

Polymer Communication

Fabrication of the periodic nanopillar arrays by heat-induced deformation of 2D polymer colloidal monolayer

Yue Li, Weiping Cai *, Bingqiang Cao, Guotao Duan, Fengqiang Sun

Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, Anhui, People's Republic of China

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Abstract

A strategy based on heat-deformable monolayer polymer (polystyrene) colloidal template and precursor solution-dipping is presented to fabricate large-scale nanopillar arrays. In the method, the appropriate heating time of the polymer colloidal templates is a key factor. Fe_2O_3 and silica hexagonal periodic triangular prism nanopillar arrays with an aspect ratio of about 1.5:1 were successfully fabricated. This route is also applicable for synthesis of other material nanopillar arrays and opens a new way to create patterned 1D nanostructures for applications in sensor arrays, piezoelectric antenna arrays, optoelectronic devices, superhydrophobic and self-cleaning surfaces.

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1. Introduction

In recent years, polymer colloidal crystals [1–3], as templates, have attracted much attention in fabrication of versatile specially structured functional materials. Three-dimensional (3D) colloidal crystals have usually been used both for preparation of highly periodic porous materials [4–9], which have many potential applications, such as, photonic crystals [4–6], bio-sensors [7], waveguide materials [8], optoelectronics [9], and for the 2D versatile nanopatterned surfaces [10,11]. Two-dimensional monolayer colloidal crystals, serving as more versatile fabrication templates, have also been used to generate various 2D ordered nanostructured arrays, such as, ordered pore films (by the spray-pyrolysis [12,13], the sol-gel technique [13–15] and solution-dipping template synthesis strategy [16]), the periodic metal, metal oxide, polymer nanoparticle arrays [17–19], nanoring arrays [16], nanochain, nanogap, nano overgap arrays (by metal evaporating deposition [17]) and the nanowell arrays (by CF_4 plasma striking [20]). In addition, using metal periodic nanoparticle arrays as catalyst, large-area ZnO nanorod arrays have been fabricated by epitaxial approach on different substrates [21].

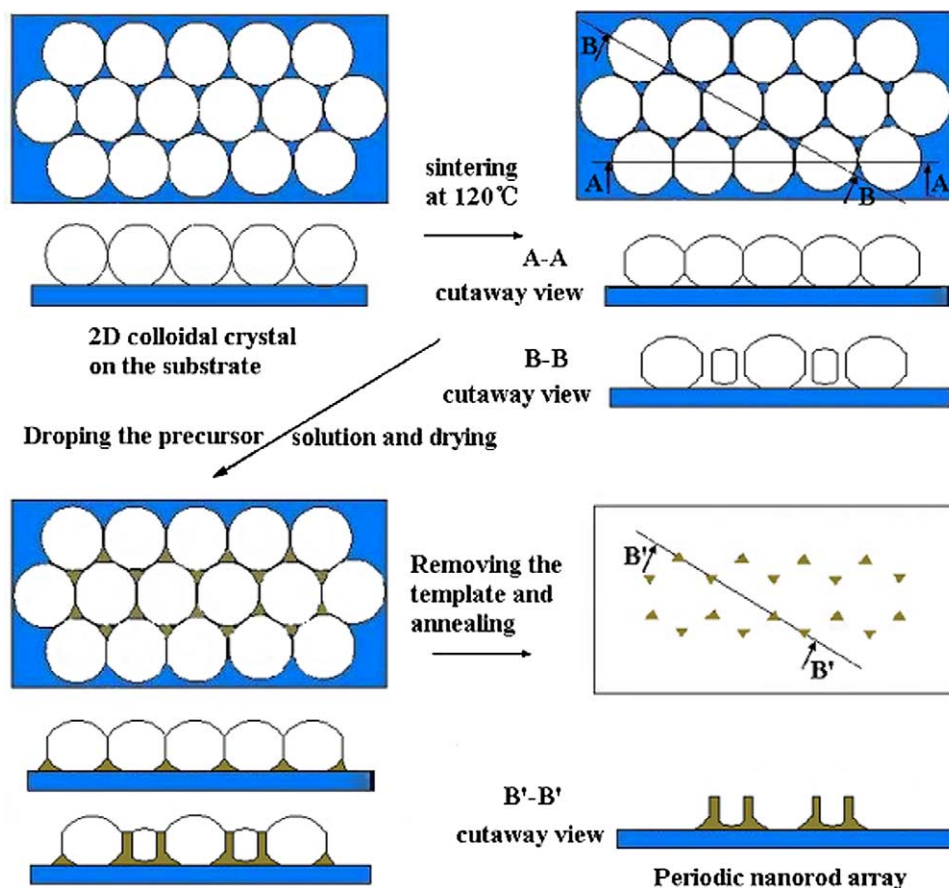
Here, we present a simple approach to prepare large-scale hexagonal nanopillar arrays by solution dipping method based on the 2D polymer colloidal monolayers, to the best of our knowledge, which is the first report for periodic nanopillar arrays directly using them as templates. In this method, the monolayer polymer colloidal spheres are deformed so much by heating that the triangular prism channels can be formed at the interstices among them. And then, using such colloidal monolayer with the channels as template, periodic nanopillar arrays can be fabricated. Taking Fe_2O_3 as an example, which is a kind of important functional material and widely studied in powders [22], $\text{Fe}_2\text{O}_3/\text{SiO}_2$ composites [23], particle arrays [24], 3D porous structures [25], the fabricating process is described in this communication. This method makes the applications of the polymer colloidal crystal templates more plentiful and opens a new way to produce patterned 1D nanostructures with small aspect ratio for potential applications in sensor arrays, piezoelectric antenna arrays, optoelectronic devices, interconnects [21], superhydrophobic and self-cleaning surfaces [26].

2. Experimental

Ordinary glass substrates were ultrasonically cleaned in acetone and then in ethanol for 1 h, as previously described [27, 28]. Polystyrene sphere (PS) suspensions (2.5 wt% in water, surfactant-free) were bought from Alfa Aesar Company (standard deviation of the diameter of PSs is less than 5%). Large-scale monolayer polymer colloidal crystals were

* Corresponding author. Fax: +86 551 5591434.

E-mail address: wpcai@issp.ac.cn (W. Cai).



Scheme 1. Schematic illustration of the periodic hexagonal nanopillar arrays.

prepared on the cleaned substrates by spin-coating [27] on a custom-built spin-coater.

The monolayer colloidal crystals on the glass substrates were put into an oven and sintered at 120 °C for a certain time, then taken out and cooled to room temperature. Subsequently, a droplet of 0.5 M $\text{Fe}(\text{NO}_3)_3$ solution (ca. 10 μl) was applied onto the sintered colloidal monolayer with a quantitative pipette, and it could infiltrate into the interstices among PSs. Finally, the sample was dried and annealed at 400 °C for 2 h to make the precursor decompose completely and the PSs template to be burnt out. The periodic hexagonal Fe_2O_3 nanopillar arrays were thus fabricated. The whole preparation process is schematically illustrated in Scheme 1.

The synthesized sample was characterized by field emission scanning electronic microscopy (FE-SEM) (Sirion 200). X-ray diffraction (XRD) spectra were measured on Philips X'Pert using $\text{Cu K}\alpha$ line (0.15419 nm).

3. Results and discussion

The inset in Fig. 1(a) shows the FE-SEM image of monolayer polymer colloidal crystal with 1000 nm PSs in diameter fabricated by spin-coating method. We can see that the spherical PSs take on hexagonal close-packed lattice structures and contact with each other by quasi point style in monolayer. Using it as template, we can only get the ordered

pore array by 0.5 M precursor solution and each pore exhibits a shape of truncated-hollow sphere (Fig. 1(a)).

However, when such monolayer polymer colloidal crystals are sintered at 120 °C for 15 min, their morphologies exhibit a large change. Due to heating at the temperature above the glass transition of PSs ($T_g \approx 100$ °C) [29–31], PSs are obviously deformed, which leads to contact evolution between neighbouring PSs from quasi point contact (see the inset in Fig. 1(a)) to facet contact (see the inset in Fig. 1(b)). Correspondingly, the interstices among the PSs in the polymer colloidal monolayer become smaller from the top view, meanwhile, triangular-shaped channels are formed among PSs.

Interestingly, based on such deformed templates and the strategy shown in Scheme 1, we obtained the ordered nanopillar arrays, as illustrated in Fig. 1(b) and (c). Their morphologies are very different from those obtained by the templates without heating. Such nanopillars are of triangular prism shape with an aspect ratio of about 1.5:1. The whole arrays also exhibit hexagonal alignment. The nanopillars do not grow directly on the substrate, but on the nodes of the skeleton network surrounding the previous bottoms of the sintered PSs. However, if over-heating the colloidal monolayer (say 25 min), the channels will almost disappear in the templates (see the inset in Fig. 1(d)). Correspondingly, no pillars will be formed due to no channels in the over-heated template and the morphology takes on regular network, as shown in Fig. 1(d).

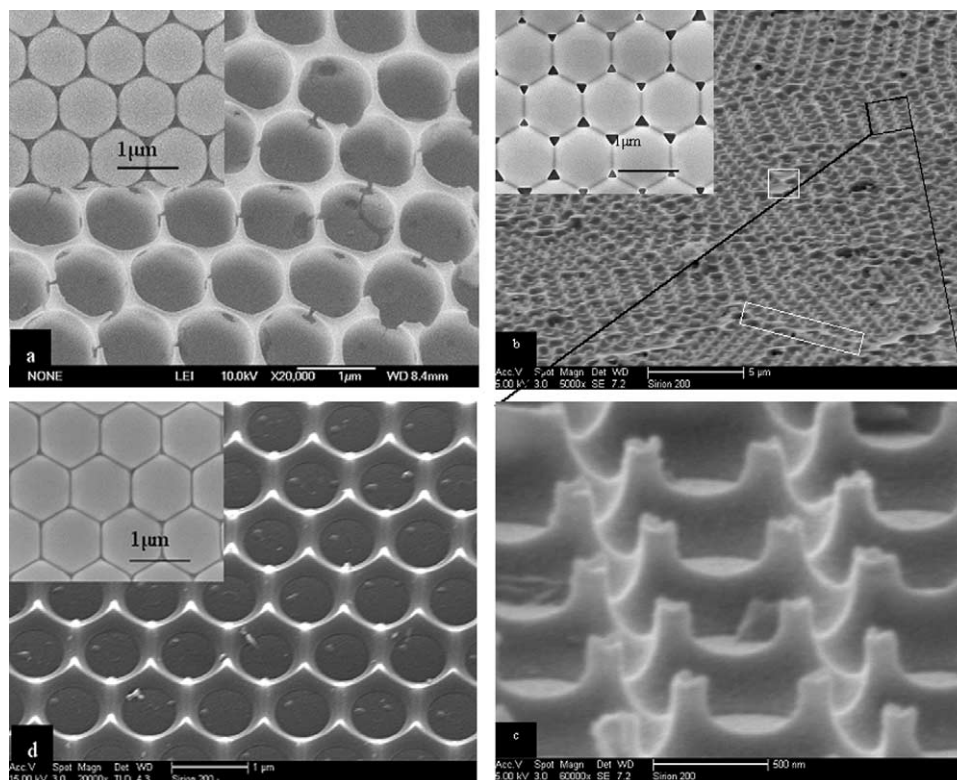


Fig. 1. FE-SEM images of Fe_2O_3 ordered patterns fabricated with 0.5 M $\text{Fe}(\text{NO}_3)_3$ precursor solution, based on monolayer polymer colloid crystal with 1000 nm PSs in diameter sintered for different time at 120 °C. The insets in (a), (b), (d) are colloidal crystal sintered for 0, 15, 25 min, respectively, and (a), (b), (d) are corresponding periodic nanostructures prepared using such templates, (c) is the local magnification of (b).

For these periodic nanopatterns obtained by this method, the corresponding X-ray diffraction peaks are in agreement with the standard values of bulk $\alpha\text{-Fe}_2\text{O}_3$ (Fig. 2), indicating that the ordered structures consist of crystal $\alpha\text{-Fe}_2\text{O}_3$. According to the process above, obviously, the appropriate heating time of the polymer colloidal templates is a key factor to fabricate the periodic nanopillar arrays by this strategy.

Here it should be mentioned that there exist some defects in such large-scale nanopillar arrays, as marked in white frames in Fig. 1(b), which originates from the missing PSs or domain

boundary in the monolayer polymer colloidal crystals. Obviously, such defects can be overcome by improvement of monolayer colloidal crystals in quality.

In addition, if we use the monolayer polymer colloidal template with smaller PSs (350 nm), higher density Fe_2O_3 nanopillar arrays can be also prepared, as displayed in Fig. 3.

Similarly, if adding the silica precursor solution [tetraethyl orthosilicate, alcohol and distilled water (molar ratio, 1:4:20, pH=1)] onto the template (1000 nm PSs in diameter) sintered at

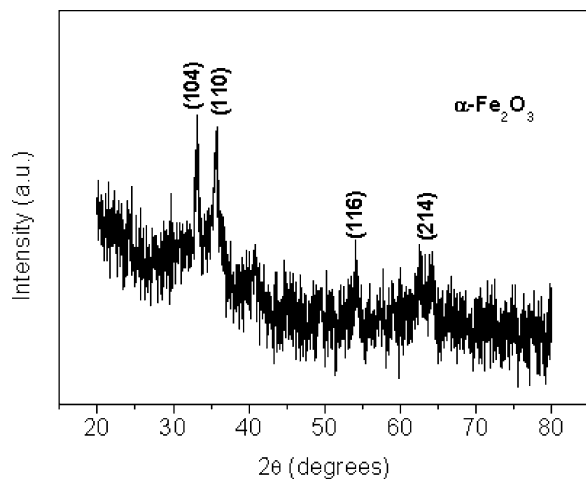


Fig. 2. XRD of ordered nanopattern films fabricated with 0.5 M $\text{Fe}(\text{NO}_3)_3$ solution after annealed at 400 °C for 2 h based on colloidal monolayer crystals.

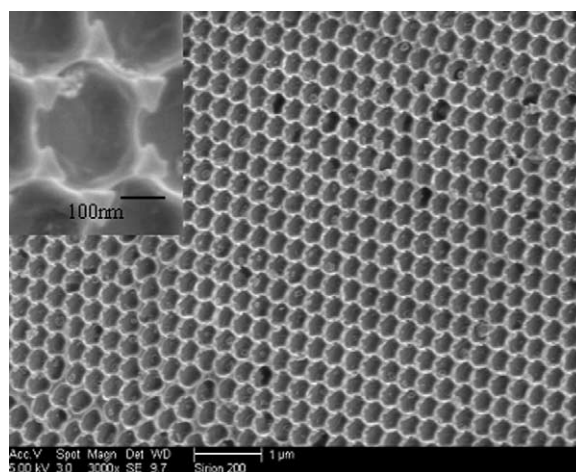


Fig. 3. The morphology of nanopillar array fabricated by monolayer polymer colloidal template with 350 nm PSs in diameter sintered at 120 °C for 6 min. The inset is a local magnified image.

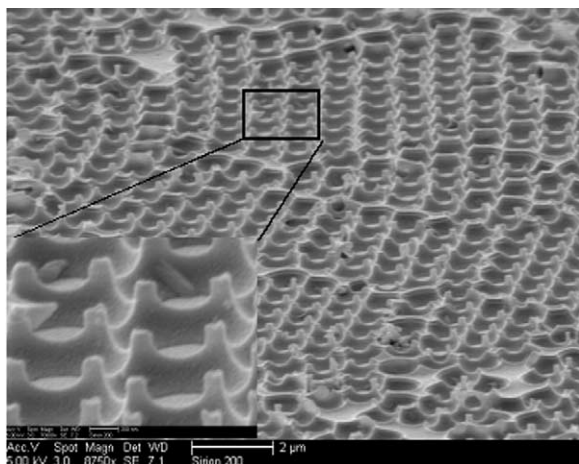


Fig. 4. Morphology of periodic silica nanopillar array formed by sol-gel based on the sintered template. The inset is corresponding local magnification.

120 °C for 15 min, and putting it into a beaker sealed with cover (solvent can evaporate very slowly) to gel (and evaporate) at room temperature for about 7 days, after removing the PSs, we can also obtain the periodic silica nanopillar arrays with an aspect ratio about 1.5:1, as indicated in Fig. 4. Here, the slow evaporation is important, otherwise, the silica gel will easily broken, due to surface stress, as extensively reported [32].

4. Conclusions

In summary, we present a strategy based on solution dipping heat-deformable colloidal monolayer template to fabricate large-scale periodic nanopillar arrays. In this method, well controlling the heating time of the polymer colloidal monolayer template is a key step. Two kinds of large-scale periodic triangular prism nanopillar arrays with short aspect ratio, Fe₂O₃ and silica, have been fabricated successfully by the approach. However, we believe that the method presented in this communication is also applicable for synthesis of nanopillar arrays of other materials. This method opens a new way to create patterned 1D nanostructures for applications in sensor arrays, piezoelectric antenna arrays, and optoelectronic devices, super-hydrophobic and self-cleaning surfaces.

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