Three-Dimensional Self-Organization in Nanocomposite Layered Systems by Ultrafast Laser Pulses

Supplementary information

Zeming Liu¹, Jan Siegel²*, Mario Garcia-Lechuga², Thierry Epicier³, Yaya Lefkir¹, Stéphanie Reynaud⁴, Matthieu Bugnet³, Francis Vocanson¹, Javier Solís², Guy Vitrant⁴, Nathalie Destouches¹*

¹ Univ Lyon, UJM-Saint-Etienne, CNRS, Institut d Optique Graduate School, Laboratoire Hubert Curien UMR 5516, F-42023, SAINT-ETIENNE, France,
² Laser Processing Group, Instituto de Optica, Serrano 121, 28006 Madrid, Spain
³ MATEIS, umr CNRS 5510, University of Lyon, INSA Lyon, University Lyon I, Villeurbanne, FRANCE
⁴ IMEP-LAHC, Minatec, Grenoble-INP, CNRS-UMR 5130, F-38016 Grenoble, France

*e-mail: nathalie.destouches@univ-st-etienne.fr; j.siegel@io.cfmac.csic.es

2D self-organized nanocomposite film.

At higher magnification, SEM micrographs (Figure S1b) of structure HS show that the observed periodic contrast is caused to a certain extend by a local collapse (closure of pores at the top surface) of the initial mesoporosity of the TiO₂ film (Figure S1a). High angle annular dark field scanning transmission electron microscopy (HAADF STEM) images (Figure 2a of the main article) show that Ag NPs buried within the film selectively grow from about 1.5 nm (initial average NP size accurately characterized in two of our recent papers¹²) up to 20 nm in the regions where the TiO₂ mesoporosity has collapsed (Fig. S1c). Atomic force microscopy (AFM) images (Fig. 2b in the main article) demonstrate that the local collapse has triggered the formation of LIPSS with a height amplitude of around 40 nm and a period of 490 nm, with the grating orientation being perpendicular to the laser polarization. Further in-depth information of structure HS is given by HAADF STEM characterizations of a cross section (Fig. 2c) prepared by focused ion beam (FIB). The latter is extracted perpendicular to the LIPSS orientation, so that the sinusoidal topography can be observed. We can clearly see that the larger NPs are located in the grooves of LIPSS, buried near the TiO₂-air interface, and that the parallel mesoporous lines observed on SEM images correspond to the ridges of LIPSS. Owing to the smooth surface morphology of the TiO₂ film and the remaining mesoporosity on the ridges, one can reasonably conclude that LIPSS are not due to matter ablation but to densification of the TiO₂ film, which results from a collapse of the initial mesostructure and a partial crystallization of the TiO₂ matrix. The film-substrate interface morphology is not affected. The film thickness is found to be smaller than the ~230 nm of the unexposed film, oscillating between 120 and 160 nm. This means that densification of the mesoporous film occurs everywhere, even though it is stronger in the grooves. A 4D STEM imaging technique³ was also implemented on this FIB cross-section to identify and map the different nanocrystals present within the nanostructured film. Figure 2d shows the result of the crystallographic analysis provided by the 4D STEM imaging procedure developed by Gatan (see methods). When recording a conventional STEM image, a nano-diffraction pattern is
captured at each probe position, enabling to reconstruct a crystalline phase map with ~1 nm resolution by applying adequate filters in the Fourier space. Reconstructed anatase TiO\(_2\) nanocrystals and face centered cubic (fcc) Ag NPs were labelled by different colors in the reconstructed bright field TEM image of Figure 2d. The two crystal phases were confirmed by high resolution TEM images (not shown). This 4D STEM analysis confirms that Ag NPs mainly grow in the crescent-shape region below the grooves where the film is denser (shown by a different contrast in STEM image of Figure 2c) and highlights the presence of some TiO\(_2\) nanocrystals in the close vicinity of the grown Ag NPs. Micro-Raman spectra of structure HS (not shown) exhibit only a single low amplitude band at 144 cm\(^{-1}\), where the most prominent E\(_g\) Raman active mode of anatase TiO\(_2\) is expected. This weak signature is coherent with the low amount of crystallized TiO\(_2\) in the film.

Figure S1: HS nanostructure. (a) Top view SEM pictures of the initial mesoporous TiO\(_2\) film and (b) of structure HS. The scale bar in (a-b) is 200 nm. The polarization direction is given by the red double arrow (c) Size histogram of Ag NPs calculated from HAADF STEM top view images. \(N_{\text{np}}\) is the volume concentration of NPs in m\(^{-3}\) and \(\Delta d\) is the bar width in nm.
3D self-organized nanocomposite film.

The average AFM topography profile of structure LS (Fig. S2a) shows that each period on the surface topography is actually split into two, featuring the presence of broad bumps in between the narrow ridges. The amplitude of these LIPSS appears much smaller than the one measured on structure LS, whose average topography profile is reported for comparison in Figure S2a. The size histogram of Fig. 2b shows that large oblate NPs up to 100 nm in diameter are generated in this structure, closer to the film-substrate interface. Electron energy loss spectroscopy (EELS) maps (Fig. S2d) were also recorded at the film-substrate interface on a FIB film cross-section of structure LS, clearly identifying the bright regions of the HAADF STEM images as Ag NPs. Small NPs are present in between the lines formed by larger NPs, at the same depth as the larger ones, close to the film-substrate interface. The thickness of the TiO$_2$ film has also decreased and is now 90 nm ± 10 nm. Raman spectra exhibit the same kind of low amplitude band at 144 cm$^{-1}$, characteristic of a low amount of crystallized TiO$_2$ in the film.

Figure S2: LS nanostructures. (a) Average topography profile of structures LS (red) and HS (blue) calculated from AFM topography. (b) NP size histogram determined from top view HAADF STEM micrographs. (c) The same HAADF STEM micrograph of the sample cross-section than in Figure 3c of the main article. (d) STEM-EELS maps of a small area located near the film-substrate interface (as indicated by the white dashed rectangle in (c)) showing separately the annular dark field (ADF) and Ag, Si, Ti signals.
Laser-induced temperature rise.

The partial collapse of the film mesostructure and the formation of TiO$_2$ nanocrystals in the two structures are both signatures of the temperature rise that occurs very locally in the film. According to literature, nanocrystallization of TiO$_2$ in our Ag doped films is expected to occur between 350°C and 450°C,$^4$ indicating that in our case a similar temperature rise is reached locally around metallic nanoparticles. Since TiO$_2$ is transparent at the laser wavelength, only silver NPs act as absorbers and cause heating through their LSPR. Absorption depends non-linearly on the NPs size and environment, dynamically changing in the course of the NP growth and self-organization. In order to consider the role of multiphoton absorption in TiO$_2$ as a possible contribution to the temperature rise we have performed experiments on mesoporous TiO$_2$ films without silver, at 10 times higher fluences. No change to the film was observed meaning that such an absorption is negligible. However, the possibility of nearfield-mediated multiphoton absorption in Ag:TiO$_2$ samples cannot be ruled out and will be considered as a possible mechanism for electron excitation. Indeed, the field intensity of the plasmon-induced optical near-field in the close vicinity of Ag NPs can be a factor 10000 times higher than that of the incident light.$^5$

REFERENCES


