New strategies for Direct Laser Writing of metallic structures

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Abstract

Direct Laser Writing (DLW) of metallic structures is a promising technique for additive manufacturing of arbitrarily complex objects with nanometric resolution [1]. In the case of gold precursors (tetrachloroauric (III) acid, $HAuCl_4$) this fabrication method is triggered by the Two Photon Absorption (TPA) process [2]. The presence of a polymeric matrix (typically polyvinyl alcohol, PVA) is crucial to keep the gold nanoparticles (AuNPs) at their place, thus preventing their free diffusion. Moreover, since the writing process occurs at the interface of the matrix with the solid substrate, it is mandatory for the last to be optically accessible.
In this study, we used bio-based hydrogel matrices (isinglass, agarose gel) instead of PVA, keeping an eye open on green chemistry. Isinglass has high transparency at the used wavelength for DLW (785 nm). Influence of different substrates (e.g. silicon, glass, silica nanowires) was also tested, evaluating the feasibility of DLW on non-transparent materials. In order to achieve the steady-state ionic concentration, the hydrogel-coated substrate was bathed in an aqueous solution of $HAuCl_4$[3]. Then, different nanostructures (linear and isolated points shapes) were printed: this step is called 'seeding' because the gold precursor acts as a photoresist and the photoreduction is the photopolymerization; the objects are created only where the TPA threshold is reached. After DLW printing, a subsequent bath in deionized water removes the non-reduced gold ions, stopping the NPs growth showing that a control of AuNPs growth kinetics is possible [4]. To better monitor the growth of the AuNPs, we did a second $HAuCl_4$ bath varying two parameters (this step is called "growing"): the duration of the bath and the concentration of the aqueous solution. A control on the ionic concentration led to an important improvement of the created structures quality. This showed that a second bath in $HAuCl_4$ allows to grow the AuNPs printed controllably (Figure 1).
We conclude that the methodology herein developed achieves uniformity of the created structures rich of gold and a good compliance with the geometrical model.

References

[1] H. B. Sun and S. Kawata, "Two-photon laser precision microfabrication and its applications to micro - Nano devices and systems," in *Journal of Lightwave Technology*, 2003

[2] T. Ritacco, L. Ricciardi, M. La Deda, and M. Giocondo, "Controlling the optical creation of gold nanoparticles in a pva matrix by direct laser writing," *J. Eur. Opt. Soc.*, 2016.

[3] K. Kaneko, H. B. Sun, X. M. Duan, and S. Kawata, "Two-photon photoreduction of metallic nanoparticle gratings in a polymer matrix," *Appl. Phys. Lett.*, 2003

[4] M. Röhrig, M. Thiel, M. Worgull, and H. Hölscher, "3D Direct laser writing of nano- and microstructured hierarchical gecko-mimicking surfaces," *Small*, 2012.

Figure

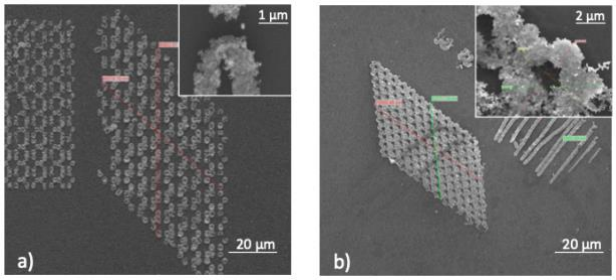

Figure 1. SEM images and their magnifications of AuNPs fabricated a) by DLW and b) after subsequent immersion in a bath of 10^{-2}M concentration $HAuCl_4$ for 24 hours.