Photoreduction: new strategies for Additive Manufacturing

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Abstract
In the industry 4.0 framework, Additive Manufacturing (AM) together with 3D printing techniques have emerged as promising processing methods and caught the attention of research investment especially for nanotechnology applications.
The DLW is an Additive Manufacturing (AM) technique for micro and nano-fabrication and here we're going to analyze a particular novel technique that allows to realize metallic structures onto solid substrates at the sub-micron scale: the two-photon photo-reduction of photosensitive metallic precursors.
Infact Additive Manufacturing combined with the Two Photon Absorption process allowed to create 3D-complex objects taking advantage of the photo reduction of the gold precursor (tetrachloroauric acid, HAuCl4) and the femtosecond pulsed NIR Erbium laser (λ = 780 nm).
A comparison with another AM technology as the stereolithography (SLA) could be, it will be interesting to test peculiarity and features of the various techniques and to choose the most efficient, easy and rapid one. In this case a different substrate (acrylic resin) is used to obtain nanostructures (AuNPs) onto it.
We pointed out the importance of the diffusive process for the created nanoparticles (NPs) growth and the necessity to have a polymeric network (polyvinyl alcohol, PVA) in order to "held" the NPs at their place, thus preventing their free diffusion. As the writing process occurs at the interface with the solid substrate, it is mandatory for the last to be optically accessible. In this new study, we preferred natural hydrogel matrices (isinglass, agarose gel), compared to PVA, keeping an eye open on the green chemistry and featuring a good transparency at the used wavelength. Moreover, a better control on the ionic concentration led to an important improvement of the created structures quality (Figure 1).

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FIGURES

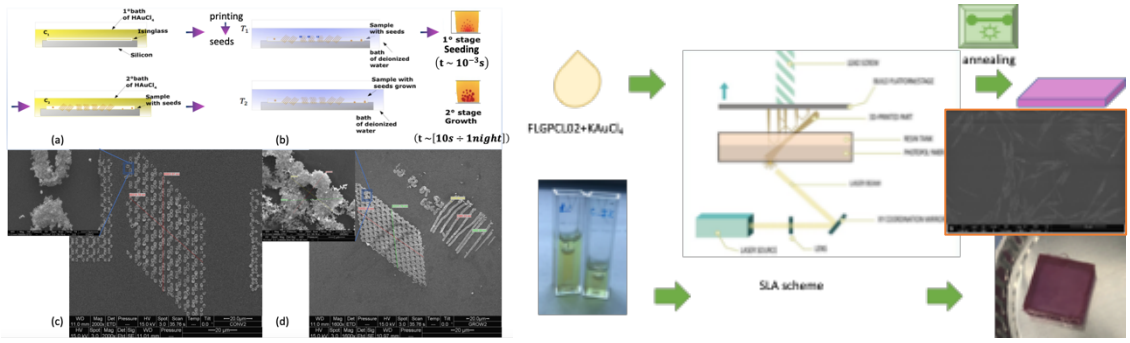

Figure 1: (a) A sketch of the of the experiment: the first bath in HAuCl4 of the silicon substrate after the spin-coating deposition of the isinglass on it and the second bath in the gold precursor to control the growth (size of GNPs: 40÷70 nm); (b) the subsequent deionized water baths to remove chloroauric ions and to stop the growth respectively. SEM images and their magnifications of some points nanostructures before (c) and after (d) the growth. On the right the scheme of the SLA technique and a SEM image of the gold NPs created inside the resin.