Two-dimensional nanopatterning by PDMS relief structures of polymeric colloidal crystals

Hye Jin Nam, Ju-Hee Kim, Duk-Young Jung, Jong Bae Park, Hae Seong Lee

*Department of Chemistry-BK21, Institute of Basic Sciences, Sungkyunkwan Advanced Institute of NanoTechnology, Sungkyunkwan University, Suwon 440-746, Republic of Korea
b Jeonju Center, Korea Basic Science Institute, Jeonju 561-756, Republic of Korea
c Department of Advanced Nanomaterials Engineering, Jeonju University, 1200 Hyoja-Dong-3Ga, Wansan-Gu, Jeonju 560-759, Republic of Korea

Received 7 November 2007; received in revised form 4 February 2008; accepted 5 February 2008

Available online 13 February 2008

Abstract

A new constructive method of fabricating a nanoparticle self-assembly on the patterned surface of a poly(dimethylsiloxane) (PDMS) relief nanostructure was demonstrated. Patterned PDMS templates with close-packed microwells were fabricated by molding against a self-assembled monolayer of polystyrene spheres. Alkanethiol-functionalized gold nanoparticles with an average particle size of 2.5 nm were selectively deposited onto a hydrophobic self-assembled monolayer printed on the substrate by the micro-contact printing (μCP) of the prepared PDMS microwell, in which the patterned gold nanoparticles consisted of close-packed hexagons with an average diameter of 370 nm. In addition, two-dimensional colloidal crystals derived from PMMA microspheres with a diameter of 380 nm and a negative surface charge were successfully formed on the hemispherical microwells by electrostatic force using positively charged PAH-coated PDMS as a template to produce multidimensional nanostructures.

© 2008 Elsevier B.V. All rights reserved.

PACS : 81.16.Rf; 81.16.Dn; 81.65.Cf

Keywords: PDMS; Microwells; Self-assembly; Micro-contact printing; Gold nanopattern; Colloidal crystal

1. Introduction

Developing soft-lithographic patterning techniques with high resolution is a challenging and attractive issue, due to their tremendous role in fabricating nanometer-scale devices such as thin-film transistors [1], MEMS [2], data storage devices [3], OLEDs [4], microfluidics [5] and optoelectronics [6]. One of the bottom-up strategies for producing patterned nanostructures is to self-assemble a two-dimensional or three-dimensional array of monodispersed colloidal nanoparticles, such as metallic, polymeric or inorganic colloids, by a variety of methods [7–12]. Multidimensional nanostructures have been constructed from the assembled colloidal templates by using soft-lithographic techniques, including micro-contact printing (μCP) [13–17], micromolding in capillaries (MIMIC) [18,19] and nanotransfer printing [20] using poly(dimethylsiloxane) (PDMS).

Many patterning techniques use self-assembled monolayers (SAMs) as resists for the selective deposition of the target materials. Assembled monolayers including metal nanoparticles or polymer spheres can serve as reactive masters for the bottom-up and top-down approaches to nanofabrication. Using a PDMS as a patterned master and a self-assembled monolayer as an ‘ink’, μCP has been successfully applied to pattern a wide range of materials, e.g., metals [13], polymers [14], colloids [16,17], proteins [12,21,22] and nanoparticles [23]. In the top-down approach, embossed patterned structures formed by melting using a polymeric solution against the assembled template have been used as ‘reactive containers’ to form an array of nanocrystals [24], and inorganic or polymeric colloidal spheres [25].
We exploited the \( \mu \text{CP} \) technique to create a hexagonal nanopatterned assembly of gold nanoparticles via a specific chemical interaction, without the use of photolithography and reactive ion etching. Moreover, self-assembled two-dimensional colloidal crystals were successfully formed through the deposition of colloidal spheres into polymeric microwells whose surface was modified by a polyelectrolyte. This method provides a facile and reproducible process to produce patterned nanostructures.

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich and used without further purification. Glass slides were cleaned with piranha cleaning solution, 3:1 \( \text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 \), to remove the residual organic impurities, sonicated for 30 min, and then rinsed with deionized water (having a resistivity of 18 M\( \Omega \)) and 100% isopropyl alcohol (Mallinckrodt). The substrates were dried in a nitrogen stream and retreated with an oxygen plasma using a Harrick plasma cleaner. The 10 wt% aqueous suspension of 488 nm polystyrene (PS) microspheres was purchased from Microparticles GmbH (Germany), and their sizes were measured to be 454 ± 2 nm by the SEM with a calibrated length used in our previous study [26]. The replica molds were prepared from PDMS (Sylgard 184, Dow Corning). Sulfuric acid, 35% hydrogen peroxide (J.T. Baker), dodecanethiol (Aldrich) and tridecafluoro-(1,1,2,2)-tetrahydrooctyltrichlorosilane (United Chemical Technologies, Inc., Bristol, PA) used as a perfluoroalkylsilane were used as received. Alkyl thiol-functionalized gold nanoparticles were synthesized by a two-phase liquid–liquid system [27], following the procedure described in a previous report.

2.2. Arrays of gold nanoparticles on SAM-patterned surfaces

A colloidal monolayer of 454 nm PS microspheres was prepared by spin-casting at 2000 rpm for 30 s on glass substrates. The PS arrays were heated in a conventional oven at 70 °C for 1 h, in order for them to be reliably adhered onto the glass substrate by melting them slightly, and used as a template for PDMS molding. The PDMS prepolymer solution was poured and treated under a vacuum for 30 min to remove the trapped gas bubbles and cured in an oven at 70 °C for 40 min. The cured PDMS molds were peeled off from the PS crystals, which show an iridescent color when exposed to visible light due to its being scattered in all directions. A schematic illustration of the fabrication of the microwell arrays by the soft-lithographic technique using the PS colloidal monolayer as a master for the patterning process is shown in Fig. 1. An octadecyltrichlorosilane (OTS) solution with a concentration of 10 mM in hexane was coated on the PDMS molds by spin-casting. The pattern of OTS-SAMs was transferred by the \( \mu \text{CP} \) method. The OTS-patterned substrate was dipped into the gold colloidal solution for 18 h, followed by washing with toluene and drying under an \( \text{N}_2 \) stream.

2.3. Two-dimensional colloidal crystals on microwells

We produced a self-assembly of polymethylmethacrylate (PMMA) 380 ± 2 nm microspheres on the microwell of the PDMS mold by dip-coating in the PMMA colloidal solutions. To improve the adhesion of the PMMA microspheres on the microwells, we first modified the surface of the microwells by treating it with a poly(allylamine hydrochloride) (PAH) solution having a concentration of 0.1 mg/mL at room temperature for 10 min, and then the modified PDMS...
microwell was immersed in the PMMA colloidal solution at room temperature for 2 h. The PMMA deposited PDMS microwells samples were washed with deionized water to remove any double- or multilayered microspheres and dried at room temperature.

2.4. Characterization

Scanning electron microscope (SEM) measurements were taken using a JEOL JSM 7000F FE-SEM instrument operating at 15 kV. Before imaging, the samples were coated by sputtering with Pt. AFM images were obtained using a Nanoscope IV multimode AFM (Digital Instruments Co.) in tapping mode using a silicon cantilever with a curvature of 10 nm (MikroMasch Inc.) and a “J” scanner with a scan limit of 125 µm. Phase contrast TEM images of the gold nanoparticles were obtained using a side-entry JEOL high-resolution TEM operating at 300 kV. The size distribution of the Au core was measured from the enlarged TEM image photographs including at least 100–200 individual nanoparticle core images. The electrophoretic mobility of the obtained PMMA particles was measured using a Malvern Zetasizer 4. The \( \zeta \)-potential was calculated by the conversion of the electrophoretic mobility, \( \mu \), with the Smoluchowski relation: \( \zeta = \frac{\mu \eta}{e} \), where \( \eta \) and \( e \) are the viscosity and permittivity of the solution, respectively [28].

3. Results and discussion

3.1. Two-dimensional PS colloidal crystal

We optimized the experimental conditions for the fabrication of a well-ordered PS monolayer array over a large area by controlling three major factors: the spinning speed, spinning time, and concentration of the colloidal solution. The best result for the monolayer assembly of the 454 nm PS microspheres was obtained in 10 wt% PS colloidal solution at 2000 rpm for 30 s on the plasma treated glass surface. At spin speeds below 2000 rpm, double-layered coatings were also formed in a portion of the area together with the monolayer, whereas a non-covered area was produced at higher speeds. Colloidal solutions with a concentration of less than 10 wt% gave less dense packing of the PS in the monolayer under similar conditions [26].

A PS monolayer array with a uniform, hexagonal close-packed array over a large area was obtained, as shown in Fig. 2. The high-magnification SEM image indicated that the PS microspheres were slightly deformed from a spherical to a nearly hexagonal shape, since the contact area between the microspheres increased after annealing at 70 °C for 1 h. The average diameter of the annealed PS microspheres in the longitudinal direction was approximately 435 ± 2 nm, showing 4.2% shrinkage compared with the value of 454 nm before annealing. In the horizontal direction, the average diameter was 447 ± 2 nm, corresponding to 1.5% shrinkage due to the void space among three microspheres. The height of the monolayer array was approximately 435 ± 3 nm, resulting from an elastomeric deformation.

The AFM data of the PS array are schematized in Fig. 3. The hexagonal close-packing was confirmed by the angle among the triangular points of maximum heights in the AFM data, which was approximately 60 ± 0.1°. The line profile in the edge-to-edge direction showed that the average feature size of the hemispherical part is 457 ± 2 nm in width and 156 ± 2 nm in height. The discrepancy in the data between AFM and SEM is ascribed to the difficulty in accomplishing the length calibration for the SEM data.
3.2. Two-dimensional PDMS microwell

The casting of the prepolymer against the PS arrays produced well-ordered PDMS microwells with an embossed surface and their SEM data are shown in Fig. 4. One hexagon in the microwell consisted of the six walls formed by the contact between two PS microspheres and the six protrusions formed by the void space among three adjacent microspheres. We prepared the PDMS prepolymer solution with 20% curing agent, which is higher than the conventional ratio of 10%. The 20% prepolymer presents less viscous characteristics, thereby allowing for its improved penetration into the voids of the PS arrays by capillary action during the replica molding. The resulting solid PDMS molds are harder and less adhesive to the embedded PS microspheres, thus allowing for facile peel-off. The structural features of the hexagonal patterns were a corner-to-corner distance of approximately $486 \pm 3$ nm and an edge-to-edge distance of $410 \pm 4$ nm. The size change is thought to result mainly from the additional thermal deformation of the PS microspheres during the PDMS curing steps.

The cross-section line profiles of the AFM data shown in Fig. 5 revealed that the diameter and depth of the negative hole are $449 \pm 3$ nm and $103 \pm 4$ nm, respectively, indicating that the pattern was transferred with excellent fidelity using this replica method. The width and height of the protrusions with pyramidal-shape geometry were $288 \pm 2$ nm and $35 \pm 3$ nm, respectively, indicating the effective penetration of the PDMS prepolymer solution into the void space among the three microspheres.

3.3. Hexagonal gold nanopattern by micro-contact printing

The transferred pattern depends on the topography of the elastic stamp and, thus, PDMS stamps with diverse widths, heights and topographical patterns could be fabricated by controlling the topology of the master PS colloidal crystal pattern. Microwell arrays were used as the elastic stamp for µCP, where the OTS molecules were deposited onto the six protruding walls of the hexagons in the microwell and printed onto the surface of the substrate by contact with the substrate. Fig. 6 shows a schematic illustration of the fabrication of the gold nanopatterns by µCP of OTS by dip-coating in gold colloidal solutions.

The printed pattern of OTS-SAMs was confirmed by the pattern of deposited gold nanoparticles. The OTS molecules have hydrophobic alkyl chains, and gold nanoparticles capped with alkyl-terminated surfactants were deposited in the OTS printed area. The gold colloidal solutions were stable, showing little decomposition or aggregation even over a period of months. The HR-TEM data revealed that the gold nanoparticles are 2.8 nm in diameter and have a spherical shape with a narrow particle size distribution (see Appendix, Fig. A.1).

A submicrometer-scaled Au pattern was successfully generated on the surface of the OTS-SAMs deposited silicon substrate by dip-coating, as shown in Fig. 7. The hexagon-like gold arrays were formed over a large area, indicating that successful pattern transference was achieved by the µCP method. The nanoclusters of gold nanoparticles consisting of close-packed hexagons have an average diameter of 10 nm, and the resulting patterned hexagons have a smaller diameter of $370 \pm 2$ nm, as compared to the width of the microwells, viz. $449 \pm 3$ nm. The smaller diameter of the patterned gold hexagons than that of the template used is due to the elastic deformation of the soft PDMS stamp during the µCP process. In addition, the smaller nanostructures formed on the boundaries of the hexagons, as compared to those obtained using the PDMS template with broad micron-sized line patterns, are ascribed to the elastic deformation induced by...
pressing during the μCP process using the elastic PDMS microwells with nano-sized sharp walls. The elastic deformation is one of the known disadvantages of the PDMS stamp. Metal or polymer patterns obtained by μCP using a PDMS stamp with micron-sized line patterns or with a flat surface have flat and non-close-packed patterns, due to the use of templates with a micrometer-scaled regular spacing [13,15–17], but we successfully established a method of fabricating ordered nanopatterns consisting of closely packed assembled nanoparticles by using a self-assembled pre-patterned porous film.

3.4. Two-dimensional assembly of colloidal particles on modified PDMS surface

By using the patterned PDMS microwell, we also achieved the fabrication of an ordered 2D assembly of PMMA colloidal spheres on the hydrophobic PDMS microwells. In the self-assembly process using colloidal particles, there are three major forces operating on the colloidal particles as the liquid medium is dewetted: gravitational force, capillary force and electrostatic force. Among these three, the gravitational force is negligible in the case of latex particles, due to the similarity of their density to that of water. Although the capillary force plays the most important role in the self-assembly process, an additional effect such as a repulsive electrostatic interaction is needed to remove the particles randomly adhered to the surface of the substrate. From this point of view, it might be necessary to modify both the surfaces of the colloidal particles and the substrate by applying an appropriate functional group, and this procedure has been demonstrated in several reports [29,30]. We treated the non-charged microwell surfaces with PAH in order to obtain a positive surface charge for the sake of ensuring the reliable adhesion of PMMA with negative surface charge, resulting in electrostatic assembly between the particles and the patterned PDMS. The PAH layer was formed when a PDMS microwell was immersed in a PAH solution for 10 min, which is ascribed to the hydrophobic attraction between the PDMS surface and the adsorbing polymer chains in PAH. The PMMA surfaces have negative potentials of $-50 \text{ mV}$ [31], presumably due to the termination of the polymer surface by the sulfate group of the initiator.

The SEM images of the PMMA assembled on the PDMS samples are shown in Fig. 8. The microwell with structural dimensions of 449 nm in width and 103 nm in depth for one hexagon, as shown in Fig. 5, produced the self-assembled PMMA crystals with non-close-packing hexagonal arrays in the microwells. The center-to-center distance between the PMMA particles was $500 \pm 2 \text{ nm}$, which is larger than the diameter of one particle, indicating the formation of a non-close-packed array of the colloidal particles in the crystal, due to the interparticle spacing between the particles. Each microwell has only one PMMA particle. Both capillary and electrostatic attractive forces [32–34] act toward the moving colloidal particles and the surface of the microwells as the
liquid medium is dewetted by meniscus-thinning and, thus, the particles that floated from the substrate due to the repulsive electrostatic interaction are trapped into the microwells by absorption due to the capillary action, and the excess ones in the top layer, which are in physical contact with the ones adhered in the microwells, are taken away along with the dewetted liquid, resulting in the deposition of only one colloidal particle per microwell.

Self-assembled particle arrays using patterned templates formed by lithographic etching [32] or electrodeposition [33] have been demonstrated in several studies, but these methods require special techniques which are complex and generally produce micrometer-scaled patterned templates as well as requiring a long time to obtain a desirable result, even several days. We present a feasible and time-saving self-assembly technique which can be used to obtain highly ordered colloidal crystals using PDMS microwells. Moreover, the prepared crystals having regular intervals can serve as templates to produce multidimensional nanostructures through layer-by-layer growth using monodispersed [35] or binary colloidal particles [36,37].

4. Conclusions

We demonstrated a facile and reproducible method of fabricating self-assembled 2D gold nanopatterns with an ordered hexagonal array on a silicon substrate from a patterned PDMS microwell by combining two well-established methods, µCP and dip-coating, by means of which successful pattern transference and the formation of nanopatterned structures by the soft-lithographic technique were accomplished. We present a self-assembly technique for ordered two-dimensional arrays of spherical polymer particle assemblies on pre-patterned PDMS relief structures modified with a poly-electrolyte, showing self-assembly by electrostatic particle–surface interaction. The electrostatic particle–surface interaction induced by the surface modification of the substrate may dominate the interaction between the colloidal particles. These highly ordered 2D particle assemblies have applications in many areas, such as optoelectronics, photonics and biotechnologies.

Acknowledgements

This research was supported from the Brain Korea (BK) 21 program, KISTEP (Program No. M1-0214-00-0228), the Korea Research Foundation Grant funded by Korean government (MOEHRD) (KRF-2005-005-J11902) and the National Research Laboratory Program of Korea Science and Engineering Foundation (Program No. ROA-2007-000-10020-0).

Appendix A

See Fig. A.1.
References