2020 NANOPORTUGAL CONFERENCE ONLINE

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PHOTOREDUCTION: NEW STRATEGIES FOR ADDITIVE MANUFACTURING

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Introduction

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.

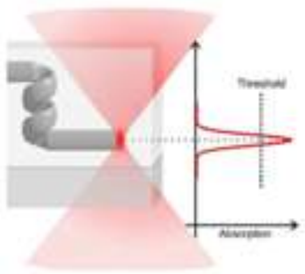
The Direct Laser Writing (DLW) is an Additive Manufacturing (AM) technique for micro and nano-fabrication and here is presented a particular novel method that allows to realize metallic structures onto solid substrates at the sub-micron scale: the two-photon photo-reduction of photosensitive metallic precursors. The Two Photon Absorption (TPA) process triggers this fabrication method, and using an Au precursor and a polymeric matrix a specific protocol is defined to create Au NPs clusters with a fine-tuning of ionic density inside the network.

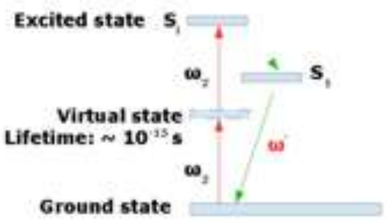
A comparison with another AM technology as the stereolithography (SLA), it will be interesting to test peculiarity and features of the various techniques and to choose the most efficient, easy and rapid one. In this case a different substrate (acrylic resin) is used to obtain nanostructures onto it.

Natural hydrogel matrices are preferred, 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.

TWO PHOTON ABSORPTION PROCESS (TPA)

- NIR laser *(780 nm)*
- Polymeric matrix *(isinglass, agarose gel)*

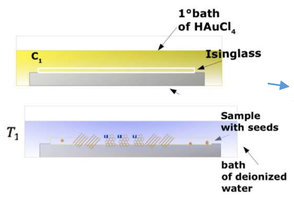


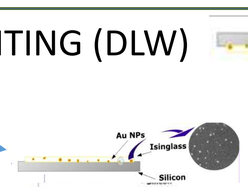


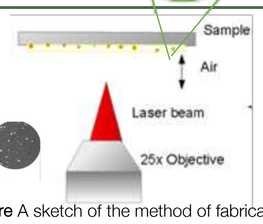
M. Göppert-Mayer, "Elementary processes with two quantum transitions," Ann. der Phys., 2009.

TP-DLW system

DIRECT LASER WRITING (DLW)







▲ **Fabrication procedure** A sketch of the method of fabricating nanocomposites by *TP-DLW*. a) A silicon substrate, with a thin film of hydrogel deposited on it, is bathed in a tetrachloroauric acid aqueous solution until the achieving of the steady-state ionic concentration between the hydrogel film and the bath. b) A near-infrared femtosecond laser beam (red) is focused into the voxel and the gold precursor is reduced. Nanoparticles are formed, complex 2D and 3D structures are fabricated by scanning the laser in two and three dimensions. c) Then, as last step, the deionized water bath is used to stop the growth of the NPs.

PHOTOREDUCTION

gold precursor → gold NPs *($KAuCl_4$/$HAuCl_4$)*

$$(Au^{3+}Cl_4)^- + h\nu \rightarrow (Au^{3+}Cl_4^-)^*$$

$$(Au^{3+}Cl_4^-)^* \rightarrow (Au^{2+}Cl_3^- \dots Cl)$$

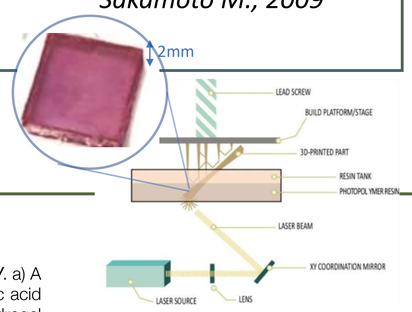
$$(Au^{3+}Cl_3^- \dots Cl) \rightarrow (Au^{2+}Cl_3)^- + Cl$$

$$2(Au^{2+}Cl_3)^- \rightarrow (Au^{3+}Cl_4)^- + (Au^{+}Cl_2)^-$$

$$(Au^{+}Cl_2)^- + h\nu \rightarrow Au^0 + Cl^- + Cl^0$$

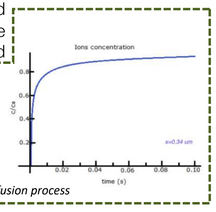
$$nAu^0 \rightarrow (Au^0)_n$$

Sakamoto M., 2009



$$\frac{dc(x,y,z,t)}{dt} = D_{ion}\nabla^2 c(x,y,z,t)$$

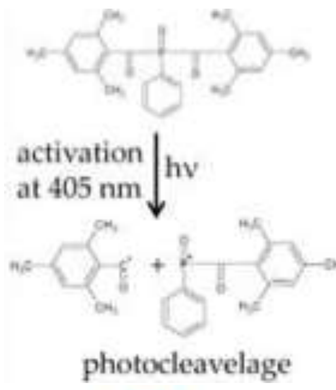
$$c(r,t) = c_0\left(1 - \mathrm{erf}\left(\frac{r}{4D_{ion}t}\right)\right)$$



The *second Fick's law that rules the diffusion process*

PHOTOPOLYMERIZATION

- photo-induced cross-linking
- acrylic resin *(FLGPCL02)*



Taormina G., 2018

STEREOLITHOGRAPHY (SLA)

◀ **Fabrication procedure** A sketch of the method of fabricating nanocomposites by SLA. A system of lens and mirrors to focus the UV-light (λ = 405 nm) from the laser. The light heats the resin tank where the photopolymer resin mixed with the gold precursor is contained. Photopolymerization and photoreduction are activated.

▲ **Fabrication procedure** Other fundamental elements of the process. The sonication, useful to have an homogeneous mixture of the resin and the gold precursor. The annealing in the UV-oven, it allows to complete the polymerization process.

Experimental Details

The *TPA* is a threshold non-linear optical process, whose cross-section depends on the square of the intensity of the laser beam (NIR femtosecond laser → λ = 780 nm).

When the ultrafast near infrared (NIR) laser is focused on a UV-sensitive resin or a photosensitive material, polymerization is activated only in a very small volume inside the focus of the laser beam (volume-pixel → «voxel»). A resolution below hundred nanometers is achieved for the nanostructures.

The *photoreduction* is the result of photo induced chemical reactions, infact in the first case TPA with the gold precursor optically synthetizes gold nanoparticles (GNPs). In the second case (SLA) activates the cross-linking with the photosensitive resin.

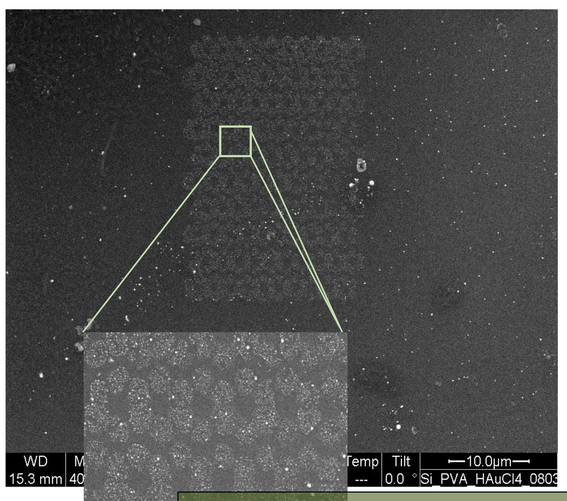
The *photopolymerization* with SLA works with UV light (λ = 405 nm). Composites are formed when two or more monolithic materials are combined such that a stronger and rigid reinforcement phase is dispersed in a weaker continuous phase, referred to as the matrix.

Results

Isolated point structures

Creation of high quality structures rich in gold NPs is made.The samples are then characterized by Scanning Electron (SEM) and Atomic Force (AFM) Microscopy. Printing parameters have been optimized.

SEM characterization



Isolated points structures: "pulsed mode"; exposure time (ET) and laser power (LP) are the printing parameters

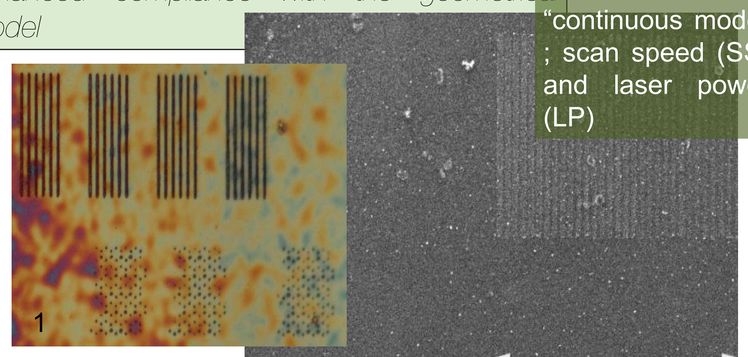
SEM ▲

SEM images of the created structures with various shapes on the silicon substrate, in particular an isolated points shape structure and a magnification of it.

Linear structures

Dosing delivered energy with LP to prevent damaging, burnt or swelling structures and clustering of GNPs. Unpreceded uniformity and enhanced compliance with the geometrical model

linear structures: "continuous mode"; scan speed (SS) and laser power (LP)

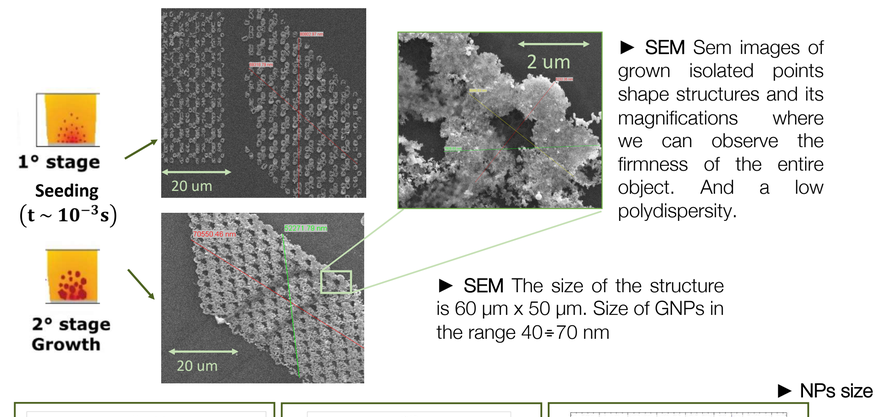


► SEM and optical microscope SEM image of a linear shape structure and optical microscope images (1,2,3) of the isolated points structures and linear structures obtained with LP=80 (1,2),

and the same image between crossed polarizers (2). The same isolated points patterns (3) obtained with LP=100.

Seeds Growth and NPs size

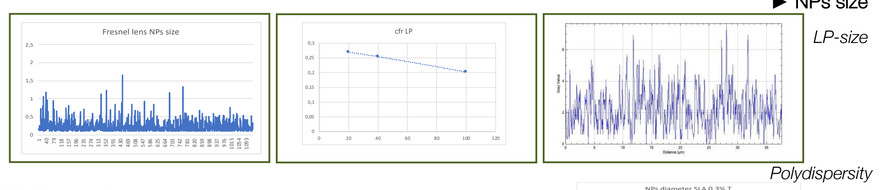
Another $HAuCl_4$ bath could be done to let the seeds grow acting on two parameters: the duration of the bath and the concentration of the aqueous solution. Improvement of quality of created structures, rich of gold. NPs size analysis is done for both the procedures.



► SEM Sem images of grown isolated points shape structures and its magnifications where we can observe the firmness of the entire object. And a low polydispersity.

► SEM The size of the structure is 60 µm x 50 µm. Size of GNPs in the range 40÷70 nm

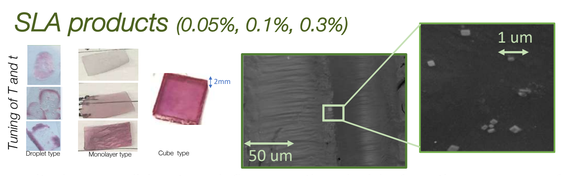
► NPs size

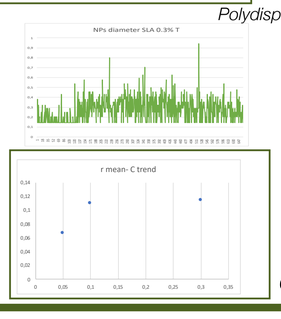


LP-size

Polydispersity

SLA products (0.05%, 0.1%, 0.3%)





C-size

It is possible to define a threshold for the range of concentration that doesn't inhibit polymerization [0.05%-0.3% $KAuCl_4$]. Analysis of the size of the NPs is done → they decrease in size with lower concentration.

► NPs size

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