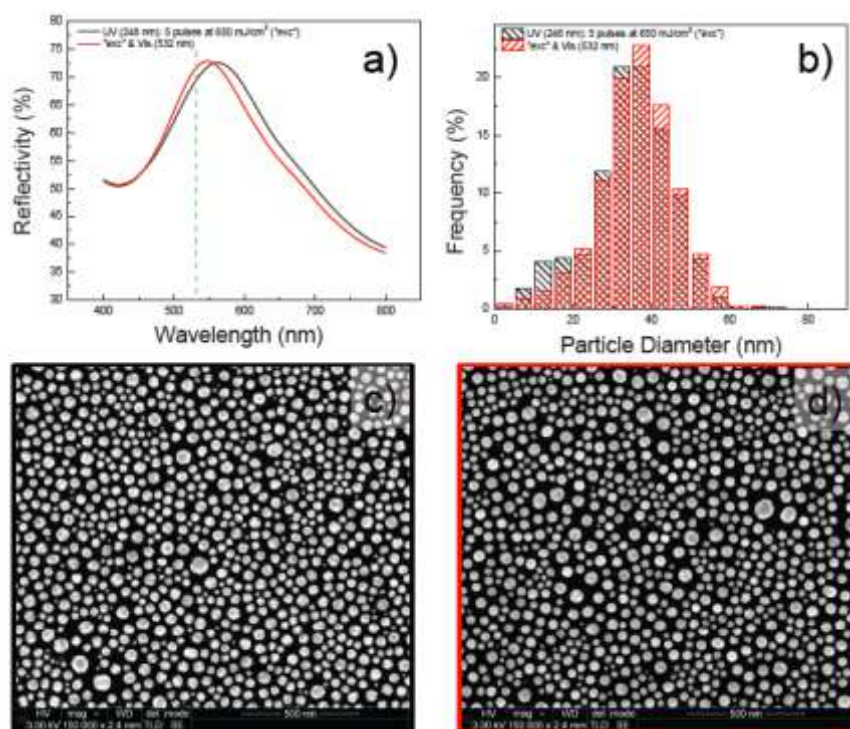


Figure S26. (a) ORS of the UV LA, 5 pulses at 650 mJ/cm^2 (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm^2 (red line). The green dashed line sets the 532 nm mark (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

10 pulses of UV & 10 pulses of UV plus VIS treatment

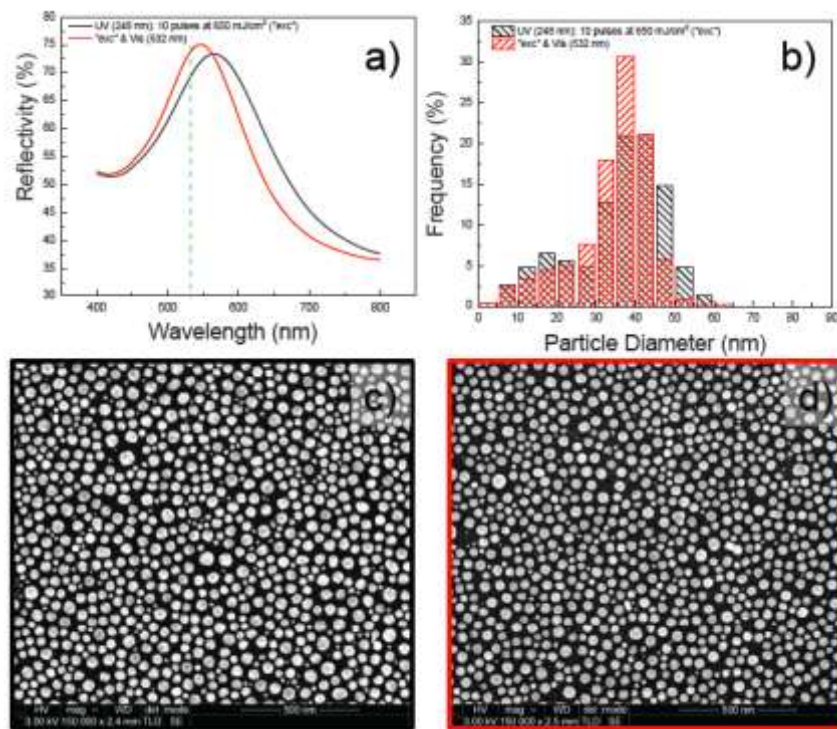


Figure S27. (a) ORS of the UV LA, 10 pulses at 650 mJ/cm^2 (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm^2 (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

15 pulses of UV & 15 pulses of UV plus VIS treatment

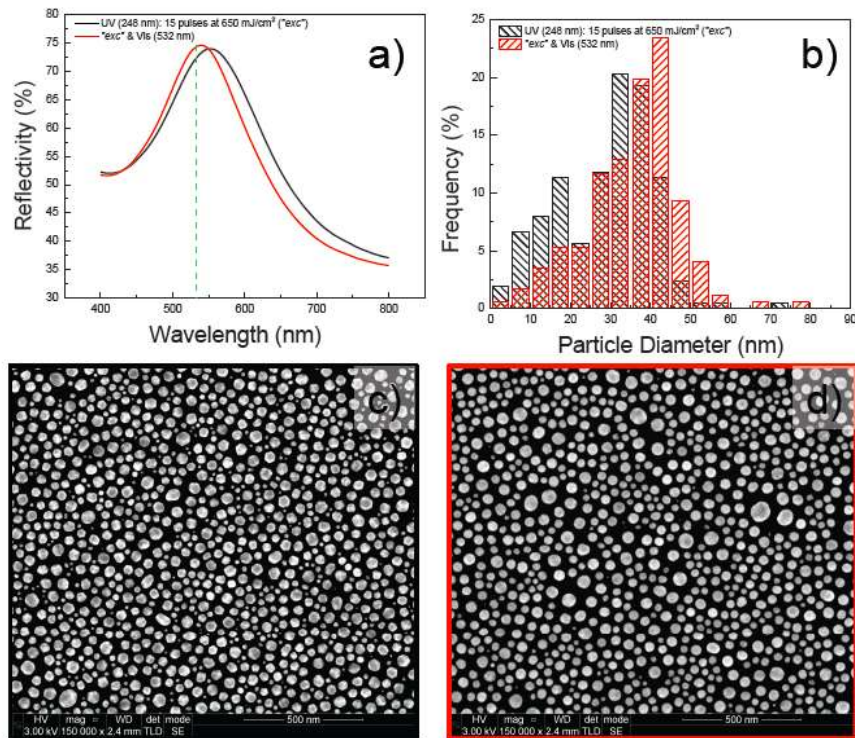


Figure S28. (a) ORS of the UV LA, 15 pulses at 650 mJ/cm^2 (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm^2 (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

LISA / UV MONA-LISA (248 nm, 800 mJ/cm²)

1 pulse of UV & 1 pulse of UV plus VIS treatment

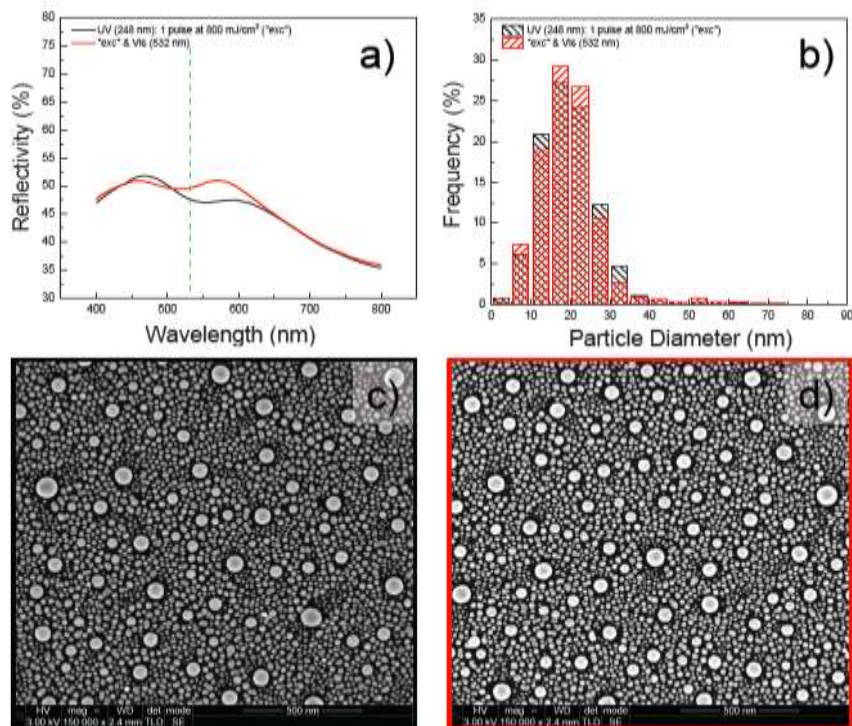


Figure S29. (a) ORS of the UV LA, 1 pulse at 800 mJ/cm² (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm² (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

2 pulses of UV & 2 pulses of UV plus VIS treatment

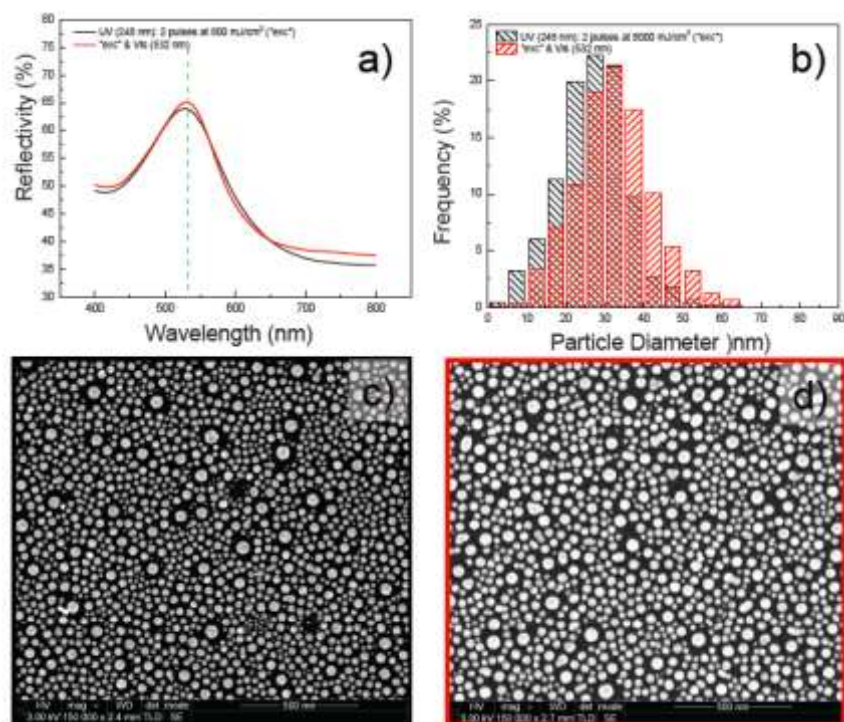


Figure S30. (a) ORS of the UV LA, 2 pulses at 800 mJ/cm^2 (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm^2 (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

3 pulses of UV & 3 pulses of UV plus VIS treatment

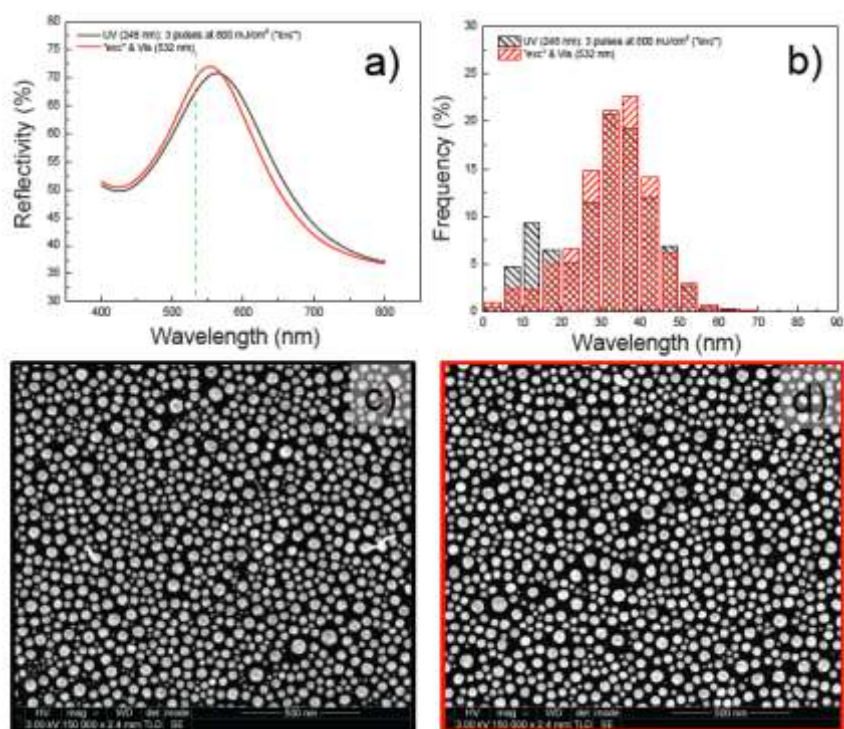


Figure S31. (a) ORS of the UV LA, 3 pulses at 800 mJ/cm^2 (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm^2 (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

5 pulses of UV & 5 pulses of UV plus VIS treatment

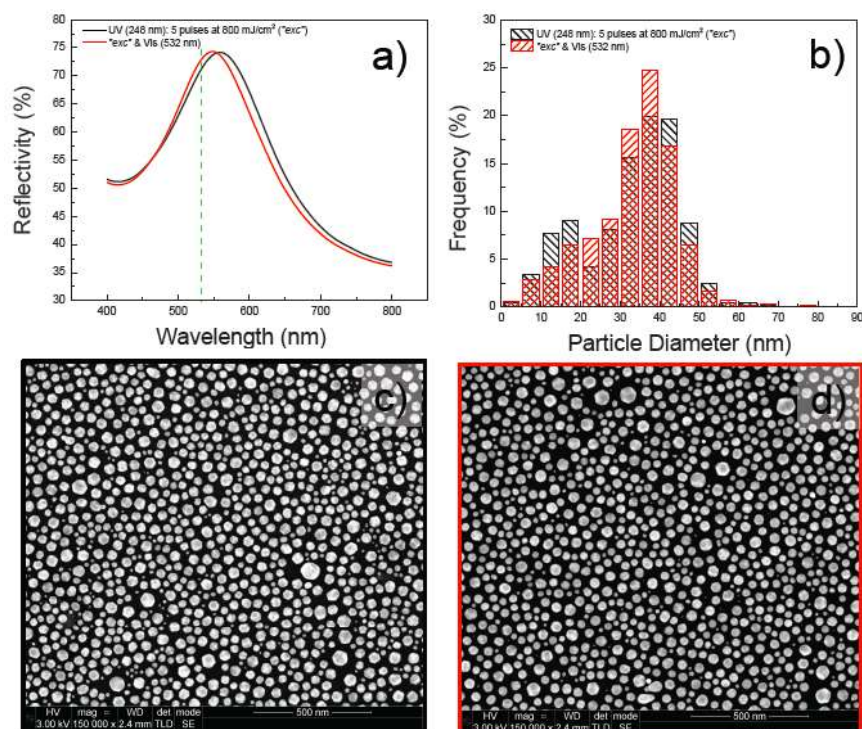


Figure S32. (a) ORS of the UV LA, 5 pulses at 800 mJ/cm² (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm² (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

10 pulses of UV & 10 pulses of UV plus VIS treatment

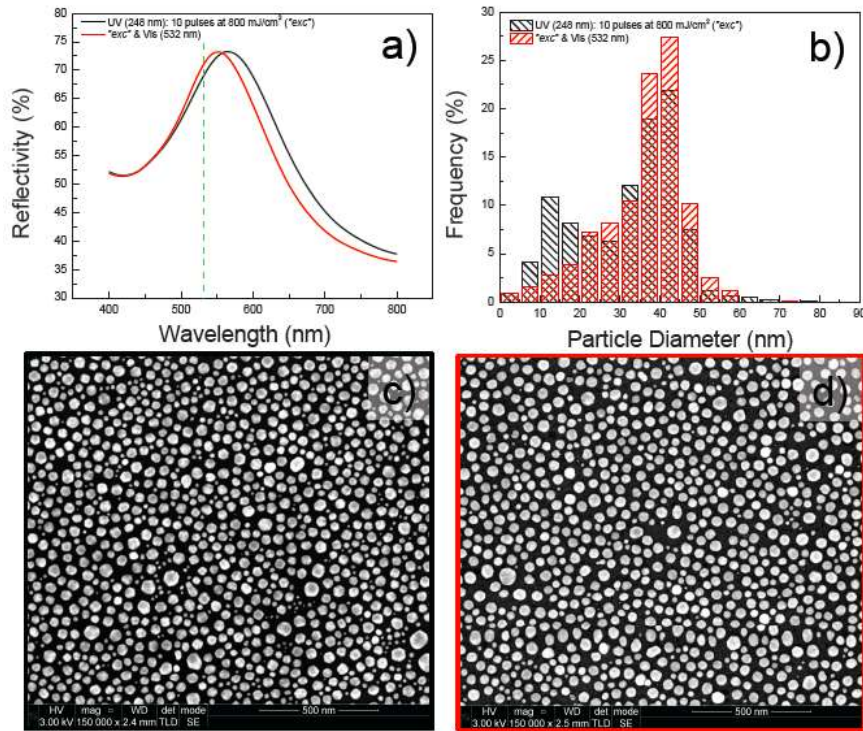


Figure S33. (a) ORS of the UV LA, 10 pulses at 800 mJ/cm² (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm² (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

15 pulses of UV & 15 pulses of UV plus VIS treatment

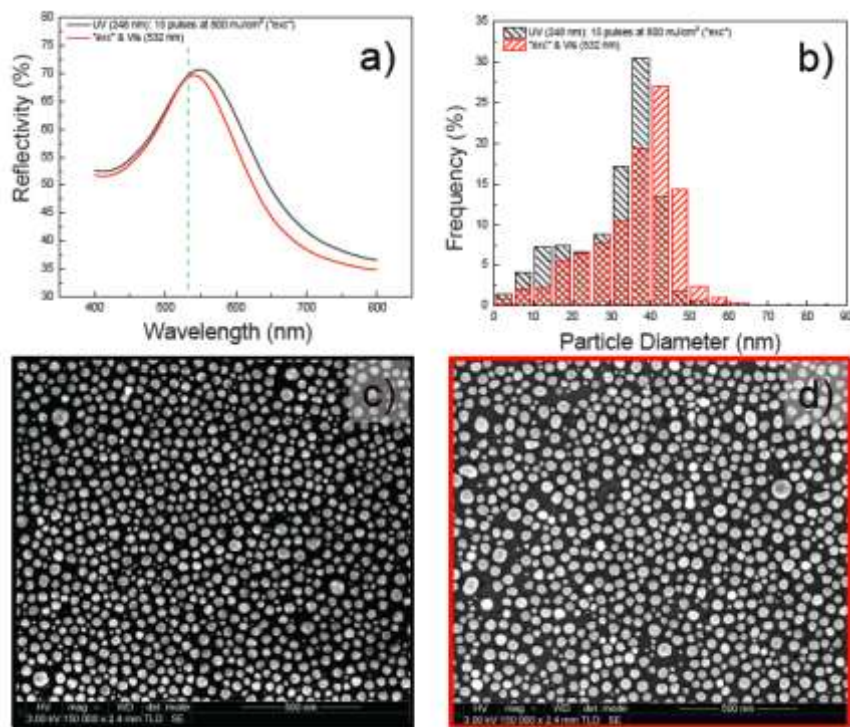


Figure S34. (a) ORS of the UV LA, 15 pulses at 800 mJ/cm² (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm² (red line). The green dashed line sets the 532 nm mark. (b) Particle size distributions derived from SEM imaging analysis of the sample processed with the UV LA (black shaded bars) and the sample treated with the UV LA and the VIS LA (red shaded bars), (c) SEM image of the UV LA processed sample and (d) SEM image of the UV LA and VIS LA processed sample.

ii. Ag thin films deposited by alternative techniques

A Ag thin film, 10 nm of effective thickness, was deposited by e-beam evaporation (EBE) to assess the generic approach of the *MONA-LISA* process. Two initial UV LA conditions were chosen as templates to be subsequently used for the VIS LA; 15 pulses at 500 mJ/cm^2 and 5 pulses at 800 mJ/cm^2 . Both templates were then exposed to VIS LA (532 nm) for 500 pulses at 125 mJ/cm^2 . The result of *MONA-LISA* is confirmed.

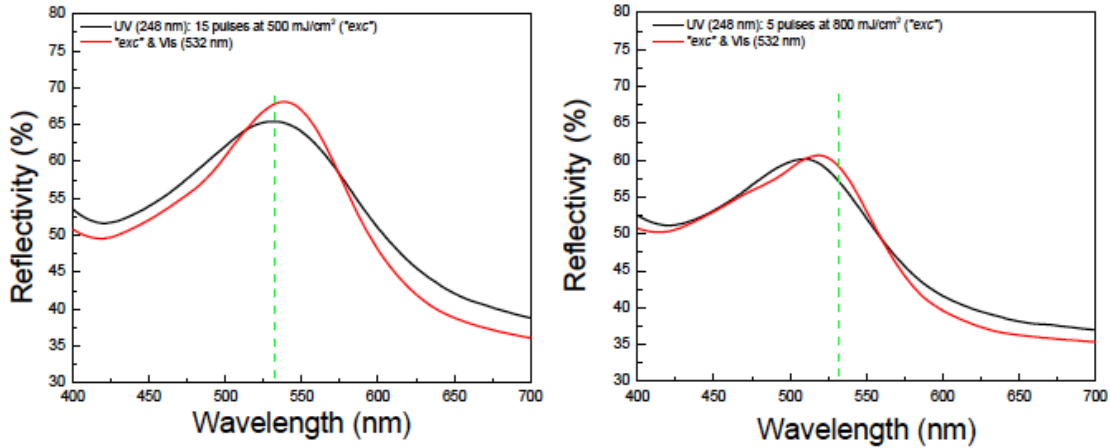


Figure S35. ORS of a Ag (10 nm) thin film fabricated by EBE of (a) UV LA, 15 pulses at 500 mJ/cm^2 (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm^2 (red line) and (b) UV LA, 5 pulses at 800 mJ/cm^2 (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm^2 (red line).

Additionally, we used a further alternative method; that of Ag deposition by chemical reduction of AgNO_3 on commercial n-type Si (100) wafers by drop casting of an AgNO_3/HF aqueous solution. In this case the chemical reduction produces nanoparticles, hence the UV LA is not required. VIS LA is applied only.

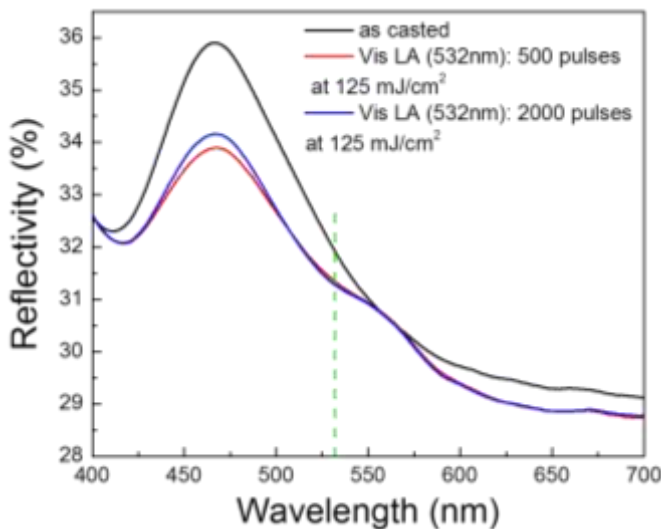


Figure S36. ORS of a Ag nanoparticles deposited by chemical reduction of AgNO_3 on to Si wafers by drop casting (black line) and subsequently processed with VIS LA (532 nm), 500 pulses at 125 mJ/cm^2 (red line) and 2000 pulses at 125 mJ/cm^2 (blue line). Again the result of *MONA-LISA* is confirmed.

2.2 Combined irradiations of UV (248 nm) and VIS (532 nm) on Au thin films

The VIS *MONA-LISA* process has also been tested for Au thin films (shown on Fig. S37). An initial UV process of 15 pulses at 500 mJ/cm^2 was followed by a VIS irradiation of 500 pulses at 125 mJ/cm^2 . The results of *MONA-LISA* process are confirmed by the narrower and higher reflectivity observed after the VIS LA, for the case of Au, as well. The inset figure presents the LSPR peaks after background subtraction. The corresponding values for the FWHM are also shown in the inset for comparison.

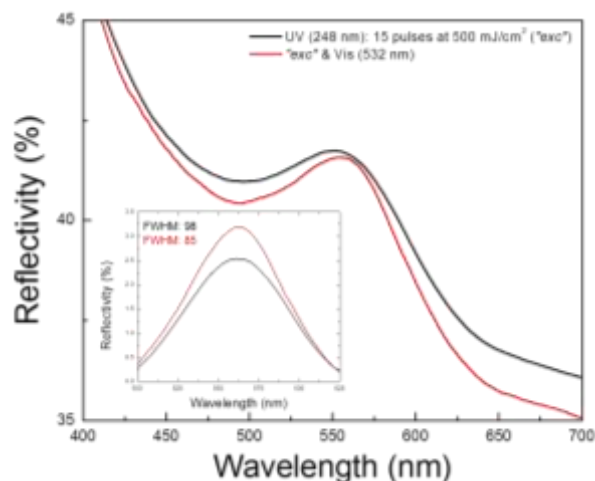


Figure S37. ORS of Au 5nm thin film fabricated by magnetron sputtering processed with UV LA, 15 pulses at 500 mJ/cm^2 (black line), used as a template for the subsequent VIS LA process, 500 pulses at 125 mJ/cm^2 (red line).

2.3 Combined irradiations of UV (248 nm) and VIS (620 nm) on Ag thin films

The *MONA-LISA* process has been, finally tested with a second VIS wavelength (620 nm). For this particular reason, a Ag thin film (10 nm), initially processed at UV LA (248 nm, 2 pulses at 350 mJ/cm^2), was subsequently processed with VIS LA (620 nm, from OPO) with 100 and 200 pulses at 120 mJ/cm^2 . As shown in Fig. S38 below, a shift towards the processing wavelength and a narrower bandwidth is observed, similar to the case of the 532 nm VIS LA, thus proving the general concept of VIS *MONA LISA*.

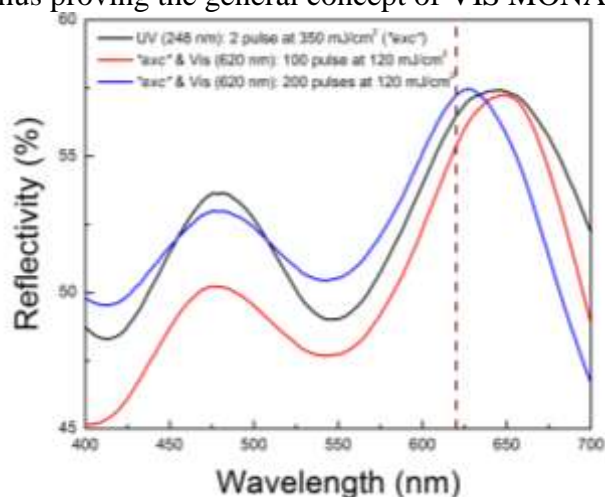


Figure S38. ORS of a Ag (10 nm) thin film fabricated by magnetron sputtering and UV LA, 2 pulses at 350 mJ/cm^2 (black line), used as a template for the subsequent VIS LA process, 100 pulses at 120 mJ/cm^2 (red line) and 200 pulses at 120 mJ/cm^2 (blue line). The dark red dashed

line sets the 620 nm mark. The effect of *MONA-LISA* is confirmed again by shifting the main resonance band towards the processing wavelength.

3. Reproducibility tests

Fig. S39 presents statistical analysis of the LSPR spectral position and LSPR reflectivity percentage for 30 samples produced by identical UV laser annealing conditions on the same Ag (10 nm) coated Si(100) wafer.

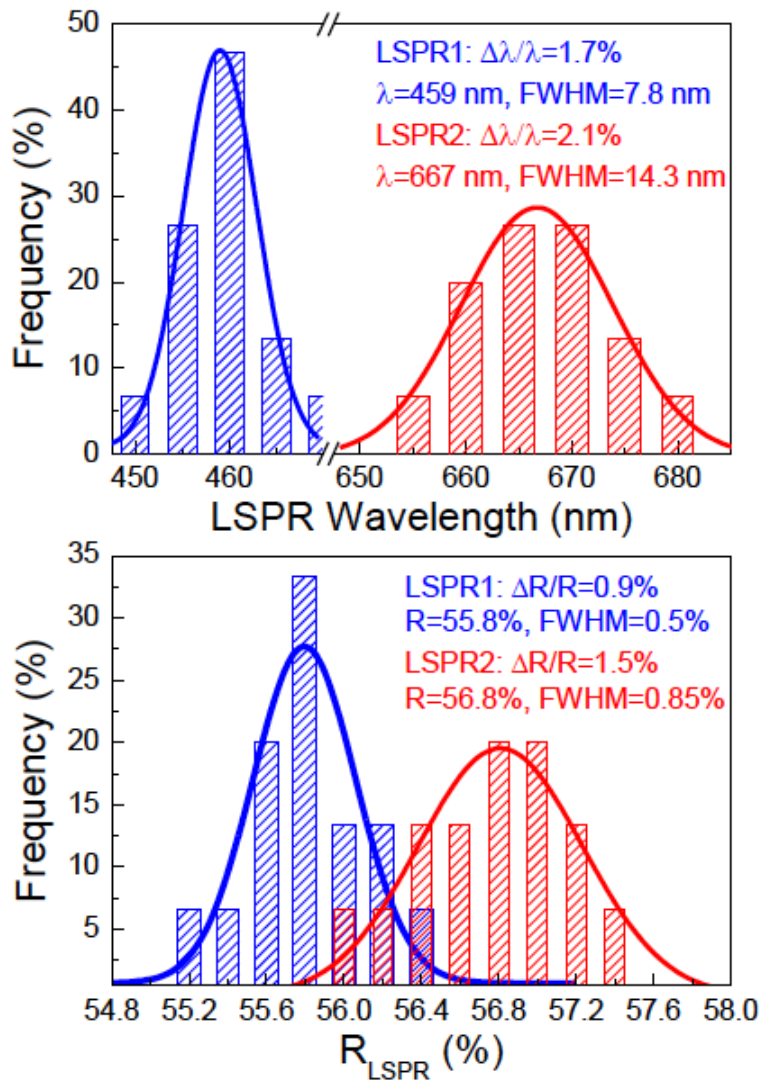


Figure S39. Reproducibility tests regarding the spectral position and reflectivity percentage of LSPR from 30 plasmonic templates produced by UV *MONA-LISA*.

4. Microscopy evaluation

Considering that the high-energy beam used in the SEM experiments (3 keV) could have an impact on the samples' morphology, we present results from an alternative microscopy technique, namely Atomic Force Microscopy (AFM). The AFM measurements were performed with a Dimension FastScan Scanning Probe Microscope (BRUKER). The AFM was placed on an anti-vibrational air stable granite stage housed inside an acoustic enclosure. Tapping mode was utilized for better image acquisition using extra sharp rectangular silicon cantilevers (nominal tip radius: 8 nm), with a constant force of 40 N/m.

Fig. S40c presents results of particle size distributions of the same sample (248 nm UV LA processing: 15 pulses at 650 mJ/cm^2) derived from AFM (Fig. S40a) and SEM (Fig. S40b). The red bars represent the results of the analysis on the SEM image, whereas the black bars represent the results of the analysis on the AFM image. Clearly, a good agreement between the two experimental techniques is observed and therefore we can be confident that the SEM is not altering (“destroying” or “creating”) the morphology of the nanoparticles as created by the LA processes. In addition to that, we present in Fig. S40d a SEM image captured immediately after zooming out of the area of interest, where it is also clearly shown that the particle sizes within the darker box are identical to those in the surrounding areas. All these results suggest that the produced nanoparticle arrays are not harmed by either the mechanical forces applied by the AFM tip during measurement, neither by the high energy electron beam used in SEM.

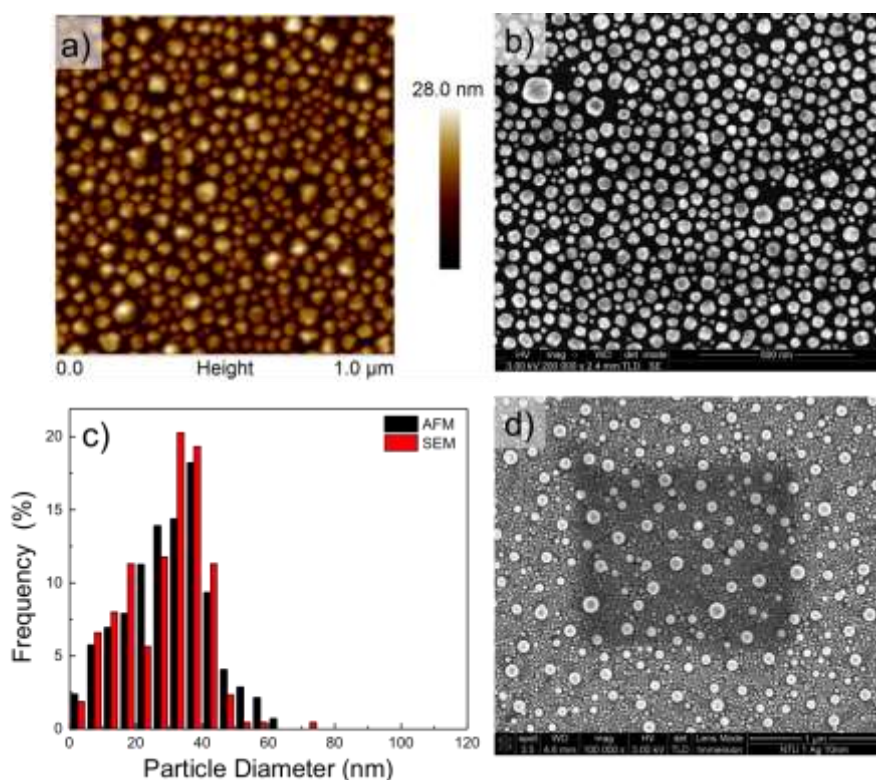


Figure S40. (a) AFM image of sample processed with a 248 nm UV LA (15 pulses at 650 mJ/cm^2), (b) SEM image of the same sample, (c) particle size distributions from AFM imaging (black bars) and SEM imaging (red bars) showing good agreement between the two experimental characterisation techniques, (d) SEM image captured immediately after zooming out from the area of interest showing that SEM does not alter the samples' surface morphology.

5. Details of the Excimer Laser Annealing experimental set up

UV Laser Annealing (LA) was carried out with an Excimer laser (LAMBDA PHYSIK LPX 305i) which is capable of delivering unpolarized light (pulse length of 25ns) and up to 1200 mJ/pulse at 248nm (KrF) or up to 600mJ/pulse at 193 nm (ArF). The raw beam is approximately 30mm x 15mm with a Gaussian like profile on the long axis and an almost top-hat profile on the short axis. The beam delivery system consists of a variable attenuator, a beam homogeniser and a mask-projection system. The variable attenuator employs a partially reflective first plate that can be angled, at various positions, reflecting more or less of the laser beam and a second plate that compensates for the parallel displacement of the beam caused by the first plate. The attenuator has a variable throughput from 0% up to 90% of the original beam. The beam homogenizer (Exitech Ltd., type EX-HS-700D) employs a pair of cylindrical lenses that expand the short axis of the beam to match the entrance aperture of the lens arrays to follow. The lens arrays consist of 64 separately closed pack spherical lenses mounted tightly together. The first array segments the input beam into 64 separate beamlets, each of which is focused and then re-expanded to intercept its corresponding lenslet of the second array. A condenser lens is placed immediately after the second lens array in order to intersect all the beamlets on the optical axis at the homogenizer output plane. As a result each beamlet is expanded and caused to overlap at the homogenizer output plane, providing a laser spot of predetermined size (13 mm x 13 mm), at a predetermined distance from the condenser lens and with top-hat profiles on both axes (better than 2% uniformity). This homogenized beam was arranged to coincide with a mask, which was then projected onto the sample via a combination of a field lens and a projection lens. A X-Y-Z stage was used in order to manipulate the sample and laser process different areas on it. The laser spot delivered onto the samples was set, by an appropriate mask and projection lenses, to be a $2.5 \times 2.5 \text{ mm}^2$ spot.

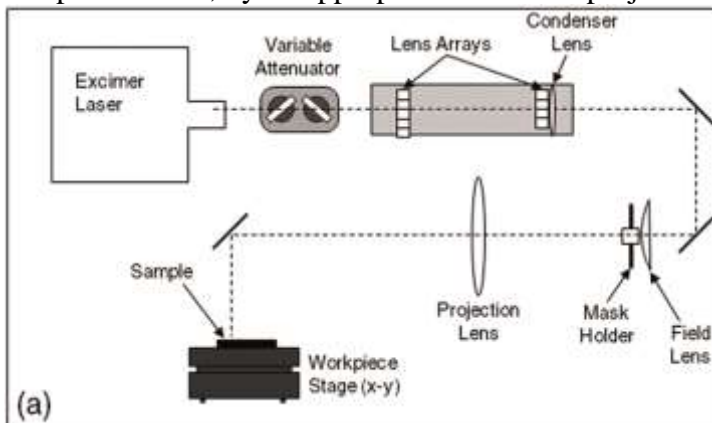


Figure S41. Schematic of the excimer laser annealing apparatus and optics.