

## Dip-Pen Nanolithography: “Writing” Molecules, Biological Entities and Nanomaterials at the Nanometer Scale

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New methods for micro- and nanofabrication are essential to scientific progress in many areas of biology, physics, chemistry, and materials science. In 1999, Mirkin’s group introduced a new nanolithographic method called Dip-Pen Nanolithography (DPN).<sup>1</sup> DPN is a direct-write scanning probe-based lithography in which an AFM tip is used to deliver chemical reagents directly to nanoscopic regions of a target substrate. For example, this technique has been used to pattern alkanethiol self-assembled monolayers (SAMs) onto gold surfaces with sub-100 nm resolution and registration. To date, these nanostructures have been used as molecular templates for creating, for example, metal and semiconductor nanostructures, biological nanoarrays (including proteins, DNA, and viruses), and arrays of different nanoscale building blocks (such carbon nanotubes, nanoparticles, etc.).<sup>2,3</sup> Furthermore, DPN has allowed the direct deposition and location of proteins, DNA, polymers and nanoparticles on different surfaces.<sup>4</sup> More recently, we and other groups have transformed this technique from a serial to a massively parallel process through the use of both one- and two-dimensional cantilever arrays.<sup>5</sup> As shown in Figure 1, any desired micro- or nanostructure can be reproduced over an area of 1 cm<sup>2</sup> by using simultaneously an array of 55.000 pens.

Recently, our group has used the direct-write capability of DPN to show that one can fabricate nanoarrays of magnetically active materials, such as ferritin proteins and Mn<sub>12</sub>O<sub>12</sub>-based clusters, at the sub-100 nm scale.<sup>6</sup> Nanoarrays of both materials have been fabricated on different surfaces, such as gold and silicon, by using parallel DPN and characterized by using several techniques, such as TOF-SIMS and FE-SEM. The direct-write capability of DPN is currently being used to direct position such arrays onto μ-SQUID devices. The precisely control on the positioning of such structures on the active areas of the μ-SQUID devices increases the sensitivity of these devices, and allows us to measure and study the magnetic properties of a small and controlled number of such proteins or clusters.

The DPN technique has also been used to directly create nanoarrays of fluorescein onto gold substrates (see Figure 2). Fluorescein is a fluorescent compound with two states featuring different optical properties after protonation/deprotonation. Therefore, its structuration on surfaces offers the possibility to design a surface molecule sensor.<sup>7</sup> The fluorescent properties of the resulting DPN-generated arrays have been investigated by confocal fluorescence microscopy, revealing a fast and a sensitive response to acid/base gas flows.

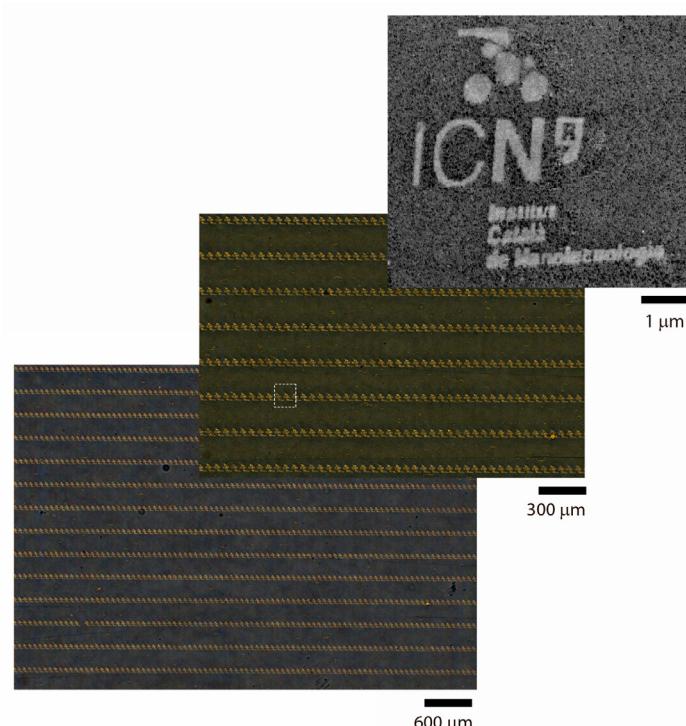
In this contribution, a general overview of the DPN technique, the recent results as well as the recent technological advances will be shown.

### References:

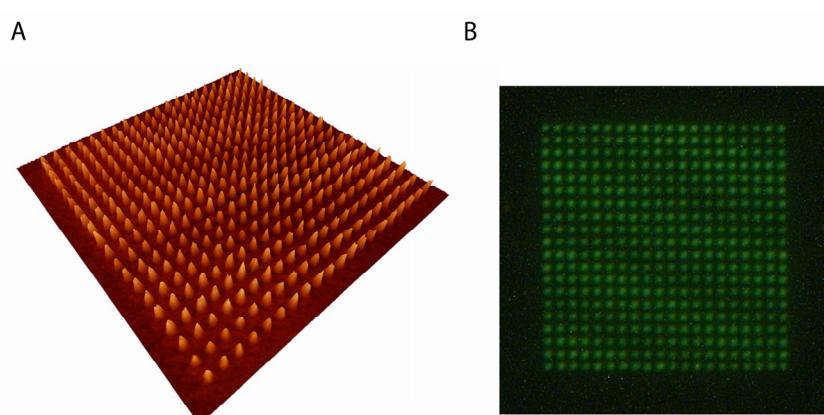
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**Figures:**



**Figure 1.** Optical image of a representative region of the substrate on which approximately 55000 duplicates of the logo of the “Institut Català de Nanotecnologia” have been generated. On top there is a high-resolution SEM image of a representative replica.



**Figure 2.** (A) 3-D AFM tapping mode image of a fluorescein nanoarray on Au surface and (B) the corresponding fluorescence image. The distance between dots is 1 μm.