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Physical phenomena ruling the optical creation of gold nanoparticles, by multi-photon photoreduction

T. Ritacco[1,2], P. Pagliusi[1,2] and M. Giocondo[1]

[1] Consiglio Nazionale delle Ricerche, Istituto di Nanotecnologia - Nanotec, SS di Cosenza Ponte Pietro Bucci Cubo 31/C, 87036 Rende (CS), Italy
[2] Università della Calabria - Dipartimento di Fisica Ponte Pietro Bucci Cubo 31/C 87036 Rende (CS), Italy

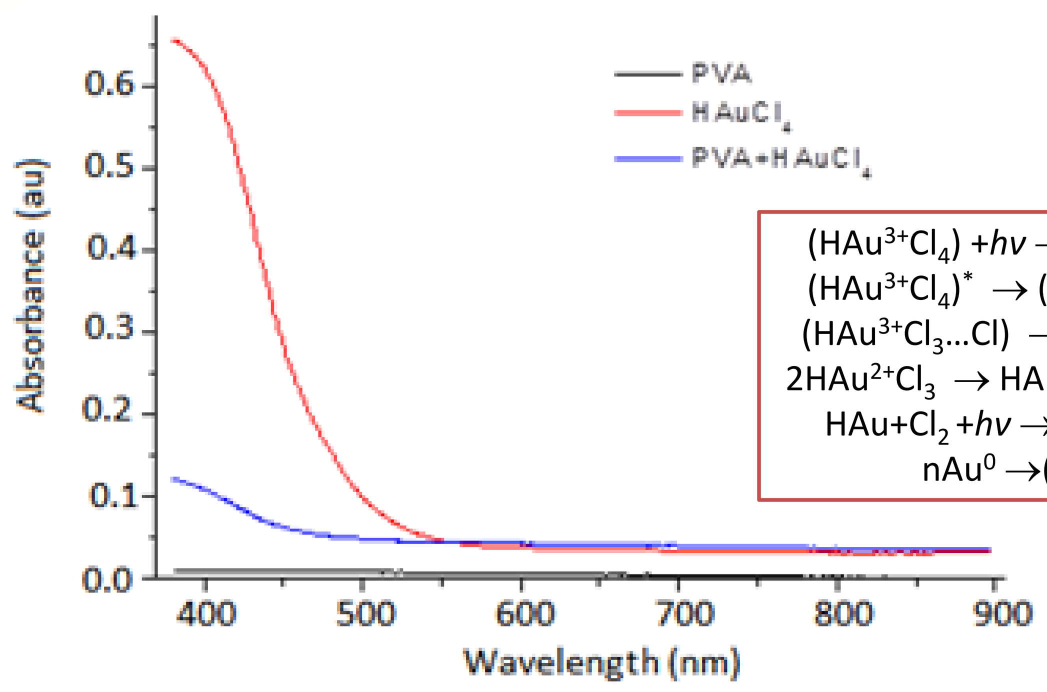
Consiglio Nazionale Ricerche

CNR NANOTEC INSTITUTE OF NANOTECHNOLOGY

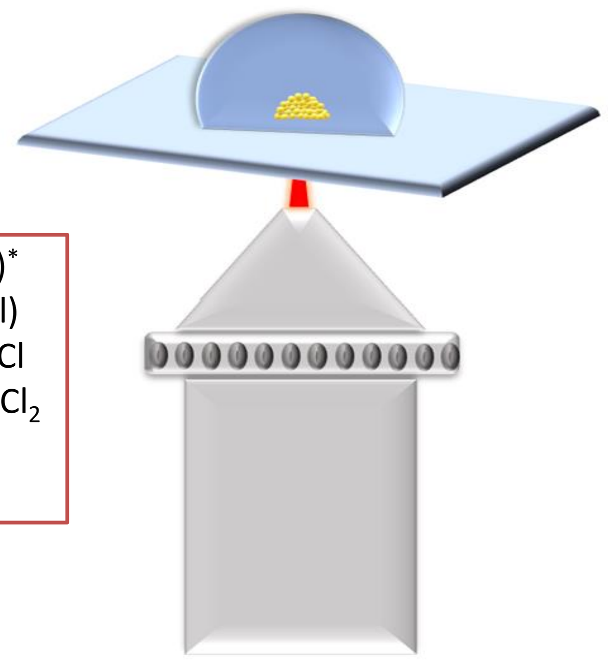
Abstract

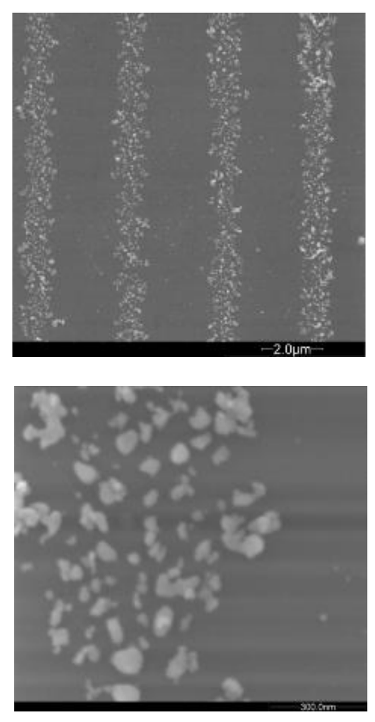
Additive Manufacturing refers to a group of technologies that build physical objects directly from 3D Computer-Aided Design (CAD) data. In the field of nanotechnologies Multi-Photon Direct Laser Writing (MP-DLW) is the most advanced optical technique for creating arbitrarily complex 3D materials featuring details well below the diffraction limit, in organic resists. [1-3] The possibility to include metallic details or even to create metallic structures would pave the way for the fabrication of metallic/polymeric nanocomposites for advanced optics, plasmonics, thermo-plasmonics and sensing.[4-7]
Here we report about the study on the physical features of gold nano-particles created by MP-DLW in a polymeric matrix, doped with a suitable metallic precursor.
Our experiments are performed in a free surface drop cast or cell segregated thin film onto a glass substrate, in which we create 1D gratings made by stripes of gold nanoparticles (GNPs) with single or multiple laser sweep.[8-10] We also analyze the influence of the exposure time over the created nano-particles size distribution and density and we show that by suitably adjusting the exposure time it is possible to maximize the frequency of a given diameter.
Finally, we point out the key-role of thermal and diffusive processes. In particular, the localized photoreduction is the cause of the concentration gradient of the gold precursor; while, at the same time, the local temperature increase during MP-DLW generates the dehydration of the polymeric matrix. We demonstrate that, since these phenomena are characterized by different timescales, it is possible to control the size and density of GNPs by delivering the energy dose in multiply shots.

MP Photoreduction

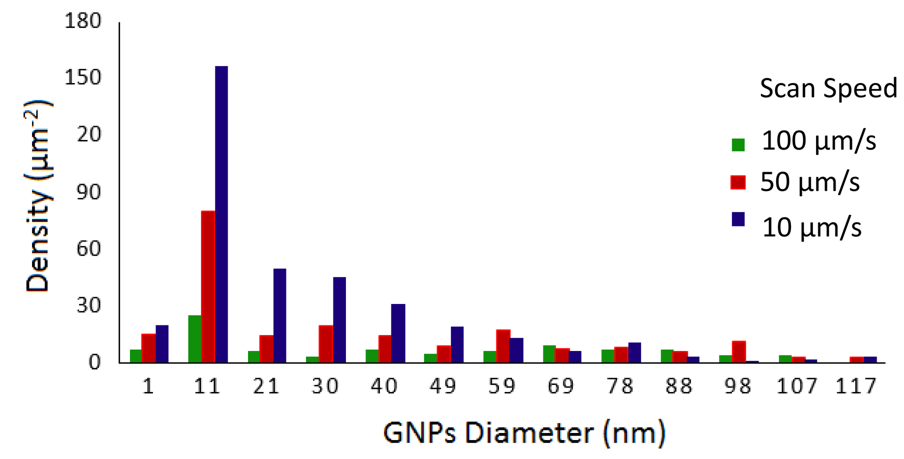


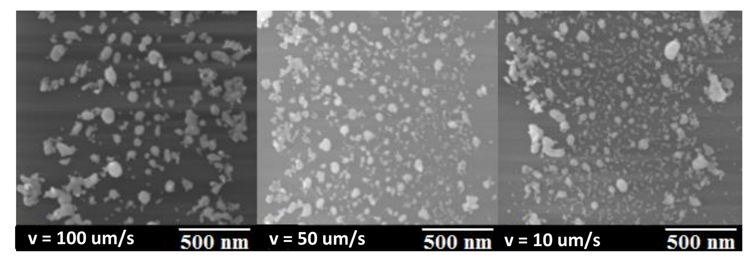
$$(HAu^{3+}Cl_4) + h\nu \rightarrow (HAu^{3+}Cl_4)^*$$
$$(HAu^{3+}Cl_4)^* \rightarrow (HAu^{2+}Cl_3...Cl)$$
$$(HAu^{3+}Cl_3...Cl) \rightarrow HAu^{2+}Cl_3 + Cl$$
$$2HAu^{2+}Cl_3 \rightarrow HAu^{3+}Cl_4 + HAu^{+}Cl_2$$
$$HAu + Cl_2 + h\nu \rightarrow Au^0 + HCl + Cl$$
$$nAu^0 \rightarrow (Au^0)_n$$



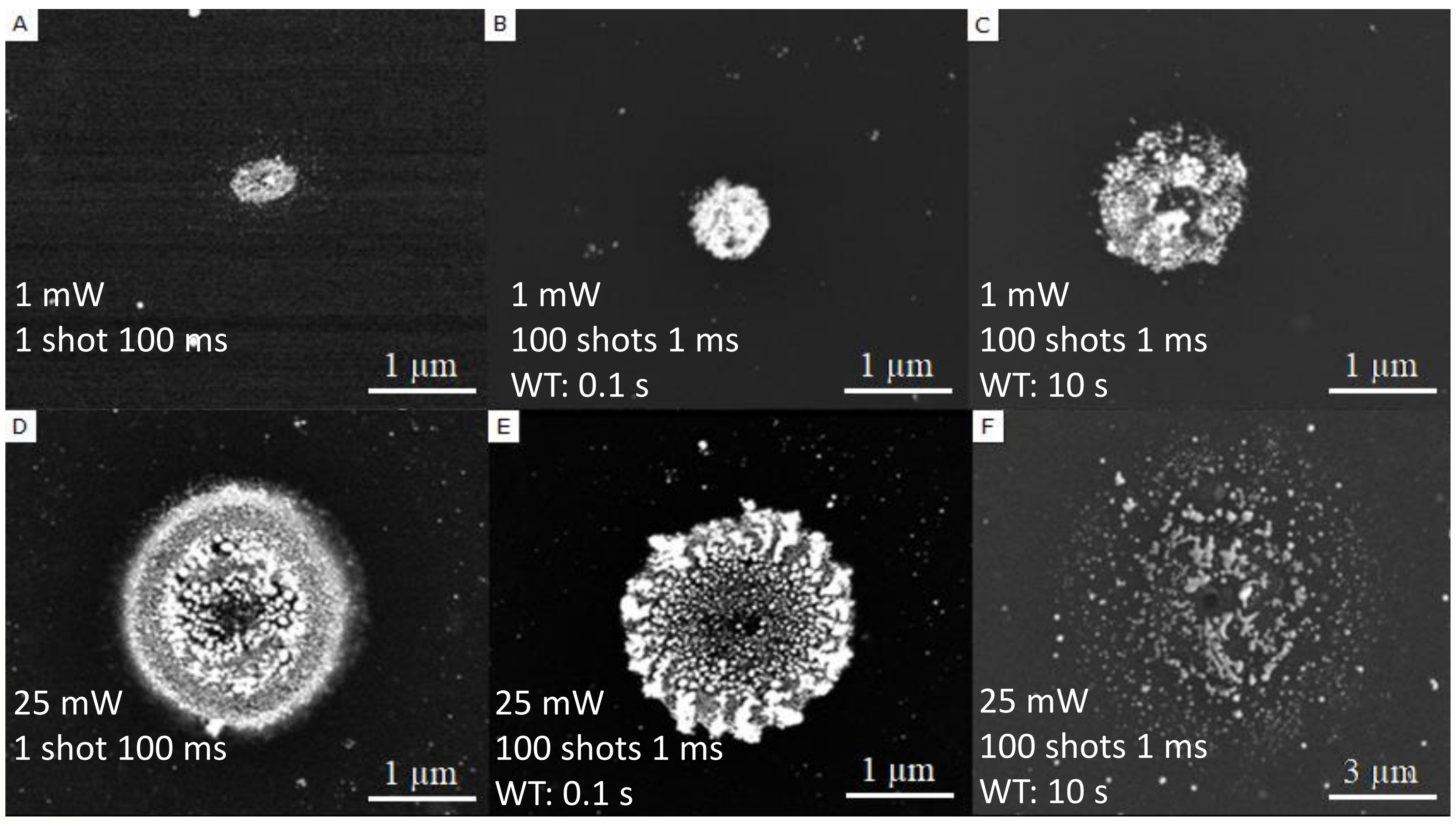


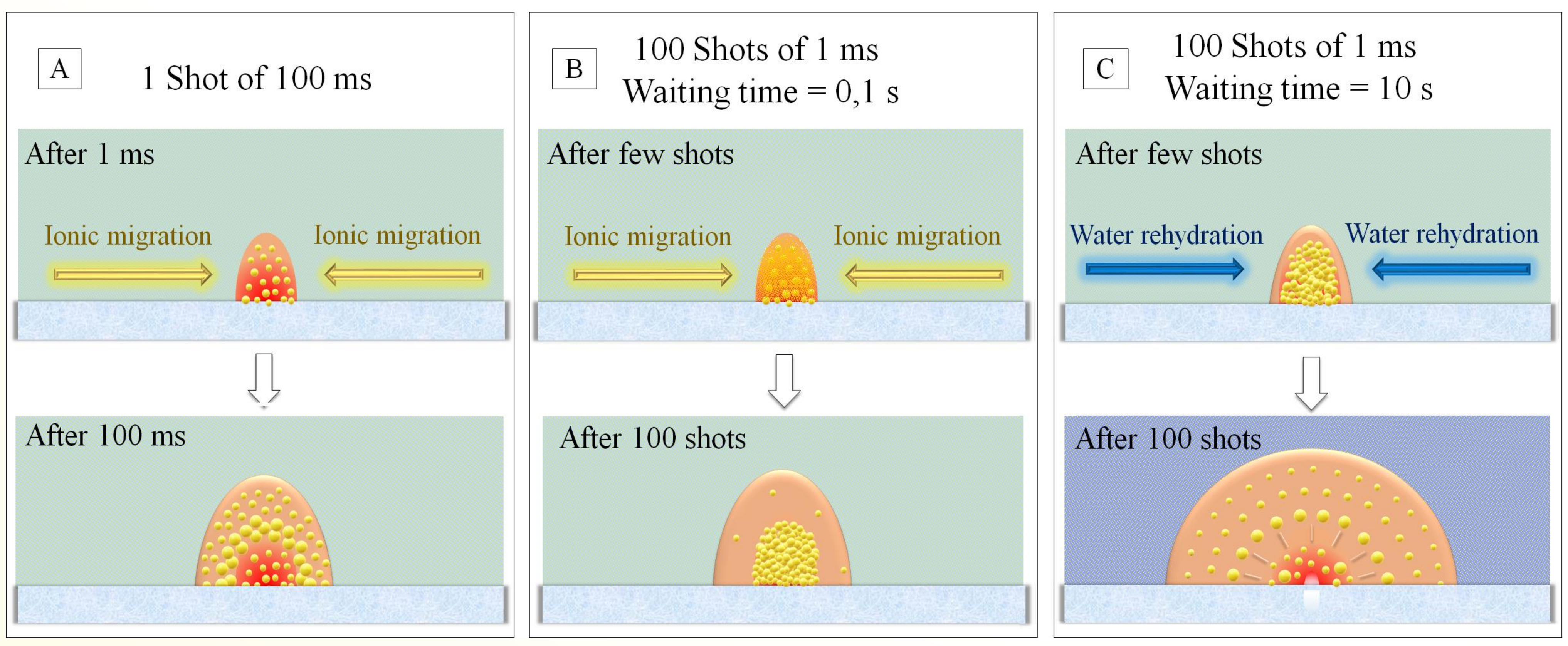
GNPs characterization





Diffusive and Blasting Effects





Conclusions

We studied the physical processes that occur during MP-DLW in polymeric matrices doped with a gold precursor. We observed that sweeping the laser inside the matrix, a stripe rich in gold nanoparticles is obtained. By suitably adjusting the exposure time it is possible to maximize the occurrence of a given diameter.
This result indicates that the local peaks of density define zones where the ionic concentration is higher and hence with higher probability of seeding and faster growing. In these zones the higher ionic and seeds concentration feeds the growth of the larger GNPs at a higher rate. Slower scan speeds are effective in activating seeds in the lower concentration zones, where smaller nanoparticles are grown thanks to the ionic diffusion. Therefore, the ion diffusion plays a key-role in the creation of the GNPs aggregates by MP-DLW. To improve the control on the growth of GNPs, we delivered the energy dose in multiple shots. This method allows the chloroauric ions to diffuse in the voxel during the time between consecutive shots, restoring the initial condition of the system. Tuning the waiting time (WT) between each shot, it is possible to monitor the concentration of gold ions photo-reduced by each fraction of energy, and get a finer control on the density and size of the nanoparticles created. As a consequence, it is possible to obtain denser aggregates of GNPs, with reduced polydispersity.
However, we observe that when the WT is comparable with the water diffusion, the polymeric matrix is rehydrated and a blasting wave originating in the laser focus takes place at each shot, strongly affecting the resulting GNPs spot geometry.
Therefore, we define that to create dense cluster of monodispersed nanoparticles, which find a multiply of application from photonics to sensing, a multi-shot procedure is the best way to work, however the laser power has to be kept to minimum values to avoid an exceeding temperature arising and the waiting time has to be in the order of the ionic diffusion.

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