Reproducible growth of gold nanoparticle arrays by laser irradiation

Matteo Tonelli and Hicham El Hamzaoui

Gold (I) and (III)-precursor-doped silica matrices enable fast direct writing of reproducible nanoparticle arrays in 2D or 3D depending on the wavelength of the laser used.

Gold nanoparticles (GNPs) have received a great deal of attention over the past few decades due to their interesting properties and potential applications in numerous fields, from catalysis to cancer therapy. Many fascinating possibilities are related to localized surface plasmon resonance (LSPR), which gives rise to intense extinction bands in the visible or near-IR wavelengths, making GNPs attractive for analytical and bioanalytical applications due to their potential as optical markers. When embedded in transparent solid matrices, the nonlinear optical properties of GNPs make them well suited for devices such as ultrafast optical switches, applicable to optical telecommunications, data storage, optical computing, and information processing. Finally, GNPs also exhibit high electric field enhancements at their surfaces, making them extremely useful for spectroscopy: increased Raman signals can be harnessed for SERS (surface-enhanced Raman scattering); IR for SEIRA (surface-enhanced IR absorption spectroscopy); and fluorescence can be used for MEF (metal-enhanced fluorescence spectroscopy).

Whereas a large number of synthetic routes exist to prepare GNPs in the liquid phase with controlled sizes and shapes, their inclusion in solid host matrices is not a trivial task. In our previous work, we obtained this result by impregnating a mesoporous silica monolith with a solution of hydrogen gold chloride and sodium carbonate and then irradiating the samples with a pulsed femtosecond laser operating at 800nm. Unlike other methods, this technique requires no annealing process after irradiation. The GNPs are obtained at room temperature exclusively in those areas scanned by the laser beam, which makes it possible to obtain reproducible GNP microarrays

Figure 1. Top: Gold precursor-doped silica matrix. Bottom: Schematic of the optical setup used for laser irradiation.

Figure 2. Schematic of the experimental setup for laser-induced growth of gold nanoparticle arrays.

(see Figures 1 and 2). GNP clustering after irradiation is prevented by the mesoporous nature of the host matrix. The silica monoliths we prepare in our laboratory, using a sol-gel route followed by annealing at 850°C, present a narrow pore size distribution averaging 5.7nm.

Our current research extends this work by making use of easily synthesizable gold (I) and (III) precursors that lead to GNP formation even when no reducing agent is included within the silica matrix. Moreover, we have shown that, by use of

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these precursors, GNP microarrays can also be obtained with continuous laser sources (CW) with visible (532nm) and UV (266nm) wavelengths.

As our results suggest, the mechanism of gold reduction varies with the wavelength of the laser beam impinging on the sample: it is of thermal nature at 532nm and photochemical when the UV laser is employed. As shown in Table 1, it is possible in both cases to obtain reproducible GNP microarrays, but only when the beam is focused at the surface of the sample. This limitation can be overcome with the pulsed laser at 800nm. In this case, there is no linear light absorption from the matrix, scattering effects are minimized, and gold reduction is due to multiphoton absorption processes. These also occur when the focal point is embedded deep inside the matrix, making 3D micropatterning of GNPs possible.

However, 2D and 3D GNP microarrays would be of little or no use if it were not possible to remove the gold precursors from the host matrix. They might be reduced under intense light exposure, and their chemical stability cannot be guaranteed beyond several months. We have shown that washing the silica host matrix to elute the precursors is possible by immersing the irradiated samples into a fresh solvent solution. This washing affects neither the GNP micropatterning, nor the transparency of the silica monolith. As shown in Figure 3, tests of the thermal resistance of the GNP microarrays reveals that they are stable at least up to 500°C, thus further confirming the outstanding ability of these matrices to prevent GNP aggregation.

In summary, by using focused laser irradiation on sol-gel silica monoliths post-doped with appropriate gold precursors, direct writing of 2D and 3D nanoparticle microarrays has been obtained. The resulting samples are transparent and do not require any subsequent heat treatment. Presently, we are trying to extend this technique to bimetallic nanostructures and to the possibility to use such 2D/3D microstructures for data storage.

The porous nature of the silica host makes it possible to remove unreacted precursor molecules with a simple washing. Once removed, it should be possible to impregnate the matrices

Table 1. Summary of the results obtained during laser irradiation with two different gold precursors. It should be noted that in all cases, gold nanoparticles (GNPs) of red color (indicating that the particles are less than 100nm in diameter) and a distinct localized surface plasmon resonance band were obtained with the gold (I) precursor. CW: Continuous wave.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Pulsed laser 800nm</th>
<th>CW laser 532nm</th>
<th>CW laser 266nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold (I)</td>
<td>3D micropatterning possible</td>
<td>2D micropatterning possible at the surface</td>
<td>2D micropatterning possible at the surface</td>
</tr>
<tr>
<td>Gold (III)</td>
<td>2D micropatterning possible at the surface</td>
<td>2D micropatterning possible at the surface</td>
<td>Large GNPs are formed, darkening of the surface</td>
</tr>
</tbody>
</table>

Figure 2. Array of parallel lines of gold nanoparticles (GNPs).

Figure 3. Optical microscope images of different spots of the GNP grid tested for thermal resistance.
with any other molecule that can penetrate into the pores. In the near future, we aim to study the interactions of these GNP microarrays with fluorophores or quantum dots, which will be deposited inside the matrix.

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Matteo Tonelli received his Erasmus Mundus master’s in advanced spectroscopy in chemistry from the University of Lille, France, and the University of Bologna, Italy (2011). He then joined PhLAM as a PhD candidate to work on laser-assisted techniques for the synthesis of metallic nanoparticles and nanoalloys.

Hicham El Hamzaoui received a PhD in organic chemistry from Bordeaux University (2006). His research interests include organic, inorganic, and hybrid materials. His present research activities in the photonics group at PhLAM focus on the synthesis and characterization of high-purity sol-gel silica-based glasses for optical applications.

References