Template directed assembly of dynamic micellar nanoparticles

Kevin A. Arpin, James H. Pikul, William P. King, Hongyou Fan and Paul V. Braun

Received 8th June 2011, Accepted 12th August 2011
DOI: 10.1039/c1sm06078c

The ability to pattern functional nanoparticle arrays in multiple dimensions will enable future devices which exhibit functions that cannot be realized using unstructured nanoparticle arrays. Here we demonstrate the unique assembly properties of dynamic micellar nanoparticles by combining a top-down lithographic nanopatterning technique with a solution-based bottom up self-assembly. The templates for the directed self-assembly of the micelles consisted of arrays of cylindrical recess features fabricated by nanoimprint lithography. Silica was coated on this patterned substrate and subsequently selectively functionalized with a positively charged molecular monolayer (N-(3-Trimethoxysilylpropyl) diethylenetriamine) to regulate the micelle-surface interactions. The self-assembled block co-polymer polystyrene-b-poly(4-vinyl pyridine) (PS$_{480k}$-PVP$_{145k}$) micelles were approximately 325nm in diameter in aqueous solutions (pH = 2.5) and 50nm in diameter in the dry state. The average number of micelles assembled per feature increased from less than 1 to 12 with increasing feature diameter in the range of 200nm–1μm. Using a 2D model for maximum packing of circles in circular host features, the effective sphere size of the micelles during assembly was calculated to be 250nm in diameter. Thus, the micelles exhibited three characteristic sizes during assembly, 325nm in bulk solution, 250nm during assembly, and 50nm in the dry state. This dramatic variation in nanoparticle volume during the assembly process offers unique opportunities for forming nanometre scale, multidimensional arrays not accessible using hard sphere building blocks.

Introduction

Multidimensional patterning with precision, speed, and reproducibility at the nanometre scale is crucial for development in many fields including memory storage, metamaterials, photonic crystals, plasmonics, solar energy harvesting, energy storage, and tissue engineering. Functional, multidimensional patterns at the nanometre scale will enable novel devices and properties that cannot be realized using unstructured materials. Conventional top-down photolithographic techniques are capable of producing features at the nanometre scale, however, are generally limited to planar geometries and select materials. Bottom-up self-assembly of materials offers unique opportunities to assemble matter in multiple dimensions at low-cost, however, understanding and optimizing self-assembly of functional structures remains an unsolved challenge and an active field of research.

Organization of matter at the nanometre scale over large areas with low defect density can be accomplished by combining top-down lithographic nanopatterning with bottom-up self-assembly. A number of research groups have followed this approach using micrometre or sub-micrometre sized rigid particles and patterned substrates. One versatile approach pioneered by Xia resulted in defect-free assembly of micrometre sized spherical particles over large areas. Using that approach, capillary forces directed spheres into lithographically defined features during de-wetting of an aqueous solution from a patterned surface. Capillary forces, however, decrease with decreasing particle size and competing effects including Brownian motion and electrostatic forces can play a significant role in assembly. Alivisatos et al. was able to control the assembly conditions, most notably, the template contact angle, to mitigate these competing factors and achieve accurate assembly of 8nm sized metallic and semiconducting nanoparticles into lithographically defined features. In all these works, the physical dimensions of the assembled building blocks remained constant during the assembly process.

Herein, we investigate the potential for the template directed assembly of dynamic objects, namely self-assembled micelles. The micelles consist of a hydrophobic core (polystyrene) and a positively charged, hydrophilic shell (polyvinyl pyridine).
size of the micelles is closely related to the pH of the solution; at pH 2.5 the PVP chains are charged and thus repel each other, causing the shell to swell and the micelle diameter to reach 325nm. When dry, the micelles collapse to be 50nm in diameter. The dynamic PVP shell swell and condense over a range of ~275nm, changing in volume by a factor of 275, offering unique opportunities for self-assembly by allowing the formation of nanometre scale patterns and architectures that are not accessible using hard building blocks (e.g. non-close-packed structures). These micelles are also attractive as carriers of nanoparticles and other species that otherwise would not readily assemble in lithographically patterned substrates.2,28–30

Experimental

Dynamic building blocks—self-assembled micelles

Dynamic micelles for bottom-up self-assembly were fabricated using the block co-polymer polystyrene-b-(4-vinyl pyridine), PS480k–PVP145k, purchased from Polymer Source Inc. with no further purification. The block co-polymer was dissolved in N,N-dimethylformamide (DMF). An aqueous solution of HCl (pH 2) was added drop wise to the DMF/polymer mixture while stirring at 350rpm. In a typical synthesis, 5mL of the aqueous solution was added to 50mg PS-PVP block co-polymer dissolved in 1mL DMF. More extensive characterization of the micelles will be published in the near future.31

Template fabrication and selective functionalization of charged monolayers

Fig. 1 outlines the process used to fabricate templates for directed micelle assembly. A soft nanoimprint lithography approach was used to define cylindrical recess features in SU-8 (Micro-Chem, SU-8 2010) thin films using a polydimethylsiloxane (PDMS) mould. Nanoimprint lithography is a powerful, low cost technique for the fabrication of large area (10mm²) arrays of features with <100nm resolution.32,33 Various arrays were fabricated with different feature sizes, ranging from 200nm–1μm in diameter. After imprinting, ~25nm of silica was evaporated on the patterned SU8. A molecular monolayer was then printed on the top surface of the template using a planar PDMS stamp that was inked with a solution of N-(3-Trimethoxysilylpropyl) diethylenetriamine (DEAS) in hexane. Prior to printing, the silica surface was cleaned using an oxygen plasma treatment. The inked stamp was brought into conformal contact with the silica-coated patterned substrate for 30 s and then the substrate was rinsed with ethanol. During printing, only the top surface of the patterned substrates was in conformal contact with the PDMS stamp as a result of the planar stamp geometry. Thus, DEAS molecular monolayers were printed only on the top surface of the patterned substrates and generally not in the bottom of the recessed features. The monolayer printing procedures were characterized using atomic force microscopy (Asylum Research MFP-3D) and ellipsometry (Gaertner L116C fixed angle, single wavelength, 632nm) on test samples printed on silicon wafers, verifying that monolayers were being printed uniformly over large areas. AFM analysis showed RMS roughness values ranging from 0.12nm to 0.13nm and no evidence of large polymerized species. For all concentrations, the thickness of the DEAS layer was measured to be 2.5nm using ellipsometry, consistent with ellipsometric measurements performed on similar aminosilane monolayers.34,35

The patterned and functionalized templates were vertically dip coated (Fig. 2) in the micelle solution (pH = 2.5). After dip coating, the template was rinsed with copious amounts of distilled water. The assembled micelle arrays were imaged using a Hitachi S-4800 high-resolution field emission scanning electron microscope. The template feature size was measured using ImageJ (public domain image processing program downloaded from the National Institute of Health). All measurements made
using these images were calibrated using the known center-to-center distance of the imprint patterns.

**Results and discussion**

**Micelle packing in patterned substrates**

The size of the micelles was closely related to the pH of the solution; at pH 2.5 the PVP chains were charged and thus repelled each other, causing the shell to swell and the micelle diameter to reach 325 nm as determined by dynamic light scattering. However, when dry, or in higher pH solutions, these chains condensed, decreasing the overall size of the micelle. The dynamic PVP shell could swell and condensed over a range of ~275 nm, changing in volume by a factor of 275. Patterned substrates for the directed self-assembly of these dynamic micellar building blocks were fabricated using a soft nanoimprint lithography technique,\(^ {32,33}\) useful for manufacturing large area, defect free, recessed features with varying dimensions and shapes. A simple dip coating procedure was used to drive template directed self-assembly of micelle arrays (Fig. 2). Capillary forces alone during de-wetting (as the drying line passes down the substrate) were insufficient to direct assembly of the dynamic micelles into the template features. After dip coating slightly negatively charged substrates (un-functionalized silica in a pH = 2.5), directed micelle assembly was not observed; micelles non-specifically deposited in the recessed features and on the top surface of the template (Fig. 3a).

It is known that electrostatics can significantly influence template directed assembly.\(^ {34,35}\) This effect is of course strongest when the particles are highly charged, as is the case for this study. Using this effect to our advantage, we spatially modified the electrostatic environment of the template to assist with the directed assembly of micelles. A soft lithography approach was utilized to selectively functionalize the top surface of the template with a positively charged monolayer, leaving the bottom of the features slightly negatively charged (silica at pH 2.5). After printing, only the top surface of the templates experienced a charge inversion, going from slightly negative to positive. This charge inversion process was vital to achieving template directed assembly of dynamic micelle arrays. Fig. 3b presents an image of representative micelle assembly observed after dip coating onto substrates selectively functionalized with DEAS; micelles are directed into the recessed features with no micelles remaining on the top surface.

Previous studies have shown that the number of building blocks that can be assembled into a template feature is determined by the ratio between the dimensions of the template feature and the dimensions of the building block.\(^ {36}\) This relationship was studied by assembling micelles into various templates, each with a different characteristic feature dimension. The diameter of the feature, as measured at the top surface of the patterned substrates, was used as the characteristic feature dimension (\(D_{\text{Template}}\)). Not surprisingly, the average number of micelles per feature (\(N_{\text{AVG}}\)) increased as \(D_{\text{Template}}\) increased from 200 nm to 1 \(\mu\)m. The average number of micelles per feature was calculated by manually counting the number of micelles observed in at least 50 features. The counted averages were plotted as a function of the area per template feature (calculated using

\[ D_{\text{Template}} = \text{NAVG} \]

\[ D_{\text{Template}} \] and displayed in Fig. 4. The relationship between \(N_{\text{AVG}}\) and feature size was reproducible over large areas of each substrate and multiple samples. Representative distributions of count data for three different feature sizes (0.25 \(\mu\)m, 0.61 \(\mu\)m, and 1.04 \(\mu\)m in diameter) are presented in Fig. 5. The distributions of the count data were close to normal around the calculated averages demonstrating that the data is generally not clustered and is uniformly distributed over large areas.

Due to the dynamic nature of the micelles, the characteristic size of our building blocks during template directed assembly was significantly different from the characteristic size either in bulk solution or the dry state. We considered assembly after monolayer printing using a solution of 0.2 mM DEAS in hexane to be the case of maximum packing. The effect of DEAS concentration on micelle assembly is presented in Fig. 4 and will be explained, in detail, in the next section. To summarize, lower solution concentrations of DEAS resulted in non-specific attachment of micelles on the top surface of the patterned substrates. However, at higher solution concentrations of DEAS, we suspect some DEAS is deposited in the bottom of the features, altering the micelle-surface interaction, and decreasing the observed \(N_{\text{AVG}}\). The assembly data acquired for this
concentration of DEAS (0.2mM) was compared to a 2D model for the maximum packing expected for circles in circular features. Since the depth of the cylindrical features (250nm) is less than the diameter of the micelles in bulk solution (325nm), and the micelles are repulsive, we expect monolayer packing and thus we can use this 2D model to understand the micelle assembly. Using this 2D model, the ratio between the diameter of a host circle and the diameter of circles being packed was plotted in Fig. 6 as a step function. The average number of micelles per feature as a function of the ratio between the diameter of the host feature and the diameter of the micelles (black dots). Assuming a micelle diameter of 250nm, the counted data for $N_{AVG}$ as a function of this ratio matches closely to the calculated maximum packing density.

The dramatic shrinking of the micelles while remaining in a defined location (Fig. 7), and note that the particles are almost never touching in the dry state (Fig. 3b), offers unique opportunities for the self-assembly of functional, multidimensional, nanometre scale arrays. Moreover, these dynamic structures represent a bridge between the larger scale of top down lithographic methods and the fine nanometre scale achievable using bottom up self-assembly. The manufacturing of nanometre scale architectures will not be possible using one of these techniques alone, however, it will be the combination of these two techniques that will be at the forefront of research involving the
DEAS monolayer printing and micelle assembly

Slight alterations in the DEAS printing protocol significantly altered the observed $N_{AVG}$ for a given template feature size. More specifically, the concentration of DEAS in hexane or the printing time altered $N_{AVG}$ observed after assembly for a given feature size. We quantified this effect by studying assembly using three different concentrations of DEAS in hexane for printing while keeping the printing time constant (30 s). The resultant $N_{AVG}$ as a function of feature size for the three DEAS concentrations are presented in Fig. 4. Increasing the concentration of DEAS in solution resulted in fewer average numbers of micelles per feature (lower $N_{AVG}$ for all feature sizes).

We hypothesize that this difference in assembly could be attributed to DEAS depositing inside the recessed features during printing by diffusing through the vapor phase. DEAS printed inside features could alter the interaction energy of the micelles with the silica surface. Micelles remain inside the recessed features during drying because the electrostatic interaction energy between the slight negative charge of the bottom of the recessed feature and the positive charge of the micelles is greater than the capillary force trying to keep the micelles in solution during de-wetting (drying). If this electrostatic interaction energy is decreased, potentially by the deposition of positively charged DEAS molecules, the capillary force may dominate, pulling micelles out of recessed features during de-wetting.

To support this hypothesis, a lower molecular weight (higher vapor pressure) amino silane, 3-aminopropyltriethoxysilane (APS), was printed on the top surface of nanoimprint templates instead of DEAS, using the same printing procedure. After dip coating, the APS functionalized templates showed almost no micelles remaining on the template (inside the recessed features or on the top surface) for all three concentrations (0.2mM, 0.3mM, 0.4mM). The APS experiment suggests that the silane volatility alters the resultant electrostatic environment of the bottom of the recessed features. While DEAS is less volatile than APS, we expect that some DEAS is diffusing through the vapor phase into the recessed features, most prominently at higher DEAS concentrations. Thus, vapor phase transport most likely contributed to the observation that increasing the concentration of DEAS in hexane resulted in few micelles per feature.

Conclusions

Here we demonstrate the template directed assembly of dynamic PS-PVP core-shell micelles into features defined via soft nanoimprint lithography. Capillary forces alone were insufficient to direct micelles into the template features. A positively charged molecular monolayer was selectively printed on the top surface of the patterned template providing a surface with coupled topographic and electrostatic features. This monolayer was essential to achieving successful micelle assembly over large areas. The dynamic micelles had 3 characteristic diameters observed at different stages of the assembly process: 325nm in bulk solution, 250nm during assembly, and 50nm in the dry state. This work here is the first example of assembly of dynamic objects into topographic features, and we expect that these three dramatically different dimensions could be exploited for applications in nanometre scale assembly that cannot be achieved using hard sphere particles.

Acknowledgements

The authors thank Dr Mark Losego, Dr Zaicheng Sun, and Andrew Carlson for experimental assistance and useful discussions. This project was funded by the National Institute for Nano-Engineering and Sandia National Laboratory’s LDRD Program. H.F. also acknowledges support from the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering. This research was carried out in part in the Center for Microanalysis of Materials, UIUC, which is partially supported by the U.S. Department of Energy under grants DE-FG02-07ER46453 and DE-FG02-07ER46471.

Notes and references

10. H. A. Atwater and A. Polman, Nat. Mater., 2010, 9, 205–213.
31 Z. Sun and H. Fan, unpublished work.