Scanning probe block copolymer lithography

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Contributed by Chad A. Mirkin, October 5, 2010 (sent for review September 3, 2010)

Integration of individual nanoparticles into desired spatial arrangements over large areas is a prerequisite for exploiting their unique electrical, optical, and chemical properties. However, positioning single sub-10-nm nanoparticles in a specific location individually on a substrate remains challenging. Herein we have developed a unique approach, termed scanning probe block copolymer lithography, which enables one to control the growth and position of individual nanoparticles in situ. This technique relies on either dip-pen nanolithography (DPN) or polymer pen lithography (PPL) to transfer phase-separating block copolymer inks in the form of 100 or more nanometer features on an underlying substrate. Reduction of the metal ions via plasma results in the high-yield formation of single crystal nanoparticles per block copolymer feature. Because the size of each feature controls the number of metal atoms within it, the DPN or PPL step can be used to control precisely the size of each nanocrystal down to 4.8 ± 0.2 nm.

scanning probe lithography | block copolymer micelles | single particle synthesis | nanopatterning

Nanoparticles exhibit size-dependent photonic, electronic, and chemical properties that could lead to a new generation of catalysts and nanodevices, including single electron transistors, photonics, and biomedical sensors (1–3). In order to realize many of these targeted applications, researchers need ways of synthesizing monodisperse particles while controlling individual particle position on technologically relevant surfaces. The challenge of positioning or synthesizing single sub-10-nm nanoparticles in desired locations is difficult, if not impossible, via current techniques including conventional photolithography (4–7). Scanning probe-based methods such as dip-pen nanolithography (DPN) (8) and polymer pen lithography (PPL) (9) are particularly attractive because inked nanoscale tips can deliver material directly to desired locations on various substrates with high registration and sub-50-nm feature resolution (10). Here we report a unique approach, termed scanning probe block copolymer lithography (SPBCL), which enables one to control individual nanoparticle growth and position in situ by using DPN or PPL to pattern attoliter volumes of metal ions associated with block copolymers in a massively parallel manner over large areas. Reduction of the metal ions via plasma results in the high-yield formation of single crystal nanoparticles per block copolymer feature. Specifically, we demonstrate that pattern dimensions and metal ion concentration dictate the size of each nanoparticle, whose diameter can be controlled with remarkable precision down to 4.8 ± 0.2 nm.

To begin, we identified a polymer with two essential properties. The material must transfer from a scanning probe tip to a surface of interest in a controllable way, and it must sequester metal ions which can be used subsequently to make nanoparticles. We evaluated the properties of poly(ethylene oxide)-b-poly(2-vinylpyridine) (PEO-b-P2VP) in this context (Fig. 1 A and B). Researchers have shown that block copolymers can be used to generate nanostructures in the 5–100 nm range (11–14). The well-defined domain structures of the block copolymer system can be used as templates to achieve patterns of functional materials including metals, semiconductors, and dielectrics (15–18). Past block copolymer work described the use of block copolymers as thin film templates for the synthesis of nanoparticle arrays in mass without control over individual particle position or dimensions. In this work, however, we demonstrate addressable and size-controllable single nanoparticle synthesis using a tip-based approach where the block copolymer acts as a delivery matrix for facile ink transfer and as a synthetic nanoreactor for forming single nanoparticles. With this PEO-b-P2VP block copolymer, the P2VP is responsible for concentrating nanomaterial precursors through metal ion association for subsequent in situ chemical synthesis (19, 20), whereas PEO acts as a delivery block to facilitate ink transport when used in a scanning probe experiment. Pure PEO is known to be a good ink matrix material for DPN (21), whereas P2VP alone is not a good transport matrix because of its low solubility in water at neutral pH. The block copolymer separates into nanoscale micelles, which not only localizes the metal ions, but also causes the amount of metal ion in each feature to be substantially lower than if the feature was made from pure metal ion ink. Moreover, the time-dependent ink transport characteristics of DPN and PPL determine the volume of transferred composite ink, which effectively controls the final feature size of the nanomaterials formed inside the polymer micelles. Indeed, the final dimensions of the metal nanoparticles that result from plasma reduction of the metal ions in the block copolymer features are smaller than those which define the original features. Importantly, feature size reduction beyond physical tip geometry constraints is achieved via this approach. It is worth noting that feature resolution for conventional DPN is limited by the tip radius of curvature and the water meniscus formed between tip and substrate; the smallest DPN feature reported to date is 15 nm in diameter for an alkanethiol self-assembled monolayer formed on a crystalline Au (111) substrate (22).

Results and Discussion

In a typical SPBCL experiment, PEO-b-P2VP (PEO MW = 2,800 g/mol and P2VP MW = 1,500 g/mol) was dissolved in an aqueous solution at a concentration of 0.5% (wt/wt). The HAuCl4 was added to the solution at a 2:1 molar ratio of P2VP:Au. The copolymer-gold salt solution was stirred for 24 h, and Si tips (Nanoink) were dipped into the ink solution, followed by drying with nitrogen. The DPN experiment was performed on an NScriptron system (Nanoink). The inked tips were brought in contact with a hexamethyldisilazane-coated Si/SiO2 surface. Due to the facile transport of PEO under environments of high humidity, the deposition of PEO-b-P2VP is rapid, and dots of uniform size were produced with a tip dwell time of 0.01 s at 70% relative humidity. This process was repeated...


The authors declare no conflict of interest.

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This article contains supporting information online at www.pnas.orglookup/suppl/doi:10.1073/pnas.1014892107/-/DCSupplemental.
1.600 times for a total patterning time below 2 min to generate a 40 × 40 area where the distance between features was 500 nm (Fig. 1C). In a representative 20-dot line generated by a single pen, each feature diameter was approximately 90 nm with a size deviation of 8%, as measured by atomic force microscopy (AFM) (Fig. 1D).

When the PEO-b-P2VP/AuCl₄⁻ inked arrays were brought in contact with a sample surface, micelles were transported to the substrates through the meniscus formed at the tip point of contact. Subsequent reduction by plasma treatment leads to the formation of Au nanoparticles within the aggregated micelles, as determined by X-ray photoelectron spectroscopy (Fig. S1). In this step, the surrounding polymer matrix was removed by the plasma, leaving square arrays of sub-10-nm Au nanoparticles on the Si substrate, as evidenced by SEM (Fig. 1E). The Fourier transform of the SEM image shows a highly ordered pattern characteristic of aligned square arrays (Fig. 1E, Inset). An SEM image at lower magnification (Fig. S2) remarkably indicates that every spot is occupied by a single Au nanoparticle in an 9 × 7 array. The PEO-b-P2VP/AuCl₄⁻ ink was also patterned on a 50-nm-thick Si₃N₄ membrane. SEM and transmission electron microscopy (TEM) images reveal that the mean diameter of the Au nanoparticles in the array is 8.2 ± 0.6 nm. One striking observation is that all of the atoms in a patterned feature go into making a single nanoparticle. The clear lattice fringes in the high-resolution TEM images of one of these Au particles are indicative of single crystal, face-centered-cubic Au with an interplanar (111) spacing of 0.24 nm (Fig. 1F). Moreover, the characteristic electron diffraction pattern (Fig. 1F, Inset) also confirms the single crystal nature of the gold nanoparticles.

Compared to conventional photolithography or contact printing, which allows one to create and duplicate preformed masks, and block copolymer lithography, which generates hexagonal arrays with spherical domains in most cases (23), we demonstrated flexibility in creating arbitrary patterns with SPBCL through piezo-controlled movement of the probe array over a substrate. This advantage of SPBCL bypasses the need for photomask fabrication and enables arbitrary pattern formation compatible with the semiconductor industry integrated circuit design standards. As an example of arbitrary pattern control, we generated the Northwestern University Wildcat logo consisting of individual sub-10-nm Au nanoparticles (Fig. 2 A and B).

The size of the nanoparticles synthesized in the block copolymer micelles depends on a number of parameters, such as the chain length of the copolymer block, the loading concentration of the metal precursor, and the type of reducing agent (24–26). The time-dependent ink transport characteristics of DPN provide an additional route for controlling the size of the nanomaterials synthesized within the deposited block copolymer nanoreactors. Because the diffusive characteristics of the block copolymer ink are similar to previous reports of feature size dependence on tip-substrate contact time, the nanoparticles synthesized using this DPN-based approach have dimensions that are linearly dependent on the square root of the tip-substrate contact time (27). In a typical DPN experiment under an environment of saturated humidity, Au nanoparticles of different diameters were produced by adjusting tip dwell time from 0.01, 0.09, 0.25, 0.49, to 0.81 s (Fig. 3). The Au nanoparticles, prior to the complete removal of block copolymer matrix, were characterized by AFM and TEM (Fig. S3). These data allow one to determine the absolute and relative sizes of the original polymer spots and resulting gold nanoparticles in a single experiment. Because feature size is dependent upon dwell time in a DPN or PPL experiment, one can control the size of the gold nanoparticles based upon the size of the block copolymer spots generated in the scanning probe experiment. Therefore, one can create an indirect, but linear relationship between dwell time and nanoparticle size (Fig. 3). In general, the nanoparticles have diameters about 10 times smaller than that of the original patterned feature. Moreover, when the block copolymer features are large enough (e.g., 450 nm in diameter), more than one Au nanoparticle can form within the original patterned area (Fig. S4). This result demonstrates that
it is possible to control the number of particles per deposited feature.

Importantly, this approach allows for sub-5-nm Au nanoparticles to be synthesized and assembled by decreasing the gold precursor concentration with all other experimental parameters remaining constant. The gold salt loading factor determines the local concentration of ions within the polymer micelle: The lower the concentration, the smaller the Au nanoparticle. Herein, HAuCl₄ was added to the PEO-b-P2VP micelle solution to obtain a 4:1 molar ratio of 2-vinylpyridine to gold instead of the previously described 2:1. After stirring for 1 d, the block copolymer-gold salt ink was transported from the pen array to the substrate followed by plasma reduction of the Au. SEM data show that sub-5-nm single crystal Au particles form on each spot (Fig. 4A). The size of each Au nanoparticle was measured by scanning TEM (Fig. 4B), and a histogram shows the average diameter of the Au nanoparticles is 4.8 nm with a standard deviation of 0.2 nm (4%) (Fig. 4C). Similar results were obtained for arrays of platinum nanoparticles by using the Pt precursor, Na₂PtCl₆, mixed with PEO-b-P2VP solution as the ink, followed by DPN deposition and plasma treatment (Fig. S5).

SPBCL, by DPN is also amenable to PPL, a recently developed high-throughput scanning-probe-based printing method that combines the advantages of DPN and microcontact printing, and eliminates many of their shortcomings. For proof-of-concept purposes, a 1-cm² polymer pen array (~15,000 polydimethylsiloxane (PDMS) pens) with 80-μm separation between tips was inked with the PEO-b-P2VP/AuCl₄⁻ ink by spin coating. Using an AFM (XE-P software, Park Systems Co.) at 80% humidity, each pen in the PPL array was used to make a 20 × 20 dot array with 2-μm spacing between the dots (Fig. 5A). The deposition time for each dot was only 0.5 s, and thus an array of approximately 25 million features (400 features per pen) was prepared in less than 5 min. The SEM image in Fig. 5B shows the formation of an array of single Au nanoparticles where the original block copolymer matrix has been removed by oxygen plasma and demonstrates that this approach is extremely high yield.

In conclusion, we report SPBCL, a unique approach to synthesize and position single sub-10-nm nanoparticles within phase-separating block copolymer inks transported to a surface by DPN and PPL. SPBCL is general and can be applied to arbitrary patterning and synthesis of sub-10-nm structures on many flat surfaces over large areas. The technique is not restricted solely to Au and Pt, and in principle can be applied to the synthesis and arbitrary patterning of sub-10-nm structures consisting of other metals, semiconductors, and potentially any material that can be synthesized within the domains of a block copolymer (28–31). This set of capabilities will allow researchers to create nanostructures on surfaces that are small enough to behave as single particle devices (e.g., sensors) that can be integrated with prefabricated circuitry and the isolation of individual biological molecules such as proteins.

Fig. 3. Size distribution of PEO-b-P2VP/AuCl₄⁻ dots and the corresponding Au nanoparticles synthesized within them as a function of increasing tip-substrate contact time. AFM topographical images of the patterned PEO-b-P2VP/AuCl₄⁻ features and SEM images of the Au nanoparticles formed after brief exposure to plasma show a time-dependent size increase (insets).

Fig. 4. Synthesis of sub-5-nm Au nanoparticles. (A) SEM image of a 3 × 3 array of Au nanoparticles with sub-5-nm diameters. (B) The size of the Au nanoparticles of the array corresponding to Fig. 3A was measured by scanning TEM. (C) Histogram showing the size distribution of sub-5-nm Au nanoparticles.
The average diameter of Au particles in the array is 9.5 nm. Block copolymer arrays which have been removed by oxygen plasma. The ink was prepared by dissolving the PEO-40 f5

Fig. 5. PPL patterning of nanoparticle arrays over large areas. (A) A dark field optical microscopy image of a large scale pattern of PEO-b-P2VP/AuCl4−dots. (The inset shows 20 × 20 dots with 2-μm spacing for each pattern with an individual pen created on a Si/SiO2 surface by a 15,000 pen array.) (B) SEM image of Au particles (bright dot) formed within the PPL-patterned block copolymer arrays which have been removed by oxygen plasma. The average diameter of Au particles in the array is 9.5 nm.

Materials and Methods

Ink Preparation. The diblock copolymer, PEO-b-P2VP, was purchased from Polymer Source, Inc., with polydispersity Mw/Mn = 1.11 and molecular weights of 2,800 and 1,500 g/mol for the PEO and P2VP, respectively. PEO-b-P2VP was used without purification. HAuCl4 (99.9995%) was purchased from Sigma-Aldrich and Na2PtCl6 (99%) was acquired from Strem Chemicals. The ink was prepared by dissolving the PEO-b-P2VP in 18 M H2SO4 at room temperature to make a 0.5% wt solution and 1.0 g of hydrosilane-rich crosslinker (vinylmethylsiloxane-dimethylsioxane -731, Gelest) and 1.0 g of hydrosilane-rich crosslinker (vinylhydroxiloxane-301, Sigma). The mixture was stirred, degassed, and poured on top of the soft pen array master. A precleaned glass slide (VWR, Inc.) was then placed on top of the elastomer array and the whole assembly was cured at 70 °C overnight. Finally, the polymer pen array was carefully separated from the pyramid master and treated with oxygen plasma for 2 min to improve inking. The ink solution of block copolymer/metal precursor was spun cast onto the PDMS tip arrays (1 mL ink, 2,000 rpm, 2 min) (Oxygen Nanotech). PPL was carried out on an AFM work station with a PPL head manufactured by Park Systems Co., using XEP software (Park, Inc.) at a relative humidity of ~80% and temperature of 25–29 °C. The leveling between the pen arrays and the sample was adjusted with an XY scanning tilting stage with a resolution of 4/1,000°.

Nanoparticle Synthesis. After DPN or PPL, the samples were exposed to oxygen or argon plasma for about 5 min in a Harrick Plasma Cleaner operated at 60 W at a pressure of 100 mtorr. Plasma treatment was used to remove the block copolymer and reduce the metal ions as facilitated by hydrocarbon oxidation (32). Any metal oxide on the nanoparticle surface can be removed by subsequent argon or hydrogen plasma treatment (26).

ACKNOWLEDGMENTS. C.A.M. acknowledges the US Air Force Office of Scientific Research, the Defense Advanced Research Projects Agency, and National Science Foundation (NSF) (Nanoscale Science and Engineering Center Program) for support of this research. C.A.M. is grateful for a National Institutes of Health Director’s Pioneer Award and a National Security Science and Engineering Faculty Fellowship from the Department of Defense. J.C. acknowledges the Natural Sciences and Engineering Research Council of Canada for a Postdoctoral Fellowship. L.R.G. acknowledges the NSF for a Graduate Research Fellowship.


