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Microcontact Printing of Uniform Nanoparticle Arrays

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ABSTRACT

Uniform, close-packed monolayer and bilayer arrays of alkanethiol-coated gold nanoparticles have been used as "ink" for microcontact printing (μCP) following the technique of Xia and Whitesides (see Xia, Y.; Whitesides, G. M. *Polym. Mater. Sci. Eng.* 1997, *77*, 596). The process is accomplished in two steps. First, a uniform monolayer of the nanoparticles is self-assembled on a water surface and is transferred intact to a patterned poly(dimethylsiloxane) (PDMS) stamp pad by the Langmuir–Schaefer (LS) method. In the case of multilayer printing, this "inking" step is repeated as many times as desired. Because multilayer arrays are assembled on the stamp pad layer-by-layer, adjacent layers may be made up of the same or different particles. The nanoparticles are transferred to a solid substrate by conformal contact of the stamp pad and the substrate. The technique has been used to print patterned monolayer and bilayer arrays on both hydrophobic and hydrophilic substrates. The quality of the transferred arrays has been verified optically and by transmission electron microscopy (TEM). This new μCP technique should be applicable to any particles that can be spread as a monolayer on a water surface and promises to be useful for nanofabrication.

Significant progress has been made in the past few years in developing synthesis and purification schemes, particularly solution-phase methods, for producing uniform populations of nanoparticles with controllable size, composition, shape, structure, and surface chemistry.[1] An important challenge that remains is to develop effective ways to self-assemble these nanoscale components into larger structures and systems. Of particular interest is a general method for fabricating patterned, close-packed arrays of nanoparticles on solid substrates.[2] Recently, we have developed a method for self-assembling on a water surface large-area (~1 sq cm), close-packed monolayers of dodecanethiol-coated gold nanoparticles that are free of holes and grain boundaries, and a method for transferring these superlattice arrays intact onto solid substrates using a smooth PDMS stamp pad.[3] Herein we report optical and electron microscopy results showing that, using a molded PDMS pad, it is also possible to print "patterned" monolayer and multilayer arrays of these nanoparticles on flat solid substrates. Recent advances in the development of elastomeric stamps for printing nanoscale patterns[4] suggest that the technique can be extended to form nanoscale patterns as well.

To date, two general techniques have been reported for fabricating patterned arrays of nanoparticles on solid surfaces. These are (1) use of a low energy electron beam to expose portions of a nanoparticle monolayer that acts like a positive resist and then employing a solvent to remove nanoparticles from unexposed areas,[5] and (2) use of a patterned molecular monolayer on the substrate as a template to guide the adsorption of nanoparticles from solution.[6] The first of these techniques can damage the particles and is serial in nature and thus not practical for many applications. The second does not yield high quality, close-packed features. Microcontact printing, which involves transfer of a molecular ink from a patterned elastomeric stamp to the substrate, would overcome both of these drawbacks, if uniform, close-packed arrays of nanoparticles could be used to "ink" the stamp.

Research at Purdue has led to the development of a method for self-assembling large area, close-packed monolayers of gold nanoparticles on a water surface.[3] The technique consists of spreading a thin film of a colloidal solution of alkanethiol-coated gold nanoparticles in an organic solvent on a water surface, which has a controlled convex curvature, and allowing the solvent to evaporate. [Typically, the colloidal solution consists of dodecanethiol (DDT)-encapsulated gold nanoparticles (~5 nm diameter and ~5 $\times$ 10^{13} particles/mL) dissolved in a 50%v mixture of dichloromethane and hexane.] As the solvent evaporates, a close-packed monolayer array of gold nanoparticles nucleates at the raised center of the water surface and grows smoothly outward. The resulting monolayer is a well-ordered, dense, hexagonal array with a center-to-center spacing of approximately 8 nm, which is the sum of the diameter of the gold nanoparticles (~5 nm) and twice the height of a SAM of DDT molecules on gold (~3.2 nm). The key characteristic of the monolayer is that with care it can be formed free of microscopic holes and grain boundaries. These monolayers can be transferred to a hydrophobic substrate by bringing the substrate parallel to the water surface and lightly touching the substrate to the

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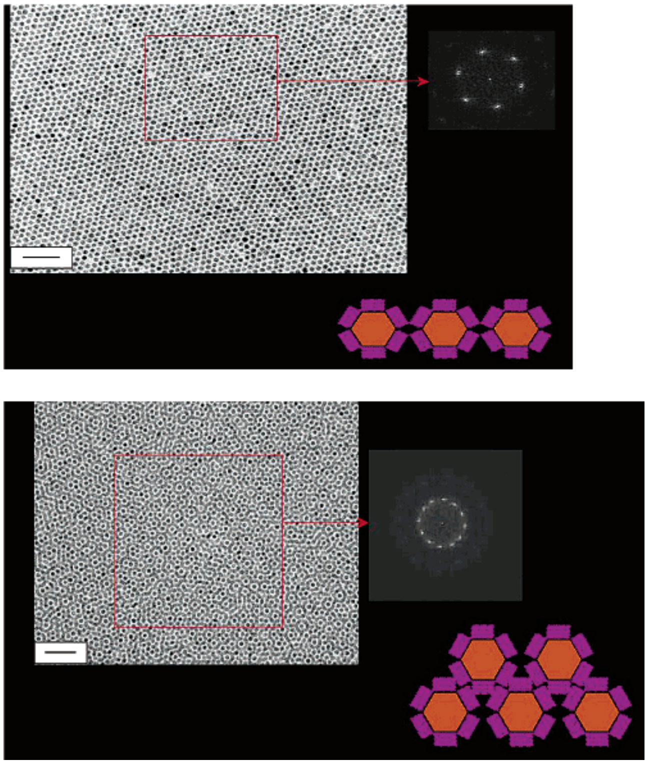

Figure 1. TEM micrographs of monolayer and bilayer films of DDT-coated, 5 nm diameter gold particles supported on thin carbon membranes. The insets are (1) Fourier transforms of selected areas of the films and (2) schematic side views of the film, drawn to indicate how the gold particles pack in each film.

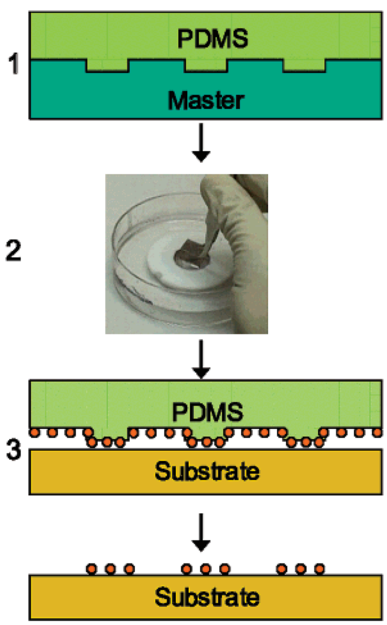

Figure 2. Schematic illustration of the process for forming a patterned nanoparticle array. (Step 1) Fabrication of a patterned PDMS stamp pad by molding on a lithographically produced master. (Step 2) "Inking" the PDMS stamp pad with a nanoparticle monolayer floating on a water surface. (Step 3) Bringing the PDMS stamp pad into conformal contact with a solid substrate for ~10 s. Finally, removal of the PDMS stamp leaves a patterned close-packed array of nanoparticles on the substrate.

nanoparticle film (i.e., Langmuir−Schaefer technique). Figure 1 presents TEM micrographs of a monolayer and a

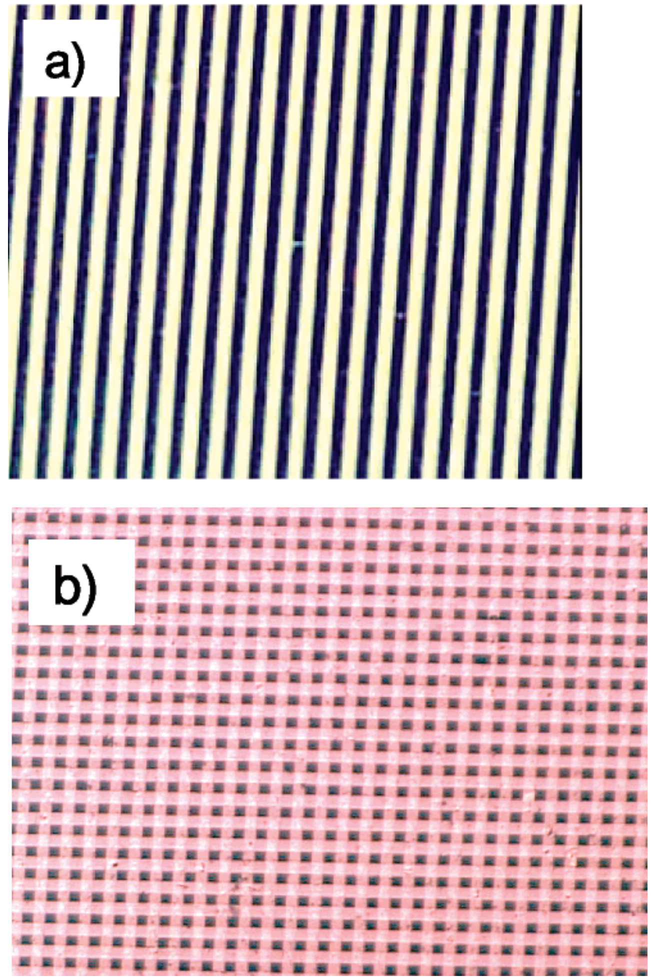

Figure 3. Optical micrographs of patterned arrays fabricated by microcontact printing. (a) Parallel *monolayer* lines. The lines have a width of ~2.5 μm and a spacing of ~3 μm. The arrays appear as the darker areas in this image. (b) Crossed *bilayer* lines formed by printing two sets of parallel lines, one on top of another, after rotating the substrate by 90° between the two printing steps. The line width and spacing are the same as in (a). The arrays appear as the lighter areas in this image.

bilayer (formed by sequentially transferring two monolayers) formed in this manner on a TEM grid coated with a thin amorphous carbon film.

These two micrographs indicate the uniformity of the transferred arrays. The monolayer films are free of multilayer regions and of microscopic voids and grain boundaries over their entire area. The bilayer films consist of two layers of particles (each having approximately the lateral spacing of the monolayer) which are locally rotated to reduce the vertical spacing between the two layers.

Using a two-step procedure in which the nanoparticle monolayer is first lifted from the water surface using a flat PDMS pad and then this pad is brought into conformal contact with the desired substrate, we have found that similar well-ordered, nanoparticle arrays can be transferred intact to both hydrophobic substrates (e.g., polymer films) and hydrophilic substrates (e.g., quartz or silicon coated with a thin SiO_2 layer). These floating nanoparticle monolayers can also be used to "ink" a patterned PDMS stamp pad that is

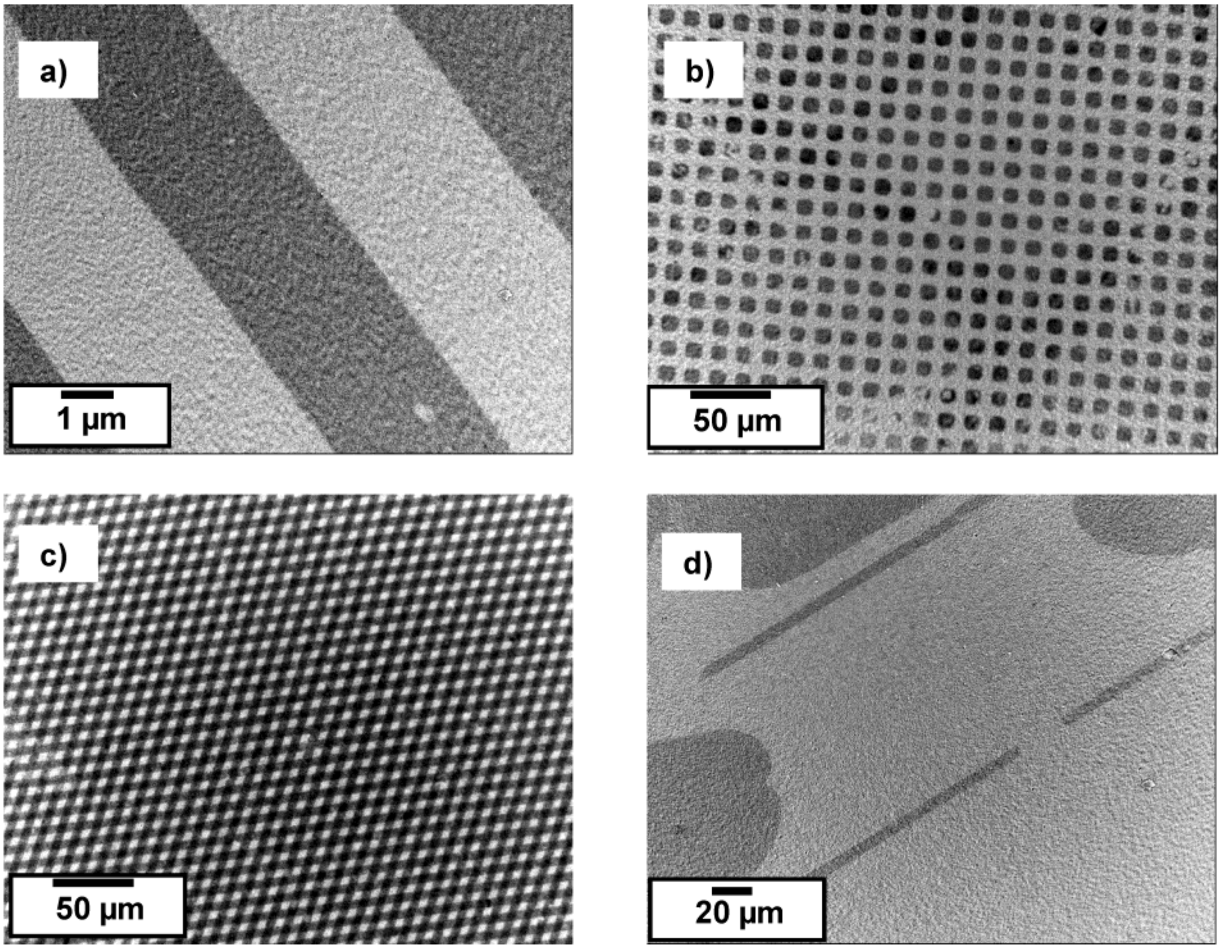

Figure 4. Low magnification TEM images of nanoparticle arrays produced by microcontact printing. The nanoparticle arrays appear darker in these images. (a) Parallel lines. (b) Square pads. (c) Cross-bar pattern produced by printing twice with a parallel line stamp pad with a rotation of the substrate between the two transfers. (d) Parallel lines spaced so that the gap between lines is considerably larger than the height of the features on the PDMS pad (∼1.5 μm).

molded from a lithographically patterned substrate, and this nanoparticle ink can then be used to print a patterned nanoparticle array onto both hydrophilic and hydrophobic substrates by applying a small pressure for ∼10 s to ensure conformal contact of the stamp pad with the substrate. Figure 2 is a schematic description of this process for printing a patterned nanoparticle array.

Steps 1 and 2 can be cycled repeatedly to ink the PDMS stamp pad with a multilayer. This also provides freedom to change the composition of the monolayer formed on the water surface in subsequent cycles, enabling one to control the composition and the number of layers in the nanoparticle array. We find that there is no need for any surface functionalization of the substrate. The transfer is observed to occur on both hydrophobic and hydrophilic substrates and on substrates that are both rough and smooth on the nanoscale, as long as conformal contact is established. The only caveat is that transfer should occur within a few hours of inking the PDMS stamp pad. The nanopartcle ink covers the entire surface of the stamp pad, i.e., both raised and recessed regions. This was observed with an optical microscope and confirmed by the deposit of nanoparticles between two desired features separated by a large gap (compared to the height of the features), due to sagging of the PDMS pad (see Figure 4d).

Figure 3 shows optical micrographs of patterned arrays of DDT-coated, 5 nm diameter gold particles. The arrays were printed on quartz substrates and the micrographs were obtained with an Olympus differential contrast microscope equipped with a CCD camera and a Kodak printer. This figure illustrates the uniformity of the transfer process on the macroscopic scale. Figure 3b suggests that the printed arrays are fairly robust, as they can be printed on top of each other. When scotch tape was applied to the surface of these printed arrays and removed, no damage was apparent.

Nanoparticle arrays were also printed onto 100 nm thick silicon nitride membrane window TEM grids (SPI Supplies) for TEM characterization. Figure 4 shows low magnification TEM images of the patterned arrays produced by this technique. The TEM micrographs were obtained using a JEOL 2000 FX operating at 200 kV. Figure 4a shows a set of parallel lines with a line width of ∼2.5 μm and a spacing of ∼3 μm. This image illustrates the sharpness of the printed lines on the micron length scale. Figure 4b shows a set of squares that are ∼10 μm on a side. Figure 4c shows crossed parallel lines that were formed by printing consecutively from

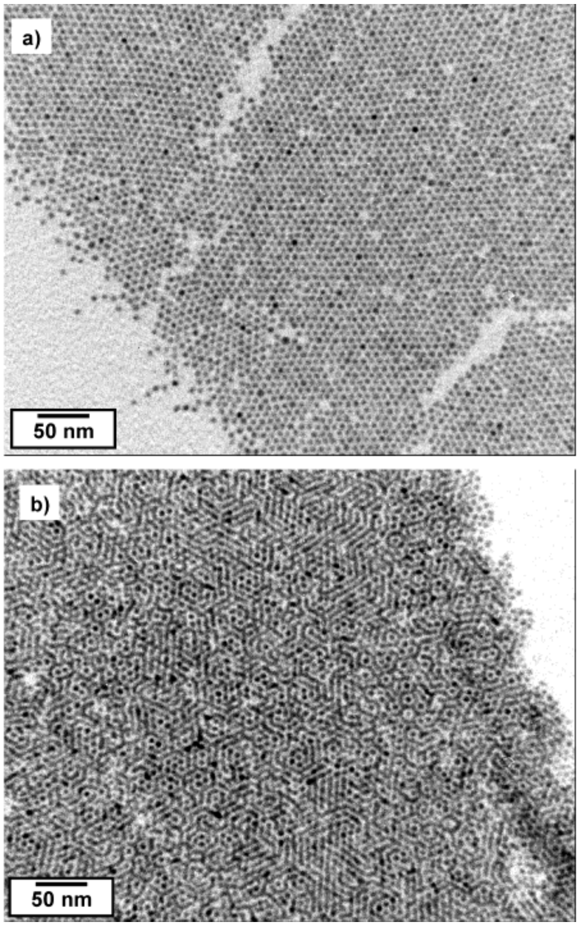

Figure 5. High magnification TEM images taken at the edge of printed lines of gold nanoparticles. (a) Monolayer array. (b) Bilayer array.

two different regions of the parallel line stamp pad and rotating the substrate between the two imprints. Figure 4d illustrates the unwanted deposition of particles between parallel lines $\sim$5 μm in width that are spaced $\sim$120 μm apart.

Figure 5a shows a TEM micrograph taken at the edge of a printed monolayer line. Figure 5b shows the edge of a printed bilayer line formed by successive transfer of two monolayers onto the stamp pad before printing. The mosaic patterns within the bilayer result from local rotation of the second layer with respect to the first layer (see Figure 1). The appearance of nanoscale cracks at the edges of the printed lines is sensitive to the pressure applied during the printing process, which deforms the PDMS stamp. The edge resolution of the stamped patterns is of the order of 20 nm. This edge roughness is not believed to be intrinsic to the technique, as the nanoparticles do not diffuse on the substrate. Edge resolution should be improved by producing stiffer PDMS pads and patterns with sharper edges.

A method for nanofabrication of patterned arrays of gold nanoparticles that is an extension of the standard microcontact printing technique has been demonstrated, wherein a uniform nanoparticle array serves as the "ink" in the printing process. Important factors that need to be considered for accurate transfer of the nanoparticle ink are the pressure applied during printing and the freshness of the ink. It is believed that the new technique can be used to print nanoscale patterns if stamp pads with nanoscale features are used. Patterned gold particle arrays have potential application as nanoscale interconnects for molecular electronics and as patterned substrates for bio-recognition applications. As an example of the latter application, the samples in Figures 3 and 4 represent hydrophobic (DDT coated particles)/hydrophilic (quartz substrate) patterned surfaces.

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