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Review

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Chemical approaches for nanoscale patterning based on particle lithography with proteins and organic thin films

Abstract: Nanopatterning methods based on particle lithography offer generic capabilities for high-throughput fabrication with thin film materials, such as organothiol and organosilane self-assembled monolayers (SAMs), polymer films, biological samples, and nanoparticles. Combining scanning probe microscopy with sample preparation based on approaches with particle lithography produces robust test platforms for ultrasensitive surface measurements. For example, nanopatterns of octadecyltrichlorosilane (OTS) can be prepared on surfaces of Si(111) using designed protocols of particle lithography combined with steps of either vapor deposition, immersion, or contact printing. Changing the physical approaches for applying molecules to masked surfaces produces nanostructures with designed shapes and thickness. Billions of nanostructures can be prepared using strategies for particle lithography, requiring only basic steps of mixing, heating, centrifuging, and drying. Arrays of exquisitely small and regular nanopatterns can be prepared with few defects and high reproducibility. For nanopatterns prepared with SAMs, the endgroups can be designed to spatially define the interfacial selectivity for adsorption of proteins, nanoparticles, or electrolessly deposited metals. Particle lithography has become a mature technique, with broad applicability for thin film materials. Images and measurements acquired with scanning probe microscopy will be described for samples prepared using particle lithography-based approaches.

Keywords: nanolithography; nanoparticles; organic thin films; particle lithography; self-assembled monolayer.

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1 Introduction

Particle lithography enables patterning of surfaces with nanoscale dimensions using processes of surface and molecular self-assembly. Strategies of particle lithography employ latex or silica mesospheres as a surface mask to direct the deposition of molecular films, polymers, proteins, evaporated metals, or nanoparticles. Particle lithography has also been referred to as colloidal lithography [1], nanosphere lithography [2, 3], evaporative lithography [4], or natural lithography [5]. To generate surface patterns with particle lithography, a surface mask or template is prepared with monodisperse mesospheres followed by steps of evaporation, etching, or deposition. One of the first reports using "natural lithography" was reported by Deckman and Dunsmuir in 1982 to prepare 80-nm silver posts using a layer of silica spheres as a deposition mask [5]. Considerable research has been reported for preparing arrays of metal nanostructures applying nanosphere lithography for optical, photonic, and surface-enhanced Raman spectroscopy (SERS) applications [6, 7]. Developments with particle lithography that have recently emerged for patterning organic thin films will be described, which generate spatially selective surface templates to deposit polymers [8, 9], metals [10–15], self-assembled monolayers (SAMs) [16–22], and proteins [23–25].

A surface mask of silica or latex mesospheres is used for preparing patterns with particle lithography. The interparticle spacing can be selected by choosing selected sizes of mesospheres. To prepare a surface mask, a solution of monodisperse spheres of latex or silica is deposited on selected substrates. As the solvent (usually water) evaporates, capillary force pulls the mesospheres together, and the spheres spontaneously assemble on flat surfaces to form periodic structures arranged in a close-packed crystalline lattice. An example of the surface arrangement of polystyrene latex mesospheres prepared on a Si(111) substrate is shown in Figure 1, viewed with an atomic force microscopy (AFM) topography frame. Even with diameters

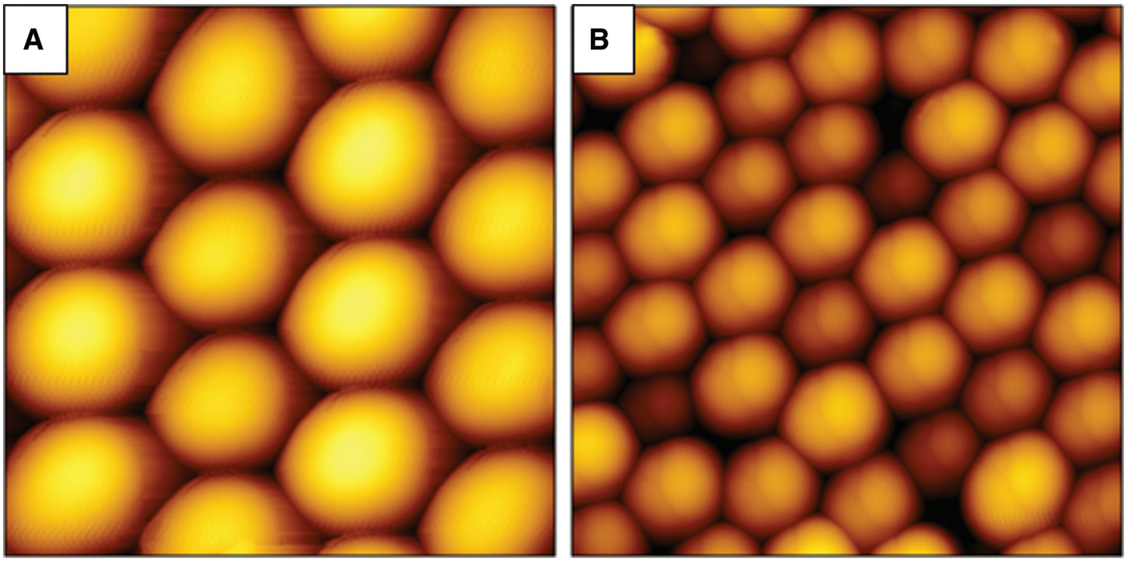

Figure 1: Masks of mesospheres prepared on mica substrates. (A) View of 500 nm latex spheres with tapping-mode AFM topograph. (B) Topography frame for 300-nm latex. Images are 2×2 μm² in size.

as small as 300 nm, the spheres assemble into a periodic arrangement. The upper surface viewed with the AFM image reveals a few missing particles (Figure 1B) and does not disclose the organization of layers under the surface. The defects of the substrate influence the packing of the latex mesospheres. It has been reported that the bottom layer will have better packing than the top surface because rows of particles are filled in from upper layers of spheres [26, 27].

An inherent advantage of patterning approaches with particle lithography is the applicability for a broad range of substrates, including metal films, glass, mica, or silicon wafers. The shapes, sizes, geometries, and inter-pattern spacing are highly reproducible for wide areas of the surface. Representative examples of nanofabrication strategies with particle lithography that have been reported are summarized in Table 1.

2 Patterning organic thin films using mesoparticle masks

Combining particle lithography with molecular self-assembly is a practical approach to pattern nanostructures of SAMs to enable spatial control of surface chemistry at the nanoscale. Strategies with particle lithography have been developed for preparing surface patterns of SAMs, which are single-layer films of molecules that spontaneously self-assemble on surfaces. The properties of surfaces coated with SAMs can be tailored by the selection of molecular endgroups, i.e., adhesion, wettability, and reactivity. Nanopatterns of SAMs can be used for attaching other molecules or nanomaterials to surfaces and can potentially be used for sensor and electronic applications [40].

2.1 Nanopatterns of organothiol self-assembled monolayers prepared with particle masks

The self-assembly of organothiols on surfaces was first reported in 1983 by Nuzzo and Allara, who discovered that alkanethiols spontaneously assemble on gold to form well-organized monolayers [41]. In assemblies of *n*-alkanethiol SAMs, thiol molecules form a close-packed, commensurate $(\sqrt{30}\times\sqrt{30})R30^\circ$ lattice on Au(111) [42]. The alkyl chains within the SAM tilt ~30° with respect to the surface normal. The reproducible geometries and well-ordered structures of organothiol SAMs provide a model surface platform, which can be applied for studying molecular, cellular, and protein binding [43–46].

Several approaches based on particle lithography have been reported for patterning organothiols [18, 34, 47]. Organothiol nanopatterns with sub-100-nm dimensions were fabricated by a particle lithography method of edge-spreading lithography (ESL) reported by McLellan [18, 33, 48]. With ESL, alkanethiol molecules were

Table 1: Examples of particle lithography.

Pattern type	Surface mask	Patterning method/approach	Mask removal	Pattern size	Ref.
Inorganic samples					
TiO_2 nanorods	PS, 350 nm–1 µm	Pulsed laser deposition	Not removed	n/a	[28]
TiO_2 nanobowls	PS, 505 nm	Atomic layer deposition, ion beam milling	Toluene etching	~460 nm diameter	[29]
Silicon nanopillars	PS, 280–440 nm	Deposition of Cr nanoparticles via sputtering followed by reactive ion etching	Sonication in CH_2Cl_2	9–60 nm diameter	[30]
Arrays of Ni, Co nanoparticles	PS, 100 nm–1 µm	Electron beam evaporation	Dissolution in THF	65–180 nm diameter	[31]
Co, Fe rings, rods, and dots	PS, 540 nm	Temperature treatment of mask, then electron beam evaporation	n/a	30–150 nm	[15]
Rings or pores of cysteine-coated CdS quantum dots	PS or silica 200–800 nm	Drop deposition of a PS/QD solution with varying ratios, followed by drying	Rinsing with ethanol or water	300–500 nm	[32]
Rings of CdSe quantum dots	PS, 200 nm–2 µm	Evaporation-induced assembly	Adhesive tape	100 nm–microns	[4]
Organic films					
Concentric rings of alkanethiol SAMs	Silica 1.6 µm	Printing with a planar PDMS stamp	Sonication in water	Ring widths of 30–340 nm	[33]
Rings and porous membrane of hexadecanethiol	Silica 800 nm	Vapor phase deposition	Sonication in water	Avg width 110 nm	[34]
Rings or pores of OTS, PEG-silane, 6-AAPTMS	PS, 100–500 nm	Chemical vapor deposition	Rinsing and sonicating in ethanol	50–250 nm ring widths	[19–22]
Porous OTS film	200–500 nm	Solution immersion	Sonication in aqueous medium	<100 nm diameter	[17]
Biomolecules					
Honeycomb rings of BSA, fibrinogen, and antimouse IgG	PS, 0.56–5.43 µm	Incubation in protein solution	Ultrasound in buffer solution	~0.5–5.5 micron	[35]
Dot arrays of streptavidin and biotinylated antibody	PS, 400 nm	Mixed SAMs of thiol derivatives on gold dot arrays, then immersion in protein solution	Sonication in THF	Periodicity 400 nm	[36]
Arrays of BSA and rabbit IgG	PS, 200–800 nm	Solvent evaporation of mixed solutions of latex and protein	Rinsing with water	100–800 nm	[24]
Ring arrays of BSA, ferritin, apoferritin, and rabbit IgG	PS	Solvent evaporation of mixed solutions of latex and protein	Rinsing with water	200–650 nm	[37]
Polymers					
Ring arrays of poly(N-isopropyl acrylamide)	PS, 5 µm	Printing initiator with a PDMS stamp	Sonication in aqueous medium	~300-nm ring widths	[38]
Nanoporous poly(3,4-ethylene dioxythiophene)	PS, 250 nm	Electrodeposition from aqueous surfactant solution	Soaking in THF for 48 h	~100-nm wall thickness	[39]

PS, polystyrene; THF, tetrahydrofuran; PDMS, polydimethylsiloxane; ECT, eicosanethiol; SHA, sulfanylhexadecanoic acid; HDDT, 12-hydroxydodecanethiol; HDT, hexadecanethiol; OTS, octadecyltrichlorosilane; PEG-silane, 2-[methoxy-(polyethyleneoxy)propyl]trichlorosilane; 6-AAPTMS, N-(6-aminohexyl)-3-aminopropyltrimethoxysilane; BSA, bovine serum albumin; IgG, immunoglobin G.

transferred from a planar polydimethysiloxane (PDMS) stamp through a particle mask to assemble on a gold substrate. The molecules deposited on the gold substrates to form ring-shaped arrangements of organothiol SAMs around the base of each silica bead, as shown in Figure 2. With longer contact times between the PDMS stamp and masked substrate, the ring-shaped area of the SAM expands laterally by spreading [18, 48]. The concentric ring patterns shown in Figure 2 were produced by successive printing of sulfanylhexadecanoic acid (SHA), 12-hydroxydodecanethiol (HDDT), and eicosanethiol (ECT) for different intervals of contact time. The widths of the rings were found to depend on the length of time for printing and the concentration of the organothiol ink.

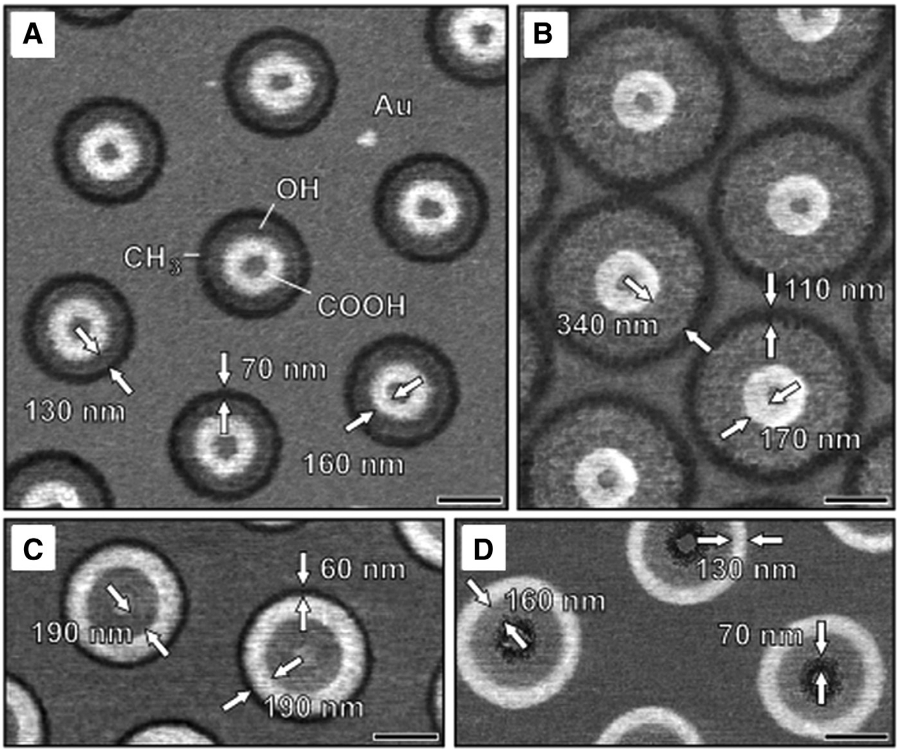

Figure 2: Concentric ring nanopatterns of alkanethiolate SAMs on gold prepared by ESL using 1.6-μm silica particles displayed with lateral force microscopy images: (A) ring patterns prepared by successive printing of SHA, HDDT, and ECT; (B) the ring width increased with longer printing times; (C) patterns prepared by changing the sequence of printing of HDDT, SHA, and ECT; (D) concentric rings produced by first printing ECT, then HDDT and SHA. Scale bars are 500 nm. Reproduced with permission from ref. [33].

2.2 Particle lithography with organosilanes

Particle lithography approaches are well suited for preparing nanopatterns of organosilanes. Films of organosilanes are highly robust due to the covalent nature of surface bonds to form a cross-linked siloxane network. Post-chemical modification of siloxane SAMs to tailor the surface properties can be accomplished with further chemical steps without destroying the original thin film. Organosilane SAMs can be prepared with a range of substrates (e.g., silicon oxide, aluminum oxide, germanium oxide, quartz, glass, gold, and mica) [49, 50]. Nanopatterns of organosilanes provide a molecular platform for integrating other molecules or nanomaterials into surface sites with designed geometries [51, 52]. Applications of organosilane SAMs encompass functional films for surface sensors [42, 53], molecular electronic devices [54], surface coatings [55], and lubricants [56].

To form organosilane SAMs, trace amounts of water are required to initiate surface hydrolysis of alkoxy or chlorosilane groups to form silanols, which then either form siloxane linkages to the surface or undergo crosslinking to effect polymerization of organosilanols [57–59]. The location of water residues on surfaces was found to influence the surface geometry of nanopatterns of organosilane SAMs prepared with particle lithography [19, 20, 22]. Changing the drying conditions of latex masks provide a means to control the distribution of water residues on mica surfaces, as demonstrated in Figure 3 with nanopatterns of octadecyltrichlorosilane (OTS). During steps of vapor deposition, the locations of water residues define the sites for depositing organosilanes to influence the thickness of the nanostructures [19, 22].

For particle lithography, areas where the spherical particles are in contact with the substrate are protected from chemical modification during the process of vapor deposition. Removal of the mask discloses the arrangement of the deposited molecules. The organosilane nanopatterns generated with particle lithography conform to the periodicity of the mesospheres used for the surface mask. The distribution of water surrounding the mesospheres has also been found to influence the surface geometries, defining sites for organosilanes to bind (Figure 3). Particle lithography combined with vapor deposition has also been applied successfully for fabricating nanostructures of OTS on Au(111), Si(111), and glass substrates [19, 21].

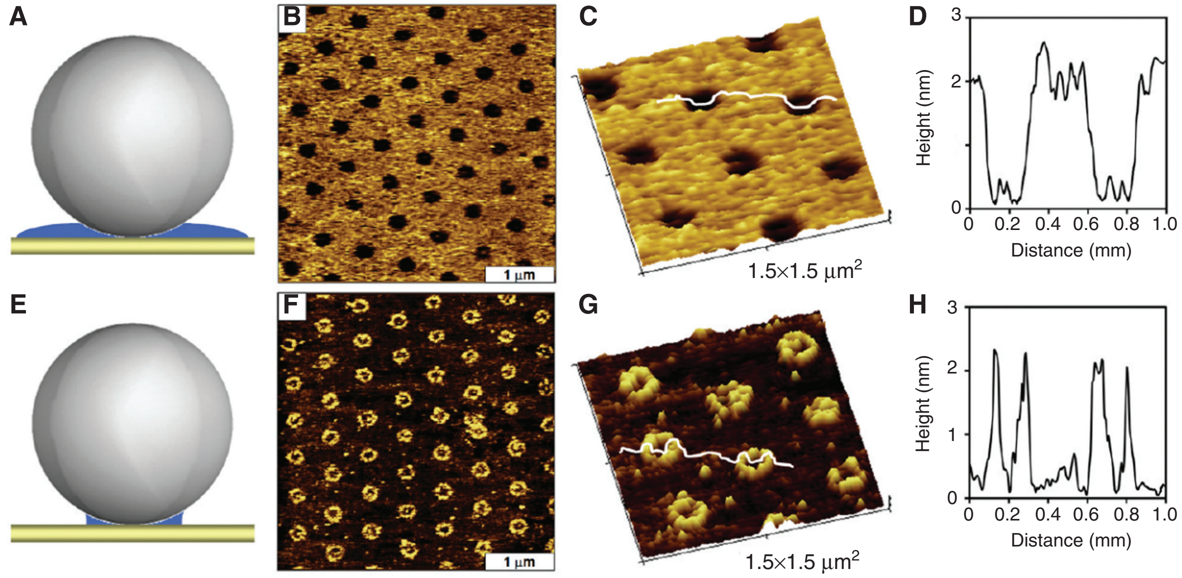

Figure 3: Nanopatterns prepared on mica(0001) with particle lithography masks (500 nm latex) exposed to OTS vapor. (A) A thin film of water covers the sites between spheres when the mask is dried briefly; (B) OTS film with periodic nanoholes of uncovered substrate shown with an AFM topograph; (C) zoom-in view of (B); (D) height profile for the line in (C). (E) A water meniscus forms around the base of mesospheres when masks are dried for several hours; (F) periodic ring patterns of OTS prepared with masks dried longer, viewed by a 4×4-µm^2 topography image; (G) close-up view of (F); (H) cursor profile for the line in (G). Reproduced with permission from ref. [20].

Nanopatterns of organosilanes with selected functional groups have likewise been produced with particle lithography combined with steps of vapor deposition [20, 22].

Procedures for particle lithography with immersion steps in which the substrates masked with mesospheres are submerged in solvents can be problematic. The adhesion between the spheres and the substrate is relatively weak, and the particles tend to rapidly detach. An annealing step can solve this problem, to temporarily solder the mesoparticles to the surface [60]. Using an annealing step, visible light photocatalysis was combined with particle lithography to generate nanostructures of polynitrophenylene on gold [61].

3 Applications of SAM nanopatterns prepared with particle lithography

The chemical and physical properties of functionalized SAM nanopatterns can be applied to prepare spatially selective sites for patterning proteins [62–64], nanoparticles [65–67], and polymers [38, 39]. Studies at the nanoscale are valuable for the development of bioconjugation chemistries, which are key for manufacturing surfaces for biochips and biosensors [68, 69].

3.1 Protein nanopatterns fabricated by particle lithography

Adsorption of proteins onto surfaces with preservation of function and activity for binding can be problematic. Proteins tend to self-aggregate and often bind irreversibly to solids with denaturation caused by the loss of tertiary structure. Approaches for binding proteins to SAMs can improve the viability of protein films and consequently increase the sensitivity of biosensor surfaces. Protein nanopatterns provide a route to increase the surface density of sensor and chip elements as well as to significantly reduce the amount of analyte required for detection. High-throughput fabrication methods for preparing protein nanopatterns offer promise for developing protein-based biosensors and biochips with efficiency and economy [70–72].

A strategy for particle lithography using a mixture approach was developed for generating protein nanopatterns of bovine serum albumin (BSA) and immunoglobulin G (IgG) [24, 37]. Changing the ratio of mesospheres and protein provides a way to tune the surface coverage and geometries of protein nanostructures [23]. An example of particle lithography with BSA nanostructures produced using 500-nm latex mesospheres as a surface template is shown in Figure 4. To prepare nanopatterns of BSA, the protein and latex mesospheres were mixed in an aqueous

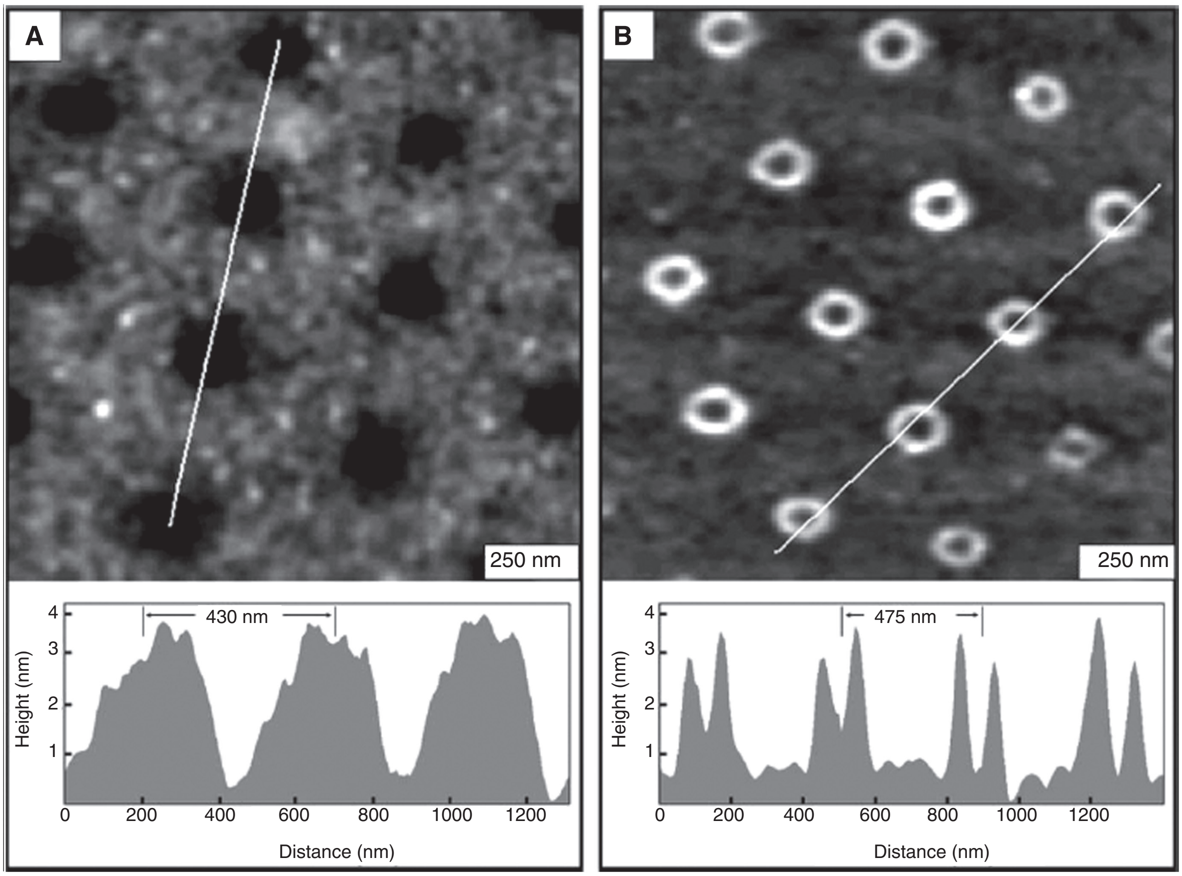

Figure 4: Periodic arrays of BSA nanostructures on mica(0001) produced with particle lithography using 500-nm latex spheres. (A) Nanoholes of uncovered substrate within a BSA film viewed with AFM topography image and corresponding cursor profile; (B) ring-shaped nanostructures of BSA formed at a low concentration of BSA, topography view and height profile. Reproduced with permission from ref. [23].

buffer, deposited on a mica substrate, and then dried under ambient conditions. During a brief drying step, the mesospheres assemble on the surface to produce crystalline assemblies, surrounded by protein. The surface template of latex spheres was removed by rinsing with deionized water. The proteins remain attached to the surface to form nanopatterns in areas surrounding and between the latex spheres. Measurements with AFM cursor profiles reveal that the thickness of protein nanopatterns produced with particle lithography corresponds to a monolayer of protein.

A strategy combining particle lithography and organosilane chemistry was developed for fabricating nanopatterns of lysozyme by Cai and Ocko [25]. A monolayer of undecenyltrichlorosilane (UTS) was prepared on a silicon substrate, in which the vinyl groups were then oxidized to carboxylic groups. Polystyrene nanospheres were deposited on the oxidized UTS to form a mask for patterning. The surface mask was exposed to methyl-terminated OTS by vapor phase deposition, and the mask was removed to generate periodic nanopatterns of oxidized UTS surrounded by an OTS resist. Lysozyme was deposited onto the surface where selective adsorption only occurred on the carboxylic acid terminated sites. To evaluate the selectivity of the surface nanopatterns, a drop of rabbit anti-hen white lysozyme antibody in 3 mM HEPES buffer was applied to the surface. Antibody adsorption was shown to occur selectively on the lysozyme nanopatterns, in Figure 5.

3.2 Periodic arrays of metal nanoparticles produced with particle lithography

Particle lithography is a practical route to fabricate nanopatterns of metal nanoparticles over relatively broad areas. Surface patterns of triangular metal nanostructures can be obtained by direct deposition of a heated metal vapor through 2D particle masks using techniques such as magnetron sputtering, electron beam evaporation, or thermal evaporation [73]. Most often, metal evaporation through surface masks produces nanostructures that are

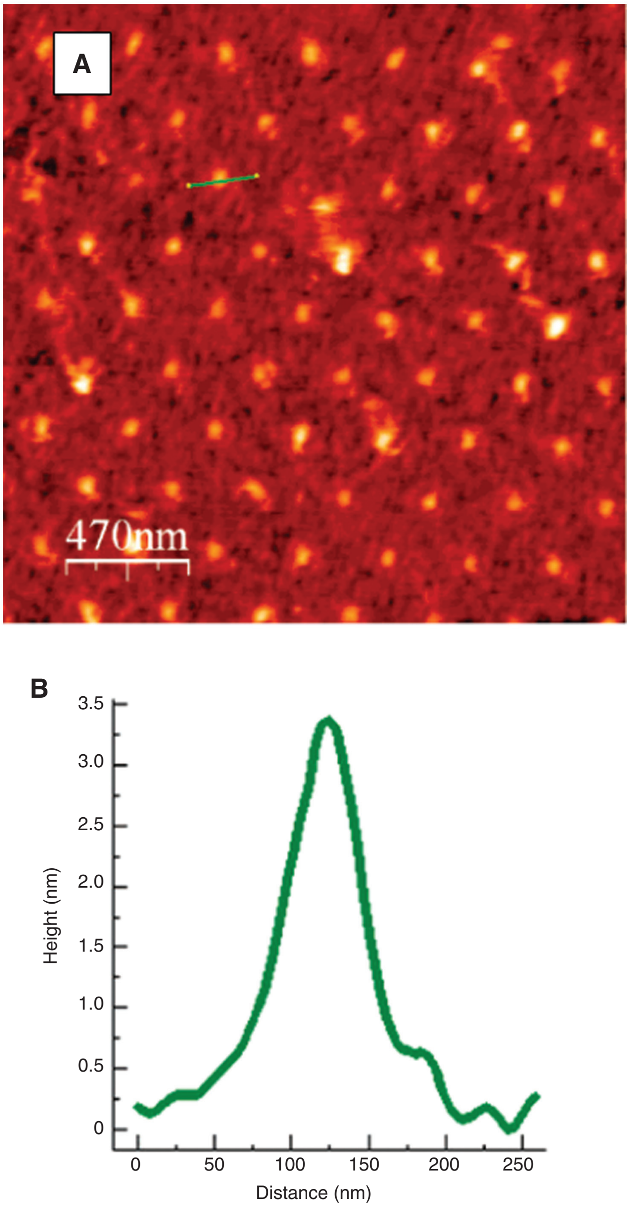

Figure 5: Adsorption of antibody on lysozyme nanopatterns prepared on silicon wafers prepared using particle lithography combined with organosilane chemistry. (A) Lysozyme nanostructures after antibody adsorption viewed with an AFM topograph; (B) cursor profile for the green line in (A). Reproduced with permission from ref. [25].

pyramidal [74], triangular [75–77], or disk shapes [15, 74, 78]. Lithographic arrays of metal nanoparticles are of importance, due to intrinsic optical properties, such as fluorescence or localized surface plasmon resonance. The properties are substantially dependent upon surface assembly on substrates. For example, light transmission was studied on a periodic array of sub-wavelength holes in a metal film reported by Ctistis et al. [79]. The authors found that the enhanced transmission is due to surface plasmons, yet the periodicity and arrangement, to some extent, controls the intensity of the transmission.

An approach using annealed latex masks was used to prepare periodic arrays of nanoparticles with pattern features as small as 30 nm (Figure 6), as reported by Kosiorek et al. [15]. For surface masks of polystyrene latex, the size of the apertures between nanospheres can be reduced by heating. The aperture between the 540-nm latex spheres was reduced from 200 to 30 nm with a heating step. Depositing a metal through the annealed latex mask was found to produce smaller nanostructures than when masks were not annealed.

Metal ring nanopatterns composed of Cu, Au, and Pt nanoparticles were prepared on Si(100) and highly oriented pyrolytic graphite (HOPG) substrates using a particle lithography strategy developed by Bayati et al. [80]. Nanorings were produced by exposing a surface template of 505-nm polystyrene spheres to a metal precursor solution (10 mM) for 2 h, followed by reduction of the metal salt with NaBH$_4$. Removal of the template was accomplished with chloroform rinses to produce arrays of metal nanorings. Examples with different metals are shown by AFM views in Figure 7.

Semiconducting nanoparticles or quantum dots exhibit unique size-dependent properties that can be useful for electronic, optical, and sensing applications [81–83]. Arrays of semiconductive nanoparticles are potential candidates for designs of solar cells and photovoltaic devices [84].

A particle lithography approach coined as “two-particle” lithography was reported by Lewandowski et al. for defining the arrangement of cysteine-coated CdS

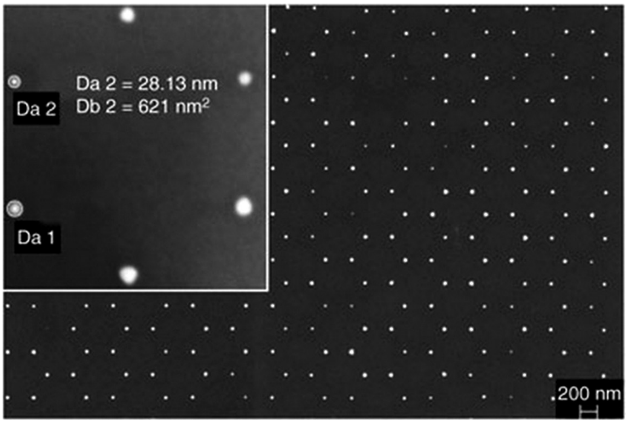

Figure 6: Arrays of Co nanoparticles on a silicon substrate prepared by evaporation of cobalt on an annealed surface mask of 540-nm latex spheres. Reproduced with permission from ref. [15].

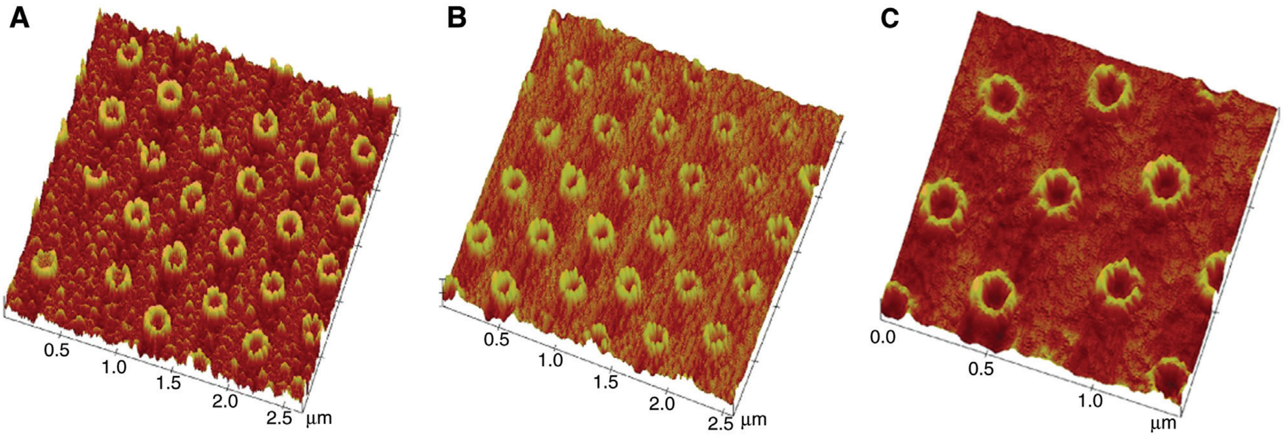

Figure 7: Arrays of metal rings produced by wicking metal precursor through the interstices between polystyrene nanospheres. Nanorings of (A) Cu, (B) Au, and (C) Pt prepared on Si(100) substrates viewed with AFM topographs; the vertical scale bars are 5 nm. Reproduced with permission from ref. [80].

quantum dots [32]. For two-particle lithography, the larger latex spheres provide a structural template to determine the arrangement of smaller nanoparticles. As a liquid mixture of two particles is dried, nanoparticles assemble surrounding the base of latex or silica spheres to generate patterns that conform to the arrangement of mesospheres. The arrangement of nanoparticles exhibit circular ring or nanopore morphologies according to the spherical shape of the meniscus sites at the base of mesospheres. Once the solution conditions are optimized, replicate samples prepared using a chosen ratio and particle diameter exhibit reproducible morphologies and periodicity.

A solution-based approach for patterning quantum dots with particle lithography was developed by Taylor et al. [85]. A film of monodisperse polystyrene was applied to a glass substrate, then a protein repellant layer of methoxy-polyethylene glycol-silane was grafted onto the surface. The mask of mesospheres was removed to form spatially selective surface patterns for defining the sites for adsorption of quantum dots. An example of the nanopatterns of quantum dots is shown in Figure 8.

Patterns of organosilanes prepared by particle lithography furnish a robust platform for binding metal nanoparticles, as demonstrated by Li et al. [20]. Gold nanoparticles were selectively attached onto designed organosilane nanopatterns, which were prepared by particle lithography combined with vapor deposition [20]. To define the spatial selectivity for binding gold nanoparticles, arrays of OTS nanostructures were prepared by vapor deposition with 300-nm latex masks. When the mask was removed, a thin film of OTS with periodically arranged nanoholes of uncovered Si(111) substrate was exposed. The areas of bare substrate were chemically modified with a second organosilane via solution immersion to define sites for binding gold nanoparticles. The nanoholes were backfilled with thiol-terminated 3-mercaptopropyltrimethoxysilane (MPTMS). The nanopatterns of MPTMS surrounded by an OTS matrix were immersed in a solution of gold nanoparticles for several hours. Gold nanoparticles were demonstrated to bind selectively on areas patterned with MPTMS, as shown in Figure 9.

3.3 Patterning polymers with particle lithography

Nanostructures of polymers have potential applications as sensors [86], electronic devices [87], and as photonic crystals [88]. Patterns of polymer thin films have prepared with methods of photolithography, electron-beam lithography, scanning probe lithography, and soft lithography [89]. Patterning protocols based on particle lithography have been reported using polymers, such as poly(N-isopropylacrylamide) [90], polycaprolactone [91], polythiophene [39, 92], and polyethersulfone [93, 94]. Approaches using microsphere arrays as a surface template were combined with surface-initiated atom transfer radical polymerization (SI-ATRP) to fabricate polymer brush microstructures of poly(N-isopropylacrylamide) [38, 95]. A colloidal template with electropolymerization was demonstrated by Roderick, followed by growing poly(carbazole) using SI-ATRP [96]. Ordered trigonal polymeric nanostructures were fabricated by particle lithography, sintering rheology, and

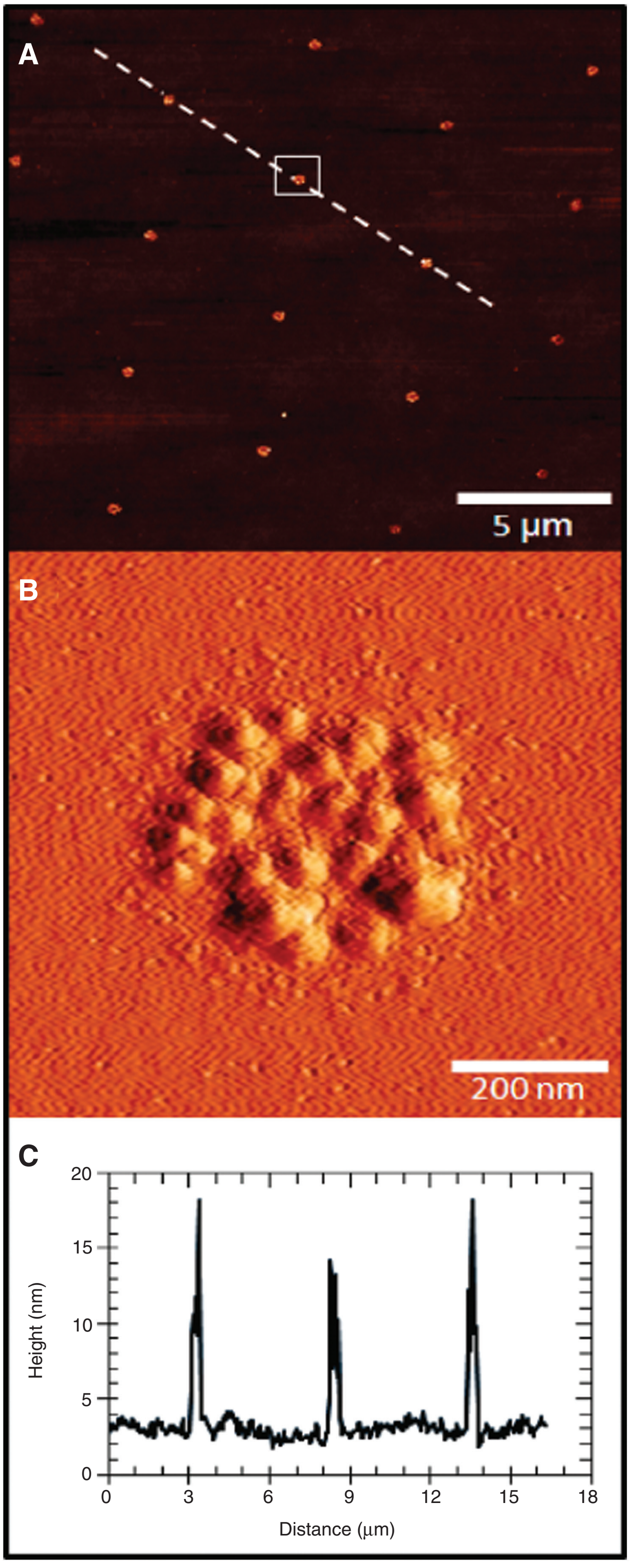

Figure 8: Dot nanostructures of quantum dots coated with IgG prepared by particle lithography with 500-nm latex spheres as a surface template. (A) AFM topography image; (B) close-up view of a single nanostructure within the box in (A); (C) cursor profile for the dotted line in (A). Reproduced with permission from ref. [85].

selective dissolution of self-assembled colloidal arrays [97]. Electro-colloidal lithography, combined with colloidal particles and electrical fields generated by alternating current (AC) and direct current (DC), was used to fabricate patterned polymer films [98]. Binary colloidal crystal lithography, containing small and large particles, was combined with plasma polymerization of *n*-heptylamine to generate patterned amine-functionalized regions on silicon or glass substrates for attachment of the globular protein, BSA [99].

A protocol using surface-initiated and site-specific Suzuki polycondensation was developed to quickly and selectively graft semiconducting and fluorescent poly[9,9-bis(2-ethylhexyl)fluorine] by Beryozkina et al. from functionalized, sub-micron surface patterns [100]. Mesospheres were arranged on Si wafers by dip coating, then, the samples were treated with octadecylsilane to coat the surface between the mesospheres. After removal of the mesospheres by sonication, [2-(4-bromophenyl)ethyl] chlorodimethylsilane was backfilled into the exposed surface areas by silane vapor deposition (Figure 10A). The samples were activated by a palladium catalyst, $Pd(PtBu_3)_2$ followed by surface-initiated polymerization (Figure 10B). No detectable amounts of polymer were formed in the solution phase using this protocol. The polymer brushes measured up to 100 nm in thickness (Figure 10C).

3.4 Approaches to minimize defect density for high-throughput patterning

Defects in the arrangement of close-packed lattices of the particle masks are introduced by variations in the sizes of the spheres; monodisperse sizes are a requirement for defect-free packing. Defects in the packing of spheres become an important consideration for developments of photonic crystals. When films of latex spheres are dried, a few cracks are formed over an area of several square microns, which are produced by shrinkage during the drying step. The roughness of the underlying substrate morphology can also contribute to shifts in registry and areas with vacancies. Surfaces which are atomically flat, such as mica(0001), generate a lower density of defects. Imperfections of the substrate, i.e., point defects, scratches, dislocations, and grain boundaries can propagate into imperfections in the packing of the spheres. Multiple approaches have been developed to produce higher-quality latex masks, and this topic has been reviewed in previous reports [73, 78, 101, 102]. Surface arrays of mesospheres can be prepared by spin coating

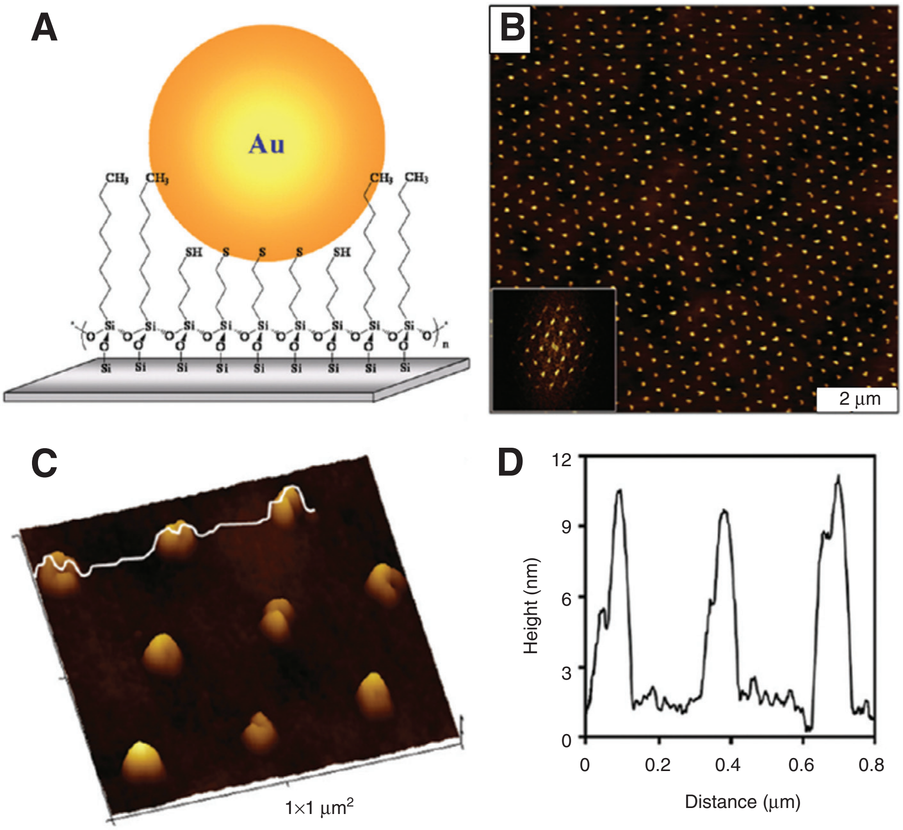

Figure 9: Nanopatterns of organosilanes were used to define the surface spatial selectivity to bind gold nanoparticles on Si(111). (A) Gold nanoparticles attached to areas with MPTMS; (B) Wide view of the arrangement of gold nanoparticles, 10×10 µm² topograph, inset is the corresponding FFT image; (C) zoom-in view of (B); (D) height profile for the line in (C). Reproduced with permission from ref. [20].

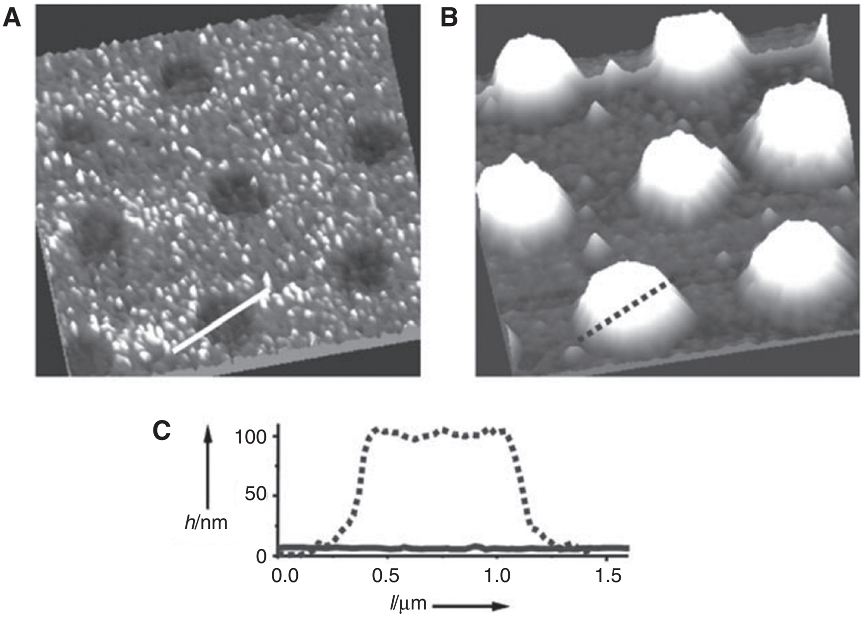

Figure 10: Surface patterns before and after steps of polymerization. Representative topography views of (A) octadecylsilane nanopores filled with [2-(4-bromophenyl)ethyl]chlorodimethyl silane; (B) surface grafted and patterned poly[9,9-bis(2-ethylhexyl)fluorine], (C) cursor profiles of patterned surfaces along the solid and dashed lines in (A) and (B). Reproduced with permission from ref. [100].

[103], drop deposition, or Langmuir-Blodgett [104, 105] protocols. Methods reported for producing defect-free arrays of spheres include driving the spheres to assemble using gravitational sedimentation [106–108], surfactants [104], or with an electric field [109, 110]. Controlling the evaporation of particles using convective assembly has also been investigated [26].

4 Future prospects

When considering requirements for manufacturing surfaces with advancements in nanotechnology, self-assembly is emerging as an indispensable approach for organizing materials at the molecular scale for practical reasons. Particle lithography provides advantages of low-cost applicability to a wide range of substrates and nanomaterials and capabilities for high-throughput construction of regularly shaped surface patterns of defined dimensions and composition. Preparing chemically selective surface sites for selective adsorption of nanomaterials can be a problem because of the potential issues of self-exchange, stability, and self-reactive properties of organic thin films. Fundamental studies of surface changes in response to environmental parameters (heat, pH, solvents) will help to address the criteria for applications with designed nanostructures. Nanoscale test platforms prepared by particle lithography are particularly suited for developing surface-based assays with biomolecules such as fibrinogen [52], and will provide advancements for highly sensitive studies for screening fluorescent markers, evaluating protein-small molecule binding and testing the selectivity of protein binding.

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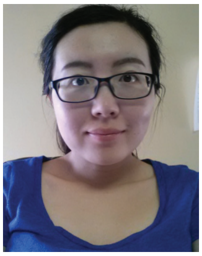

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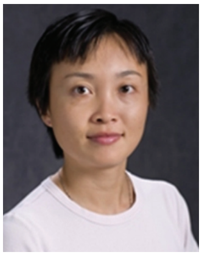

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