

# Dip-pen lithography using aqueous metal nanocrystal dispersions

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Dip-pen lithography has been successfully demonstrated on mica substrates employing hydrosols of polyvinylpyrrolidone-capped Pd nanocrystals as well as Au nanocrystals stabilized by tetrakis(hydroxymethyl) phosphonium chloride. Lines of widths as small as 30 nm and various aspect ratios have been successfully drawn by this method.

## Introduction

Metal nanocrystals with their ability to self-assemble in one, two and three dimensions are objects of intense research interest today.<sup>1</sup> Mesoscale assemblies of nanocrystals provide important insights into materials properties and a variety of applications seem possible in the area of nanoelectronics.<sup>1–3</sup> A key step in realizing nanodevices involves positioning the nanocrystals at specific locations on a surface.

Several methods have been devised for positioning the nanocrystals in specific patterns. Many of these methods exploit the affinity of nanocrystals to bind to alkanethiol molecules that have previously been set out in the desired pattern using micro-contact printing or other lithographic techniques.<sup>4,5</sup> Nanometric widths, however, are generally not achieved by these methods. Patterns with nanoscopic dimensions have been achieved by atomic force microscopy (AFM) based techniques.<sup>6,7</sup> The so called 'dip-pen' method uses the tip of a scanning cantilever as the 'nib' to deliver 'ink' on to a surface.<sup>8</sup> The inks generally chemically bind to the surface and thereby form stable patterns.<sup>9</sup> The most common inks seek to exploit the ability of long chain alkanethiols to form ordered monolayers of Au surface to create well-defined patterns. The use of bifunctional thiols as inks permits the tethering of colloids, proteins and other macromolecules at specific regions on a surface.<sup>10</sup> Ali *et al.* have reported a dip-pen nanolithography (DPN) based procedure to deposit small volumes of a sol containing Au nanocrystals on a surface, which upon evaporation of the solvent leads to circular nanocrystal patterns.<sup>6</sup> Liu and co-workers have suggested two methods to obtain linear patterns of Au nanocrystals on Au substrates.<sup>7</sup> The first method involves creating trenches in a monolayer of thiols on an Au substrate in a liquid medium containing Au nanocrystals coated with a mixture of mono- and di-thiol molecules. The second method involves direct deposition from an AFM tip, coated with nanocrystals, in trenches created by the same tip at high contact forces. Based on DPN experiments on organic dyes, Su and Dravid<sup>11</sup> have suggested that weak interactions between the substrate and the molecular ink suffice to form DPN patterns, but this proposition has not been sufficiently tested.

In this paper, we report the results of our effort to fabricate patterns of chemically prepared nanocrystals using DPN. We successfully demonstrate that suitable hydrosols of Au and Pd nanocrystals can act as inks, the patterns being stabilized by the weak interaction between a mica substrate and the nanocrystal dispersion. The present findings constitute a relatively simple approach to pattern nanocrystals on surface and broaden the choice of substrates and the nanocrystals available for patterning.

## Experimental

Pd nanocrystals capped with polyvinylpyrrolidone (PVP) were synthesized following the method of Teranishi *et al.*<sup>12–14</sup> In this method, a standard H<sub>2</sub>PdCl<sub>4</sub> solution is reduced with a mixture of ethanol and water by refluxing for three hours. The reaction is carried out in the presence of PVP. Two batches of Pd nanocrystals, both with a PVP:Pd mole ratio of 10 (based on the monomer mass of PVP), were prepared. A standard solution of H<sub>2</sub>PdCl<sub>4</sub> of 2.0 mM was prepared from PdCl<sub>2</sub> and standard HCl solution. 15 ml of standard H<sub>2</sub>PdCl<sub>4</sub> solution was reduced with 35 ml of aqueous alcohol solution of strength 20 and 25% to obtain the two batches of nanocrystals. To the brown-black sols obtained, excess diethylether was added to precipitate the nanocrystals. The precipitate was collected by filtering over a 0.45 μm nylon membrane and redispersed in water. This step ensures the removal of excess capping agent and unreacted ions.

Tetrakis(hydroxymethyl) phosphonium (THP) ion-stabilized Au nanocrystals were prepared by adopting a previously reported procedure.<sup>15</sup> To 1 ml of freshly prepared 50 mM THPC solution was added 47 ml of 6.38 mM NaOH solution and this reducing mixture was allowed to stand for 5 min. The reducing agent was then added rapidly with stirring to 2.0 ml of standard 25.5 mM HAuCl<sub>4</sub> solution. A wine-red sol was thus obtained.

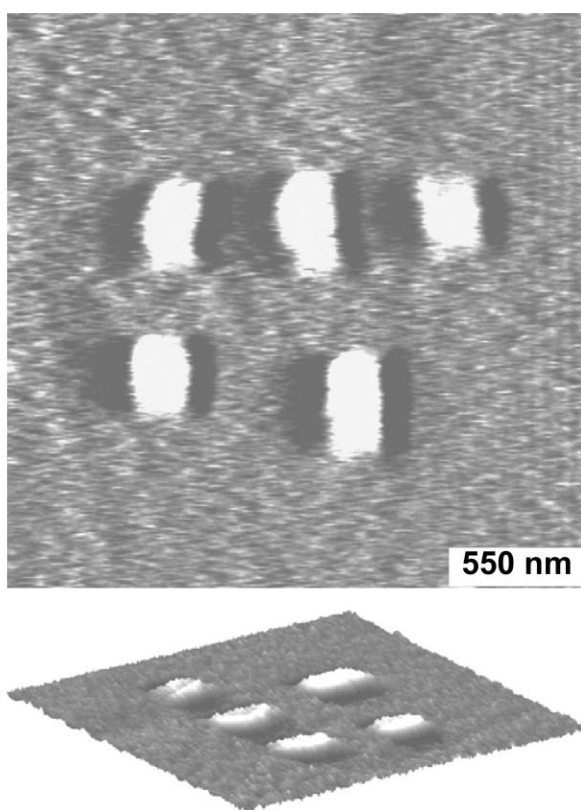
Transmission electron microscopic (TEM) measurements were carried out with a JEOL 3010 TEM, operating at 300 kV. Samples for TEM were prepared by depositing a drop of the nanocrystal sol on a holey carbon copper grid and allowing the solvent to evaporate initially in air and then in a desiccator overnight. TEM studies revealed that the Pd nanocrystals were monodisperse with diameters of 2.5 nm (20% ethanol) and 3.2 nm (25% ethanol). The average diameter of the Au nanocrystals was found to be 2.0 nm.

DPN experiments were carried out under ambient conditions (*ca.* 20 °C, humidity *ca.* 35–50%) by employing a Nanoscope-IV controller attached with a Digital Instruments multimode-head. Contact mode imaging was carried out in both normal and lateral force modes at different scan angles. Standard Si<sub>3</sub>Ni<sub>4</sub> cantilevers were coated with nanocrystals by immersing them in a nanocrystal dispersion followed by drying in air. The experiments were carried out on freshly cleaved mica surfaces. Deposition of nanocrystals was achieved by scanning an area with scan speeds of *ca.* 1 μm s<sup>-1</sup>. Subsequently, imaging was carried out by using the same cantilever and scanning a larger area with higher scan rates.

## Results and discussion

The choice of sols deserves a mention. Both the Au and Pd hydrosols could be re-dispersed in water after drying in air by simply adding water to the dried pastes. During the course of our previous investigations we have observed that such drying and re-dispersion steps do not result in any change in the diameters of the nanocrystals.<sup>13,16</sup> We believe that this ability is key to the success of a DPN experiment based on hydrosols. It is possible that when dried, these sols retain enough solvent and remain in a fluid-like state, continuing to remain as individual particles rather than as aggregates.

Fig. 1 shows an AFM image of rectangular patterns created by scanning a cantilever coated with 2.5 nm Pd nanocrystals on a mica substrate. These rectangles were produced by 8–10 min scans of the desired area ( $66 \times 100$  nm) at a slow scan velocity of  $0.5 \mu\text{m s}^{-1}$ . After each scan, the cantilever was shifted by 100 nm along either the  $x$ - or  $y$ -axis and scanning (at the slow rate) was resumed in the new area. The first four rectangles measure  $66 \times 100$  nm and are 100 nm apart in the horizontal or the vertical direction. The last rectangle of  $66 \times 120$  nm at the bottom right was created after applying an  $x$ -shift of 135 nm from the fourth pattern. The image in Fig. 1 was obtained by the same cantilever, but employing a higher scan speed ( $25 \mu\text{m s}^{-1}$ ). The rectangles exhibit an average height of *ca.* 3.0 nm. This diameter is comparable to the diameter of 3.3 nm obtained by scanning tunnelling microscope experiments carried out on these nanocrystals.<sup>14</sup> The difference in the diameter is due to the thickness of the ligand shell. We therefore suppose that the rectangles are filled with Pd nanocrystals.

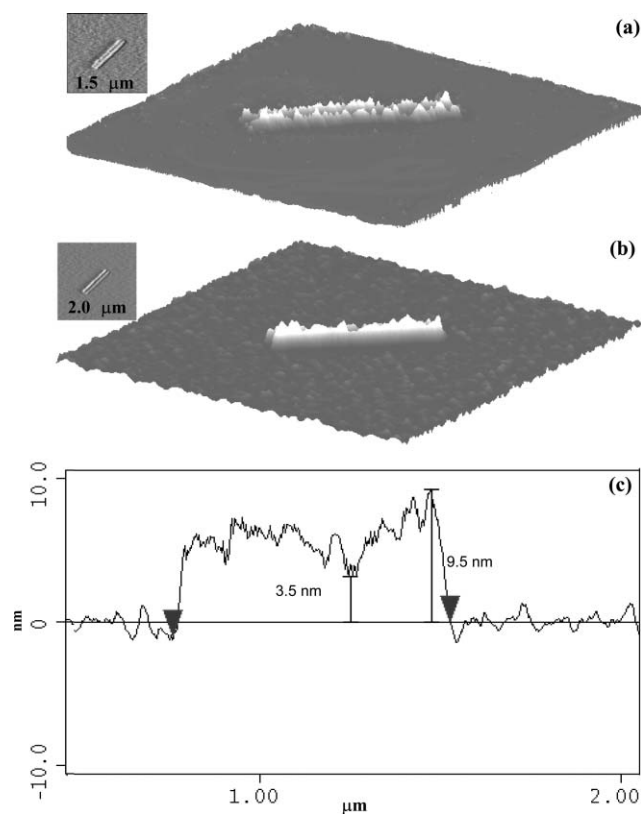


**Fig. 1** AFM images (in the lateral force mode) showing rectangles made of Pd nanocrystals. The rectangles have a constant interspacing of 100 nm in either the horizontal or vertical direction and were created by employing successive  $66 \times 100$  nm scans interspersed with 100 nm scan offset either on the  $x$ - or  $y$ -axis. The scan size employed for obtaining the second rectangle at the bottom row was  $66 \times 120$  nm. Also, the interspacing distance is 135 nm in this case. The total time required for creating this pattern was 45 min. Subsequent imaging was carried over a larger area with a tip velocity of  $50 \mu\text{m s}^{-1}$ . A three-dimensional view is shown at the bottom.

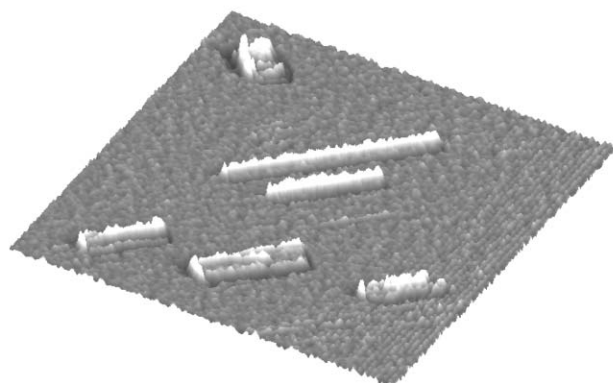
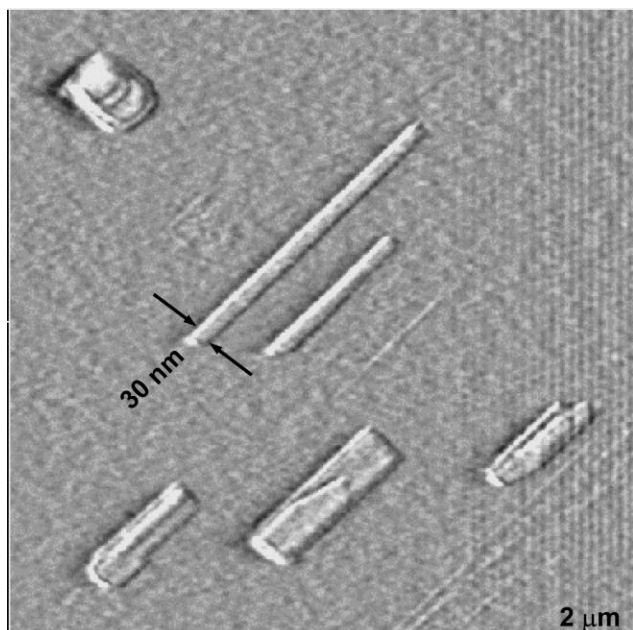
However, the individual particles are not resolved due to the mild contact forces employed to image the patterned area. A cantilever, once coated, could be used to create several such rectangles. The sharp boundaries in the patterns and the close correspondence between the scanned area and the pattern dimensions indicate that the weak non-covalent interactions between the substrate and the particles are adequate to limit lateral diffusion (which would otherwise have resulted in patterns with no correspondence to the area scanned). The small differences that are observed between the scanned area and the patterned area are due to thermal drift. The use of bigger PVP-capped Pd nanocrystals as inks yields patterns with average heights of *ca.* 4.0 nm, indicating that the ink transfer process probably depends more upon the nature of the ligand shell rather than the size of the nanocrystal. It has also been possible to obtain patterns of Au nanocrystals capped with smaller and more hydrophilic ligands such as THPC.

In addition to rectangles, this method can also create high aspect ratio structures such as lines. In Fig. 2(a) and 2(b),  $750 \times 35$  nm lines patterned with Au and Pd nanocrystals, respectively, are shown. In the case of lines made of 2.5 nm Pd nanocrystals, the height of the features along the length varied between 3.5 and 9.5 nm [see Fig. 2(c)], indicating that the pattern is made up of more than one layer of nanocrystals. The lines of the Au nanocrystals also exhibit similar behavior. It has been possible for us to create several well-defined nanostructured features on the mica surface. Fig. 3 shows another example of AFM images of a region of the substrate where several rectangles and lines of various aspect ratios and sizes have been patterned with Au nanocrystals.

The nanocrystal patterns are different from water patterns that sometimes condense on the substrate under similar scanning conditions when un-coated tips are employed.<sup>17</sup> The latter evaporate within 30 min under ambient conditions, unlike the nanocrystal patterns which are stable for extended periods. We obtained the reproducible images from nanocrystal patterns for



**Fig. 2** AFM images of lines of (a) Pd and (b) Au nanocrystals. (c) A cross sectional profile of the line of Pd nanocrystals. The vertical lines indicate the maximum and minimum heights.

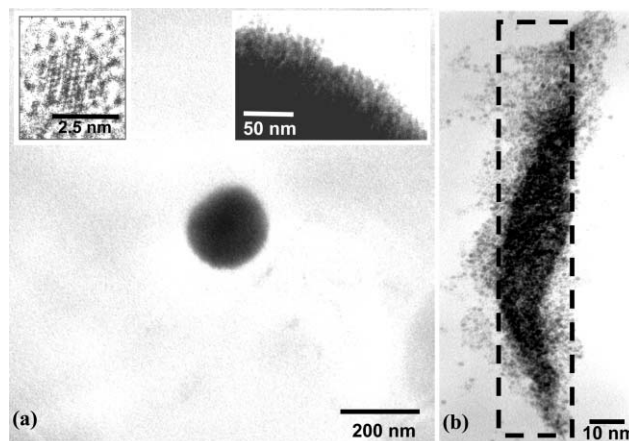


**Fig. 3** AFM image (in the lateral force mode) showing various patterns made of Au nanocrystals. The patterns were drawn by scanning the cantilever over the surface with a velocity of  $1 \mu\text{m s}^{-1}$ , under ambient conditions. Subsequent imaging was carried out over larger areas at a tip velocity of  $50 \mu\text{m s}^{-1}$ . A three-dimensional view is shown at the bottom.

several hours following patterning experiments. We have no reason to suspect that the nanocrystal patterns degrade after a few hours and we believe that the patterns are stable for long periods of time under ambient conditions. The patterns formed by water also do not exhibit the sharp boundaries afforded by the nanocrystal patterns. Furthermore, the aqueous patterns are not continuous and consist of droplets of varied dimensions.

In order to ascertain the identity of the transferred material, attempts were made to carry out patterning experiments on a holey carbon Cu grid (Fig. 3). Initial experiments involved holding the cantilever tip coated with 2.5 nm Pd nanocrystals in contact with a chosen area in the grid. The area was subsequently located on the TEM by the aid of markers created by rupturing the carbon film in neighbouring mesh regions. A scan of the grid revealed circular patterns such as the one shown in Fig. 4(a). The patterns were filled with nanocrystals and were several layers thick. Individual nanocrystals could be imaged at the edge of the circular patterns [see insets in Fig. 4(a)]. By carrying out a rectangular scan with Au nanocrystal-coated tip, the pattern shown in Fig. 4(b) was produced. TEM experiments were carried out one or two days after patterning experiments. Our studies on the grid were complicated by the rougher surface of the carbon films and also by their tendency to rupture under the scanning conditions.

On mica substrates, the patterns of nanocrystals could be



**Fig. 4** TEM images of nanocrystal patterns created on a TEM grid. (a) A circular pattern of Pd nanocrystals obtained by holding the cantilever in contact with a TEM grid for 25 min. The insets show a high-resolution micrograph of the nanocrystal pattern and that of an individual Pd nanocrystal. (b) A micrograph corresponding to a rectangle filled with Au nanocrystals. The likely area where the cantilever was scanned is indicated by dashed lines.

obtained by employing a wide range of contact forces, consistent with other DPN experiments that employ inks with chemical affinity to the substrate.<sup>8–10</sup> Based on these DPN experiments, it is believed that by holding the cantilever in contact with the substrate it should be possible to study the process of lateral diffusion of the ink. We, however, find no evidence of lateral diffusion when a cantilever coated with nanocrystals is held in contact with a mica substrate. Instead, a small dot pattern is seen whose height increases by a small amount when extended periods of contact time are employed. This behavior was independent of the contact force employed. The above observations are in sharp contrast to the reports of Ali *et al.*, who observed a strong contact force dependence of the lateral dimension of the pattern.<sup>6</sup> It is rather surprising that the weak interactions between passivated nanocrystals and mica are sufficient to limit lateral diffusion. The interaction forces are obviously substrate-dependent, as evidenced from lateral diffusion of the nanocrystal patterns on the TEM grids (see Fig. 4). It seems that the difference in behavior is due to the different wetting behavior of the nanocrystal sols on the substrate.

In conclusion, the present study demonstrates that aqueous dispersions of Au and Pd nanocrystals can form suitable inks for nanopatterning on a mica surface using dip-pen lithography. The stability and integrity of the patterns do not depend on the particle size, but are substrate-dependent. Lines and rectangles, of nanoscopic dimensions, filled with nanocrystals have been drawn on mica substrates.

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