

Frontiers of Tip-Based Nanofabrication: From DPN and Beyond

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We have been developing tip-based nanofabrication (TBN) protocols for chemically modifying and patterning surfaces with nanoscale resolution. This work stems from our initial efforts with dip-pen nanolithography (DPN). DPN is a lithographic method that uses an atomic force microscope tip as a pen to deliver the ink to the surface by way of capillary transport through a meniscus,¹ and this technique is capable of regularly producing features as small as 40 nm of a wide range of substances including DNA, proteins, viruses, nanoparticles and sols. We are now developing new TBN technologies (Figure 1), specifically polymer pen lithography (PPL), redox-activating DPN (RA-DPN), and scanning probe epitaxy (SPE) based on our initial efforts with DPN. PPL is a cantilever free method that allows one to rapidly pattern molecule-based features with sizes ranging from the nanometer to millimeter scale in a parallel, high throughput, and direct-write manner using elastomeric tips to deliver the ink. Tip arrays with as many as 10^8 tips have been made and can be used in parallel to generate features as small as 90 nm.² RA-DPN involves the modulation of a redox-active quinone surface by the DPN-assisted delivery of an oxidant to change the chemical reactivity of a surface site-specifically, which in turn reacts, in solution with the desired target. RA-DPN has been used to form protein and DNA nanoarrays.³ SPE is the atom-by-atom construction of inorganic nanostructures, including quantum dots, nanowires and carbon nanotubes. In SPE, reactions either occur on a substrate, where reagents are delivered to the substrate from the tip, or in the gas phase, where catalysts on the tip react with the gases, resulting in precisely oriented and positioned nanostructures on the surface. This presentation will report progress and challenges in developing these new TBN methods.

¹R. D. Piner, J. Zhu, F. Xu, S. Hong, C. A. Mirkin, *Science*, **283**, 661 (1999).

²F. Huo; Z. Zheng, G. Zheng, L. R. Giam; H. Zhang, C. A. Mirkin, *Science*, **321**, 1658 (2008).

³A. B. Braunschweig, A. J. Senesi, C. A. Mirkin, *Journal of the American Chemical Society*, *In Press*, DOI: 10.1021/ja809107n

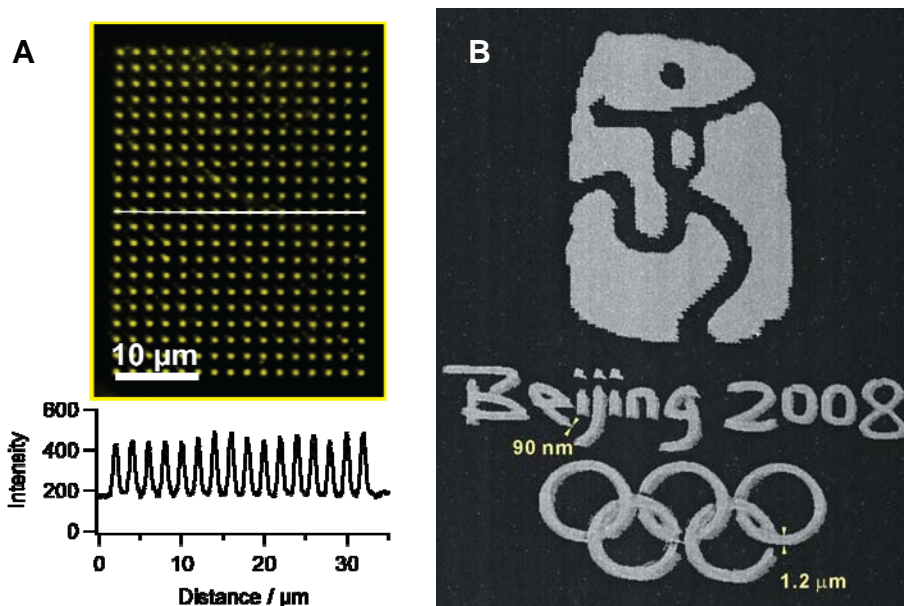


Fig 1: Beyond DPN: (A) A fluorescent DNA nanoarray prepared on a Si(111)/ SiO₂ surface by redox-activating DPN (RA-DPN), and (B) a miniaturized logo of the 2008 Beijing olympics prepared by the polymer pen lithography (PPL) deposition of mercaptohexanoic acid (MHA) on a gold surface, followed by etching of the gold where the MHA had not been deposited.