

Colloidal lithography with crosslinkable particles: fabrication of hierarchical nanopore arrays

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We demonstrate that colloidal lithography with self-assembled monolayers of crosslinkable polymeric particles can be used to create hierarchical arrays of nanopores on substrates.

Two-dimensional (2D) porous substrates have attracted great attention for a wide range of applications including chemical microcontainers,¹ surface-plasmon resonance biosensors,² catalytic supports,³ and photonic crystals.⁴ Recently, self-assembled colloidal particle arrays have been studied intensively because they provide a simple and cost-effective lithography mask to produce patterned pores.⁵ Colloidal lithography uses a 2D array of particles as a shadow mask or the interstices between the particles as open windows for reactive ions to create patterned bumps or pores on a substrate.⁶ This method allows a considerable freedom to control both the feature dimensions by varying the particle size and the shape of nanopores by using multilayered particle arrays or angle-resolved etching.^{6b}

In addition to allowing bulk nanopore arrays, the structural hierarchies are an essential step towards practical applications of these substrates.⁷ Several approaches have been developed to deposit colloidal particles selectively, including self-assembly on chemically modified surfaces,⁸ direct stamping,⁹ and colloidal photoresists.^{1b} These particle masks can produce hierarchical arrays of nanopores by colloidal lithography.

In this report, we demonstrate a photolithographic process to produce hierarchical arrays of nanopores with colloidal photoresist. Photolithography is a well developed process for precisely defined complex patterns with micrometre scales. To do this, we synthesized poly(styrene-*co*-glycidyl methacrylate) (PSGMA) particles, which were crosslinkable by themselves under UV-exposure with no need of crosslinkable monomers in a colloidal medium^{1b}

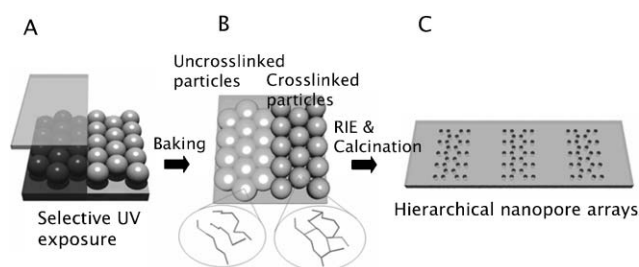
Scheme 1 shows the overall process for colloidal lithography with the crosslinkable particles. First, the PSGMA particles were deposited onto a silicon substrate and exposed to UV light through a mask (Scheme 1A). During baking at a temperature above the glass transition temperature (henceforth referred to as T_g) of the uncrosslinked PSGMA and below T_g of crosslinked PSGMA, the unexposed particles were deformed but the exposed part of the particle array retained its structure because T_g was increased by crosslinking polymerization of the epoxide (Scheme 1B). Finally, these patterned colloidal particle arrays were used as masks for

reactive ion etching (RIE). The etching proceeded only in the UV-exposed region and produced a patterned array of nanopores on the substrate (Scheme 1C).

Further details of the materials and procedures are as follows. The monodisperse PSGMA particles were synthesized by dispersion copolymerization of styrene and glycidyl methacrylate. Styrene (55 mol), glycidyl methacrylate (16 mol), and thermal initiator, 2,2'-azobis(2-methylbutyronitrile) (1 wt% of monomer) were dissolved in 100 mL of ethanol. The size of particles was controlled by a stabilizer, poly(*N*-vinylpyrrolidone) ($M_w = 49\,000$, Junsei Chemicals Co.) and ranged from 500 nm to 1 μm in diameter with a polydispersity of 1–2%. We added 1 wt% cationic photoinitiator (Irgacure 250, diaryliodonium salt in propylene carbonate) into the colloidal solution. The cationic photoinitiator, which was incorporated into the particles by diffusion, decomposed to yield protons when exposed to UV light and consequently caused the ring-opening polymerization of the epoxide in PSGMA.¹⁰

The photopolymerization was confirmed by the difference in the FT-IR spectra of PSGMA before and after UV exposure and baking. As shown in Fig. 1, considering the aromatic ring band (1500 cm^{-1}) as a reference, the decrease of the absorption peak around 915 cm^{-1} (oxirane stretch) and the peak at around 3500 cm^{-1} (hydroxy stretch) revealed the ring-opening of the epoxide, which created a hydroxy group during photopolymerization.¹¹ Meanwhile, T_g of the PSGMA particles, measured by differential scanning calorimeter (Dupont, DSC 2010) was increased from 93–95 °C to 98–100 °C after UV exposure.

The colloidal solution was spin-cast on silicon (Si) wafer. In doing this, both the spin speed and the concentration of colloidal dispersion were controlled to obtain 2D colloidal arrays. Generally, at high spin-speeds, the ethanol was washed out so rapidly that evaporation occurred over the entire substrate, resulting in a randomly organized colloidal array with a considerable defect density. We found that the evaporation of



Scheme 1 Photolithographic patterning of 2D colloidal crystals and hierarchical colloidal lithographic patterning of a substrate.

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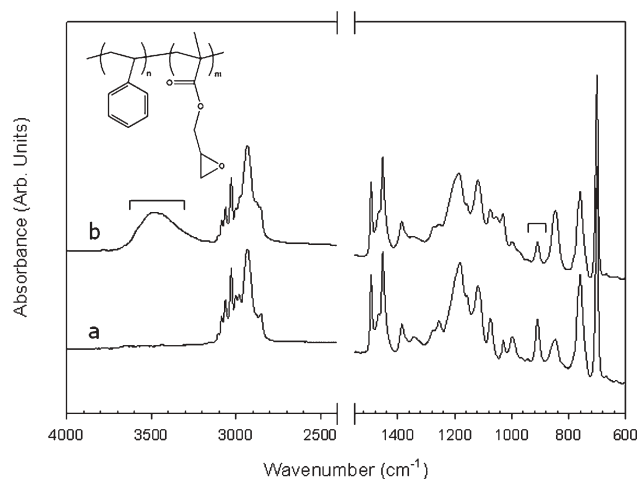


Fig. 1 FT-IR spectra of PSGMA (a) before and (b) after photopolymerization. Inset shows the chemical structure of PSGMA.

ethanol occurred from the center to the outside at a spin speed around 1000 rpm and an ordered colloidal array was able to be formed as shown in Fig. 2. The particle size was 630 nm in diameter and the average domain size was around $20 \times 20 \mu\text{m}^2$. Long range order of hexagonal close packing can be seen from 2D Fourier transform of the corresponding SEM image as shown in the inset of Fig. 2.

The colloidal array was exposed to a UV light through a grating pattern mask with a $10 \mu\text{m}$ period. Here, the deposition of decalin reduced the scattering by the colloidal particles and produced a well-defined pattern. The SEM image in Fig. 3a shows a patterned colloidal crystal after UV exposure and subsequent baking and the inset is an optical microscope image of the striped pattern. Specifically, during the baking at $98 \text{ }^\circ\text{C}$, the exposed particles in the right hand sides of Fig. 3b and 3c began to flow but soon sustained an oblate spheroidal shape since T_g increased rapidly by crosslinking of PSGMA, while the unexposed particles continued to deform and eventually fused together during melting as noted from the left hand sides of Fig. 3b and 3c. It can be clearly seen from Fig. 3c that the interstices between the unexposed particles disappeared. Meanwhile, we found that lateral expansion by forming an oblate shape suppressed the possible creation of cracks

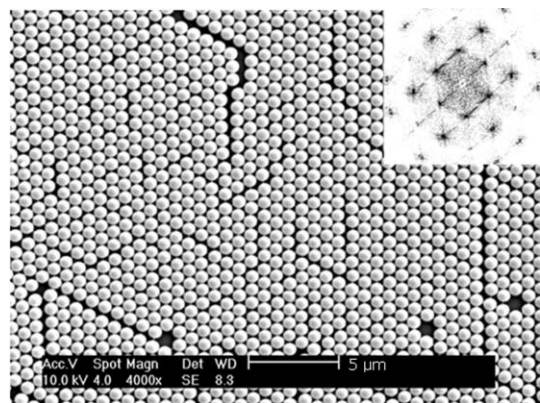


Fig. 2 SEM image of the two-dimensional colloidal assembly of PSGMA particles. Inset shows the Fourier transform of the particle array.

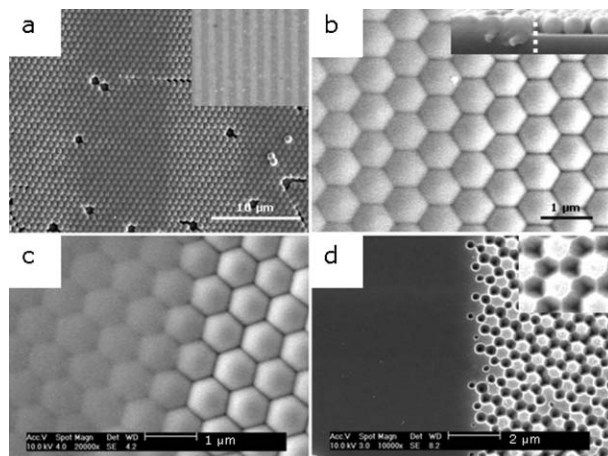


Fig. 3 (a) SEM image of the patterned two-dimensional colloidal crystal. Inset shows an optical microscope image of the patterned colloidal crystal. Magnified SEM images after post-exposure baking for 5 min (b) and for 7 min (c). Inset in (b) shows a cross-sectional SEM image around the boundary between the exposed and unexposed parts of the colloidal array. (d) SEM image of the nanobored silicon substrate by colloidal lithography using the prepatterned colloidal crystal. Inset in (d) shows the magnified image of the pore arrangement.

due to thermal expansion of the polymeric particles during annealing.¹² Moreover, micro-cracks in a closely packed domain were reduced during baking.

Subsequently, the patterned colloidal crystal was used as a mask for RIE of the Si (111) substrate. RIE with plasma was performed with a gas mixture of SF_6 (40 sccm) and O_2 (4 sccm) under a pressure of 100 mTorr at a power density of 50 W. The reactive plasma produced volatile fluorinated silicon with the substrate, and thus etched the substrate through the voids between the colloidal particles.¹³ Meanwhile, the presence of oxygen assisted the etching both of the Si substrate by increasing reactive fluorine radicals and of the polymeric particles to widen the interstices. Remarkably, as shown in Fig. 3d, the etching was achieved only in the UV-exposed regions and produced an ordered periodic array of triangular pores after removal of the polymeric particles by calcination at $500 \text{ }^\circ\text{C}$.

In summary, we demonstrated that the photolithographic patterning of 2D colloidal crystals can be used to create hierarchical arrays of nanopores by colloidal lithography. The hierarchical pattern generation was achieved by using crosslinkable polymeric particles. When the particle array was exposed to UV light through a mask, the exposed particles were not substantially deformed during baking above T_g of the uncrosslinked particles, while the particles in the unexposed region were deformed and the interstices between the unexposed particles vanished. Therefore, the RIE etching through the interstices between the particles was only achieved in the exposed regions. The present method of hierarchical patterning can be used as a practical design tool for nanopatterned substrates and could be extended to deposition of various functional materials to form patterned nanoparticle arrays.

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