

A Universal Approach To Fabricate Ordered Colloidal Crystals Arrays Based on Electrostatic Self-Assembly

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Received July 25, 2010. Revised Manuscript Received October 7, 2010

We present a novel and simple method to fabricate two-dimensional (2D) poly(styrene sulfate) (PSS, negatively charged) colloidal crystals on a positively charged substrate. Our strategy contains two separate steps: one is the three-dimensional (3D) assembly of PSS particles in ethanol, and the other is electrostatic adsorption in water. First, 3D assembly in ethanol phase eliminates electrostatic attractions between colloids and the substrate. As a result, high-quality colloidal crystals are easily generated, for electrostatic attractions are unfavorable for the movement of colloidal particles during convective self-assembly. Subsequently, top layers of colloidal spheres are washed away in the water phase, whereas well-packed PSS colloids that are in contact with the substrate are tightly linked due to electrostatic interactions, resulting in the formation of ordered arrays of 2D colloidal spheres. Cycling these processes leads to the layer-by-layer assembly of 3D colloidal crystals with controllable layers. In addition, this strategy can be extended to the fabrication of patterned 2D colloidal crystals on patterned polyelectrolyte surfaces, not only on planar substrates but also on nonplanar substrates. This straightforward method may open up new possibilities for practical use of colloidal crystals of excellent quality, various patterns, and controllable fashions.

Introduction

To date, assembly and fabrication of colloidal crystals have received considerable attention with respect to their potential applications in biochip devices, sensors, ultrahigh-density optical and magnetic recording media, etc.^{1–4} Harnessing ordered structures of colloidal crystals is also promising for creating a wide spectrum and multifunctional inversed opal structures such as superhydrophobic macroporous photonic crystals with full band gaps.⁵ In addition, the extensive study of colloidal crystals is also deemed as experimentally accessible models for stimulating and understanding interactions behind condensed matter, crystallization, for example.^{6,7}

Self-assembled 2D colloidal crystals are monolayer arrays of colloidal microspheres or nanospheres, which have drawn much attention owing to their successful applications in surface patterning.⁸ For instance, a general and cost-effective strategy named as colloidal lithography is recently well developed for preparing novel diversify structures scaling down to nanometer features, in which 2D colloidal particles provide excellent masks or templates.^{9–11} Despite great importance, a primary requirement for the success of these applications lies in the capability of fabricating colloidal

crystals with excellent quality and controlled fashion.^{12–14} Up to now, a number of methods of 2D colloidal crystals assembly have been well studied, including spin-coating,^{15,16} solvent evaporation,¹⁷ interface self-assembly,^{18,19} microcontact printing^{20,21} etc. Unfortunately, most of these methods are only applicable to planar substrates. Important work focusing on this problem done by Yan et al. showed on the basis of the use of polymer film as glue to provide an efficient interaction between the microsphere “ink” and substrate; they demonstrated a versatility method to prepare colloidal crystals on a nonplanar substrate.²¹ Other related works were recently shown by Meseguer et al., who studied the influence of nonplanar patterned surfaces on the formation of one- and two-dimensional colloidal crystals. They have used the corrugated surface of a digital versatile disk for template surface processing. When the sphere diameter is on the order of the groove width of patterned substrates, a rich variety of particle decorations appear.²² Preparation of 2D ordered colloidal crystals on nonplanar structured surface still remains a challenge.

Thanks to the simpleness and high efficiency, the electrostatic assembly technology becomes one of most important methods for 2D colloidal crystals assembly.^{23,24} The main driving force for the assembly in this technology lies in electrostatic attraction between

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colloidal spheres and substrates with opposite charges; thus, this method is capable of assembling colloidal particles on arbitrary substrates.²⁵ However, owing to this strong electrostatic attraction, the movement of colloidal particles will be confined once they are in contact with the surface of the substrate, which is unfavorable for the preparation of colloidal crystals with high quality. This random sequential adsorption was also predicted by Adamczyk et al. via a Monte Carlo simulation,²⁶ which showed colloid monolayer obtained through this way would adopt a short-range ordered but a long-range-disordered structure.

To improve the quality of self-assembled colloidal crystals, a strategy that can finely modulate interactions between colloidal particles and those with substrates in electrostatic assembly technology is highly desirable.^{27–29} Initial works were undertaken by the Hammond research group, who demonstrated modulating behavior of colloidal particles in the electrostatic assembly process.^{23,30–32} According to their experimental results, density and selectivity of particle adsorption could be controlled over by means of adjusting pH value, ionic strength of colloid suspension, and adding surfactant.²⁷ They further extended this work to fabricate composite particle arrays on patterned polyelectrolyte multilayer templates.²³ Other related works were recently shown by Akashi et al., who studied the adsorption of polystyrene nanospheres that had anionic charges from dispersions onto the surfaces of cationic polymer films quantitatively and kinetically by using a quartz crystal microbalance.³³ Himmelhaus et al. showed the addition of carbodiimide to a suspension of sulfated polystyrene nanoparticles would lead to the formation of an irregular, dense-packed monolayer of self-assembled particles on homogeneous as well as chemically patterned surfaces.³⁴ All these studies are helpful in understanding the electrostatic assembly process, revealing the mechanism and making practical usage of colloidal crystals; nevertheless, the quality of obtained colloidal crystals still needs further improvement.^{35,36}

Meanwhile, electrostatic self-assembly is considered to be able to control the number of self-assembled layers,^{37,38} but so far, ordered colloidal structures with controllable layers have not been achieved. Hattori et al. studied the preparation of composite films consisting of commercially available polyelectrolyte and colloidal silica or titania particles. In their experiment, the thickness of composite films depended on the thickness and the molecular mass of previously coated polyelectrolyte, treatment time, and the concentration of suspension. But they cannot control the number of layers and the degree of ordering.³⁹

In this paper, we demonstrate a strategy of patterning poly(styrene sulfate) (PSS, negatively charged) colloids on poly(acrylamide-*co*-diallyldimethylammonium chloride) (PMA-*co*-PDDA, positively charged in water phase) modified substrate. Combining 3D self-assembly of colloidal crystals with electrostatic layer-by-layer (LBL) assembly techniques, 2D ordered arrays of colloidal crystals are obtained. We divide the strategy into two steps: one is 3D assembly of PSS particles in ethanol phase, and the other is electrostatic adsorption in water phase. Assembly in ethanol phase avoids ionization of polyelectrolyte, thus eliminating electrostatic attractions between colloids and substrate that cause the confinement of colloidal particle in the assembly process. As a result, high-quality colloidal crystals are easily generated. Subsequently, top layers of colloidal spheres are washed away in the water phase, whereas well-packed PSS colloids that contact with substrate are tightly linked due to the electrostatic interactions, leading to the formation of ordered arrays of negatively charged 2D colloidal spheres.^{40,41} This strategy can be extended to fabrication of patterned 2D colloidal crystals on patterned polyelectrolyte surfaces, not only on planar substrates but also on nonplanar substrates. Furthermore, by immersion in PMA-*co*-PDDA water solution, the assembled colloidal spheres are positively charged over again, ensuring the circulation of these processes. Therefore, 3D colloidal crystals of certain layers can be fabricated in a LBL fashion. It is note worthy that, in the 3D assembly process, the assembled colloidal spheres can also act as a physical template, which is favorable in obtaining 3D colloidal crystals with matched lattice structure between colloidal layers. This straightforward method may open up new possibilities for practical use of colloidal crystals of excellent quality, various patterns, and controlled fashions.

Experimental Section

Materials. Silicon wafers and glass tubes used as substrates were cleaned by immersion in piranha solution (7:3 concentrated H₂SO₄/30% H₂O₂) for 5 h at 90 °C to create a hydrophilic surface and then rinsed repeatedly with Milli-Q water (18.2 MΩ cm^{−1}) and absolute ethanol. High degree of cross-linking PS colloidal spheres used in this work were prepared using surfactant-free emulsion polymerization as mentioned in our previous report,⁴² and their average sizes were measured as 247, 410, and 585 nm by SEM with a calibrated length. Poly(dimethylsiloxane) (PDMS) elastomer kits (Sylgard 184) were purchased from Dow Corning (Midland, MI). PMA-*co*-PDDA (10 wt % in H₂O) was purchased from Aldrich (1:1 mixed with Milli-Q water to dilute to 5 wt % in H₂O). Other chemical reagents such as concentrated sulfuric acid and ethanol were all used as received without any purification.

PSS Synthesis. Surface modification of obtained PS nanospheres with sulfonic group was carried out by dispersing nanospheres into concentrated sulfuric acid, stirring for 24 h, and then dialyzing in water of pH = 7 to remove unreacted sulfuric acid. The as-prepared PSS nanospheres were further purified by centrifugation and finally redispersed in ethanol with weight fraction of 1%.

3D PSS Nanosphere Arrays Fabrication. 3D PSS nanosphere arrays were prepared using the single-substrate sedimentation technique, as previously reported.⁴³ In short, surface modified silicon wafers were placed into the self-assembled container with a gradient of 60°, after which PSS ethanol latex was

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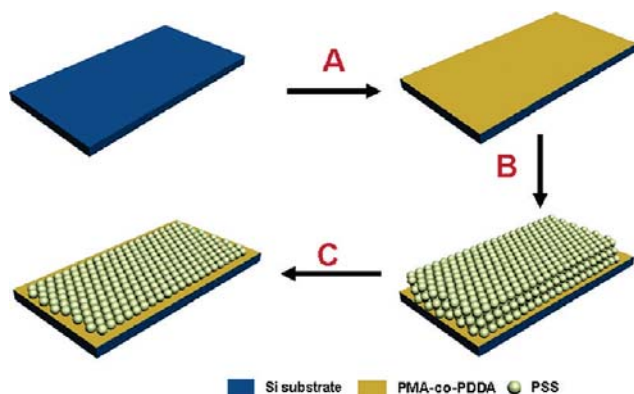


Figure 1. Schematic illustration of the procedure for the fabrication of the ordered 2D colloidal crystals: (A) growth of PMA-co-PDDA layer on silicon substrate; (B) 3D assembly of colloidal nanospheres in ethanol solution; (C) 3D colloidal crystals dispersed in water and get 2D colloidal crystals.

injected into the container. And then the container was dried in the oven at 45 °C and the humidity is 30%. After that, we obtained the 3D ordered array of colloidal nanospheres.^{44–48}

Fabrication of PDMS Samples. The stamp was fabricated by casting the precursor of PDMS on a photolithographically prepared glass master, which was patterned with photoresist. The features of the photoresist pattern were replicated on the PDMS stamp surface, after curing, and the PDMS stamp was carefully peeled from the master and was rinsed with chloroform, acetone, and ethanol before use. In the experiments, two types of patterned PDMS stamp was used: one was ordered arrays of column with diameter of 10 μm , height of 2 μm , and interspacing of 4 μm ; the second one was ordered arrays of stripes that was 20 μm in width and 2 μm in height and separated by 20 μm .

Fabrication of PMA-co-PDDA Patterned Silicon Substrate. The solution of PMA-co-PDDA in water was spin-coated on the cleaned glass slide (with spinning speed 3000 rpm for 1 min and the resulting PMA-co-PDDA film thickness being 1 μm). The glass slide was brought in contact with the PDMS stamp for 5–10 s, and then the PDMS stamp was brought in contact with the silicon substrate for 2 min. The silicon substrate was finally rinsed with deionized water to remove the excess PMA-co-PDDA and dried with N_2 .

Method. Figure 1 illustrates the process employed to fabricate colloidal arrays on planar polyelectrolyte surfaces. First, surface modification of silicon substrate was carried out by immersion in PMA-co-PDDA water solution for 20 min and then rinsed repeatedly with Milli-Q water (Figure 1A), leading to the formation of positively charged substrate in aqueous phase. Then 3D PSS nanosphere arrays were prepared using the single-substrate sedimentation technique in ethanol phase (Figure 1B). At last, 3D PSS nanosphere-coated silicon substrates were rinsed with water (Figure 1C). In that case, the surface modified with PMA-co-PDDA shows positive charge. Therefore, top layers of 3D nanosphere arrays were washed away, whereas the nanospheres that contacted with substrate were tightly linked to the substrate due to electrostatic interactions.

Characterization. SEM micrographs were taken with a JEOL JSM 6700F field emission scanning electron microscope with primary electron energy of 3 kV, and the samples were sputtered with a layer of Pt (ca. 2 nm thick) prior to imaging to improve conductivity. The atomic force microscopy (AFM) image was measured with a Digital Instruments NanoScope IIIa in contact

mode. A Shimadzu 3600 UV–vis–NIR spectrophotometer with standard mirror optics was used to measure the specular reflectance in the range of 400–1600 nm at the incidence angle of 5°. Dynamic light scattering and zeta potential measurements were performed using a Zetasizer NanoZS (Malvern Instruments) and a stylus profiler (Delctak 150, Veeco Instrument Inc.).

Results and Discussion

Colloidal particles can self-assemble into colloidal crystals during the evaporation of solvent. In the electrostatic self-assembly process, the interaction between the particles and oppositely charged substrate may affect the degree of ordering of colloidal crystals. Our experiment started from the synthesis of cross-linked PSS nanospheres with sulfurous groups, a strong polyanion. The PSS nanospheres are highly cross-linked, so they swell little in ethanol. Because the surfaces of the PSS nanospheres are strongly hydrophilic, the PSS nanospheres can be redispersed easily into the water or ethanol phase after they are dried or centrifugally extracted. Sulfo groups on the surface of PSS nanospheres give a net negative surface charge. When in the presence of an oppositely charged surface, such as that presented by the cationic PMA-co-PDDA, the PSS nanospheres undergo an adsorption process driven by the electrostatic attraction.⁴⁹ When the colloidal slurry is allowed to evaporate on the oppositely charged substrate surface slowly, if the interparticle capillary forces introduced by the thinning liquid layer overpower the electrostatic attractions between colloidal particles and the surface, these capillary forces may enable the formation of well-packed colloidal arrays.⁵⁰ The polyelectrolyte used here is PMA-co-PDDA, a strong polycation. It can be ionized in water, whereas it cannot be ionized in ethanol.

In our experiment, PSS nanospheres of 410 nm in the ethanol solution are used to fabricate the 3D ordered arrays of colloidal crystals on the PMA-co-PDDA surface. As shown in Figure S1, it is found that the Z electric potentials of the PSS nanospheres in the water and ethanol have a negligible difference, that is, -72.8 and -72.2 mV, respectively, while the Z electric potentials of the PMA-co-PDDA in water and ethanol are evidently different, that is, 64.5 and 0 mV, respectively. There are hardly any electrostatic attractions between the PSS nanospheres and PMA-co-PDDA modified substrate in ethanol, while strong electrostatic attractions between the PSS nanospheres and the surface of PMA-co-PDDA substrate exist in water. The thickness of PMA-co-PDDA film was measured by the stylus profiler, and it varied from 14 to 16 nm on planar silicon.

Colloidal Crystals Monolayer on Substrate. To generate well-packed 2D colloidal crystals, the fabrication of the ordered arrays of 3D colloidal crystals in the first step is of great importance. In vertical deposition and related methods, evaporation-induced self-assembly of colloidal particles is driven by the capillary forces and convective assembly in the meniscus. It is well-known that holding the evaporation rate at an optimal value is crucial for high-quality colloidal crystals.⁴⁴ Excessively high or low speed of the solvent evaporation induces the stacking faults and macroscopic cracks in the colloidal crystals. Parameters such as temperature, humidity, solvent, horizontal angle of the substrate, etc., are necessary for keeping the evaporation rate steady to obtain the optimal growing conditions for colloidal crystals growth.^{43–46} According to the above theory, we have got the optimized protocol: high-quality 3D colloidal crystals can be fabricated at 45 °C with the humidity of 30%, the PSS nanospheres solution weight fraction is

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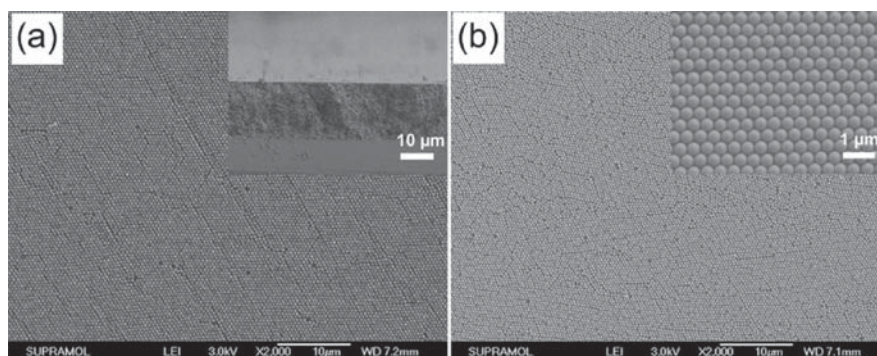


Figure 2. SEM images of 3D and 2D ordered arrays of colloidal crystals on the planar substrate. (a) Top view and inset cross section SEM images of 3D ordered arrays of colloidal crystals. (b) Top view and inset magnified top-view SEM images of 2D ordered arrays of colloidal crystals; the average diameter of PSS sphere is 410 nm.

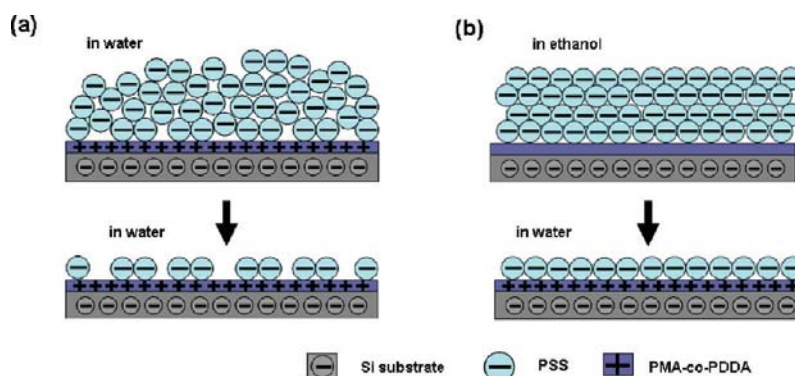


Figure 3. Schematic illustration of the procedure to fabricate 3D and 2D colloidal crystals on PMA-co-PDDA modified silicon substrate in different liquid-phase system. (a) Fabrication of 3D ordered arrays of colloidal crystals in ethanol (b) and then obtained 2D ordered arrays of colloidal crystals in water.

1% in ethanol, and inclination angle of the substrate is 60° . As shown in Figure 2a, following the experimental conditions above, high-quality 3D colloidal crystals was obtained on a planar silicon substrate. It is the experimental basis of fabricating 2D ordered arrays of colloidal crystals. Because the surfaces of the PSS nanospheres with sulfo groups are strongly hydrophilic, when putting the assembled 3D colloidal crystals into water, top layers of PSS nanospheres can be redispersed. Nevertheless, the PSS nanospheres which are in contact with the substrate will still be adsorbed due to the strong electrostatic attraction between the PSS nanospheres and the PMA-co-PDDA modified substrate. After the sample was rinsed repeatedly with deionized water and dried with nitrogen gas, 2D colloidal crystals were obtained.

It is known that the self-assembly behavior greatly depends on the surface property of the substrate, which varied in different solvents. The procedure for the fabrication of 3D and 2D colloidal crystals on the PMA-co-PDDA modified silicon substrate in different liquid-phase systems was illustrated schematically in Figure 3. In the water system, the surface of PMA-co-PDDA modified substrate was positively charged as shown in Figure 3a because PMA-co-PDDA can get ionized in water. Owing to the negatively charged surface of the PSS nanospheres, there were strong electrostatic attraction between PSS nanospheres and the substrate. The strong electrostatic attraction made the PSS nanospheres adsorbed on the surface of substrate, and the PSS nanospheres could not move freely during the process of colloidal crystals formation, which impeded the formation of the ordered colloidal crystals. Thus, it is difficult to fabricate large-scale 3D ordered arrays of colloidal crystals in the water

system. The SEM image of the 2D colloidal crystals fabricated in water system is shown in Figure S2. It can be seen that the 2D colloidal crystals are very disordered and incompact.

While in the ethanol system, as shown in Figure 3b, the surface of the PMA-co-PDDA substrate exhibits no positive electrical charge as PMA-co-PDDA cannot be dissolved and ionized in ethanol, though the surface of PSS nanospheres is still full of negative charge. The electrostatic attraction between the PSS nanospheres and the surface of the PMA-co-PDDA substrate was very weak in ethanol, so the PSS nanospheres will not be adsorbed on the surface of substrate. When the colloidal slurry was allowed to evaporate slowly on the substrate surface, the interparticle capillary force introduced by the thin liquid layer will overpower the electrostatic attractions between colloidal particles and the surface; thus, these capillary forces enable the formation of well-packed colloidal arrays. 3D ordered arrays of colloidal crystals were obtained and then put into water. The PSS nanospheres which contact with the surface of substrate will still be adsorbed on the surface of substrate, owing to the strong electrostatic attraction between the PSS nanospheres and the surface of substrate in water, while the above layers will be dispersed in the water. After the sample was rinsed repeatedly with deionized water and dried with nitrogen gas, 2D ordered arrays of colloidal crystals were obtained. The SEM image of the 2D colloidal crystals obtained in ethanol system is shown in Figure 2b. It can be seen that the 2D colloidal crystals are highly ordered. The SEM images shown in Figure 2b illustrate the formation of 2D colloidal crystals controlled geometry over large areas ($0.1 \times 0.1 \text{ mm}^2$). The results of the experiment are consistent with theory,

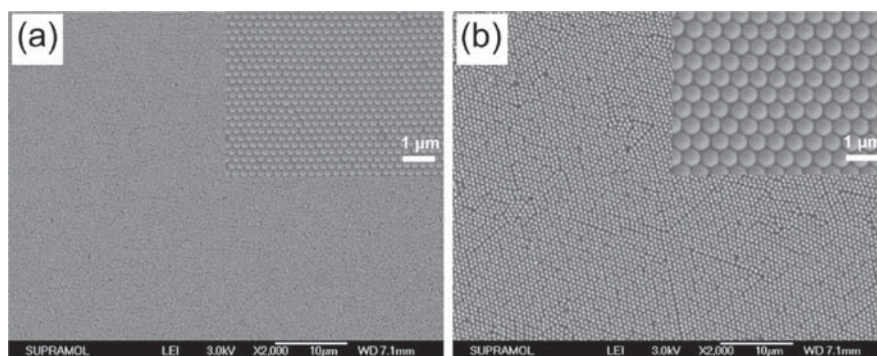


Figure 4. Top-view and inset magnified top-view SEM images of 2D ordered arrays of colloidal crystals with different sizes: (a) the average diameter of PSS sphere is 247 nm; (b) the average diameter of PSS sphere is 585 nm.

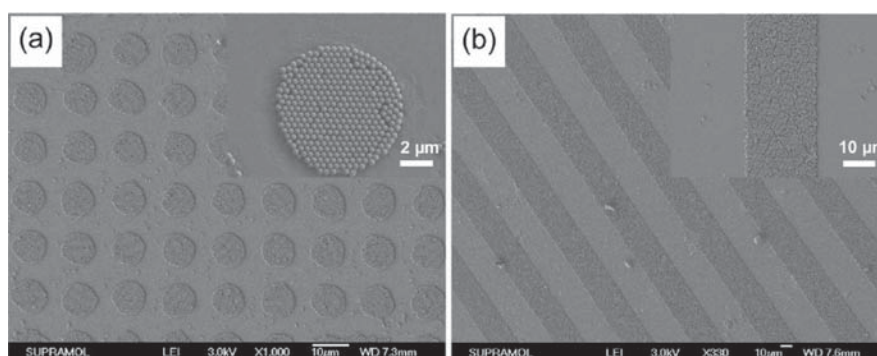


Figure 5. Top-view and inset magnified top-view SEM images of patterned 2D ordered arrays of colloidal crystals. (a) The diameter of the circle is 10 μm , the distance of the circle to the center of the circle is 14 μm , the PSS sphere (diameter is 410 nm). (b) The width of the stripe is 20 μm , the distance between the stripes is 20 μm , the PSS sphere (diameter is 410 nm).

which proves that the method can be applied to prepare perfect 2D ordered arrays of colloidal crystals.

Ordered arrays of colloidal crystals with various particle sizes were obtained on silicon substrate. As shown in Figure 4a,b, PSS nanospheres with diameters of 247 and 585 nm were used respectively to fabricate 2D ordered arrays of colloidal crystals on PMA-*co*-PDDA modified silicon substrates in ethanol system. It can be seen that 2D ordered arrays of colloidal crystals are well ordered as the above result. The SEM images shown in Figure 4a,b illustrate the formation of 2D colloidal crystals controlled geometry over large areas ($0.1 \times 0.1 \text{ mm}^2$). The experimental data prove that this method can be applied in the fabrication of multiscale 2D ordered arrays of colloidal crystals.

Patterned Colloidal Crystal Arrays. Because the 2D ordered colloidal crystals arrays can only be selectively formed on the PMA-*co*-PDDA modified areas. Patterned 2D colloidal crystals can be fabricated when patterned PMA-*co*-PDDA film was employed with the PDMS microcontact printing method on the silicon substrate. Figures S3a and S3b are the shape diagram and the altitude diagram of the PMA-*co*-PDDA pattern circle and stripe films scanned with AFM. From Figure S3a, it can be seen that the diameter of the circle is 10 μm , the distance of one circle to the center of the other adjacent circle is 14 μm , and the film is 15 nm in thickness. Figure S3b shows that the width of the stripe is 20 μm , the distance between the stripes is 20 μm , and the film is 12 nm in thickness. Because the film was very smooth, it will not influence the degree of ordering of 2D colloidal crystals.

The patterned PMA-*co*-PDDA on silicon substrate was used to fabricate patterned 2D ordered colloidal crystals arrays. The SEM images of the circle and stripe patterned 2D ordered arrays of colloidal crystals are shown in Figure 5. It can be seen from

Figure 5a that the diameter of the circle is 10 μm and the distance of one circle to the center of the other adjacent circle is 14 μm , which is consistent with the pattern of PMMA-*co*-PDDA (as shown in Figure S3a). From Figure 5b, it can be seen that the width of the stripe is 20 μm and the distance between the stripes is 20 μm , which is also consistent with the pattern of PMMA-*co*-PDDA (as shown in Figure S3b). As shown in Figure 5, the patterned 2D ordered arrays of colloidal crystals are highly ordered. There are also some nanospheres left on the surface in the nonpattern area. Such a case may occur because a little PMA-*co*-PDDA will react with the substrate instantly in the patterning process and cleaning process. The experimental data prove that this method can be used to prepare patterned 2D colloidal crystals.

Colloidal Crystals Monolayer on Nonplanar Substrate.

Using this method, 2D colloidal crystals can also be fabricated on the nonplanar substrate. Two types of nonplanar substrates were used in the experiment. The thickness of PMA-*co*-PDDA film was measured by the stylus profiler, and it varied from 13 to 15 nm on nonplanar silicon. The SEM images of colloidal crystals on the nonplanar substrate are shown in Figure 6. As shown in Figure 6a,b, 2D ordered arrays of colloidal crystals on a glass tube (inside diameter of 200 μm) are ordered and the degree of ordering is well, and the colloidal crystals on the substrate are a single layer. It can be seen from Figure 6d that the convex shape of the stripe nonplanar substrate is a trapezoid, its upper bottom is 8 μm wide, the lower bottom is 12 μm wide, and it is 3 μm high and separated by 5 μm . The colloidal crystals on the substrate are a single layer. Figure 6c shows that 2D ordered arrays of colloidal crystals on the nonplanar silicon substrate are ordered, but the degree of ordering is not so good as the 2D ordered arrays of colloidal crystals

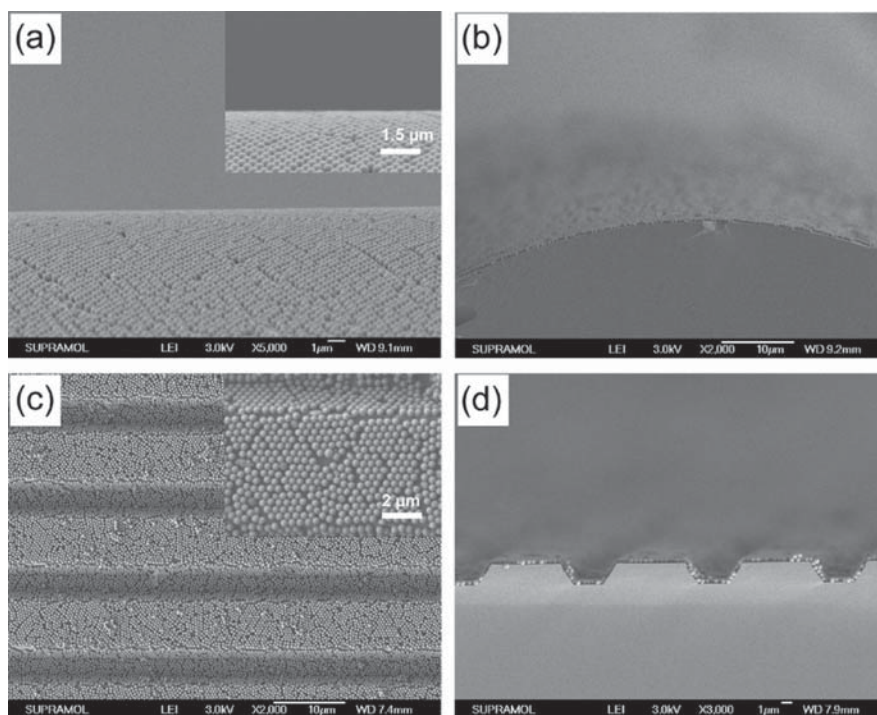


Figure 6. SEM images of 2D ordered arrays of the colloidal crystals on the nonplanar patterned surface. (a, c) Top-view and inset magnified top-view SEM images of 2D ordered arrays of the colloidal crystals on glass tube of nonplanar substrate and the stripe nonplanar patterned silicon substrate, the PSS sphere (diameter is 410 nm). (b, d) Cross-section SEM images of the 2D orderly array of the colloidal crystal on glass tube of nonplanar substrate and the stripe nonplanar patterned silicon substrate, the PSS sphere (diameter is 410 nm).

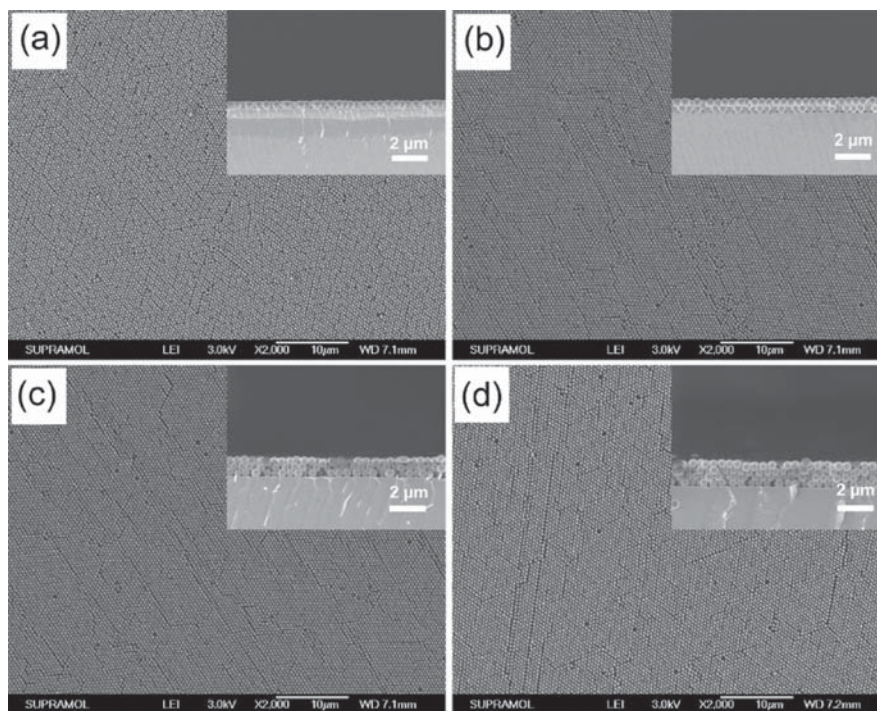


Figure 7. Top-view and inset cross-section SEM images of ordered arrays of colloidal crystals with certain number of layers: (a) one layer, (b) two layers, (c) three layers, and (d) four layers; the average diameter of PSS sphere is 410 nm.

available on planar silicon substrates. The degree of roughness of the substrate has a great impact for the self-assembly process of the ordered colloidal crystals, especially for the bottom of the order colloidal crystals. The driving forces that direct self-organization include electrostatic interactions, surface tension, van der Waals

forces, steric interactions, convective assembly, and capillary forces. Because of the rough surface, the PSS nanospheres could not move freely during the process of colloidal crystals formation, which impeded the formation of the ordered colloidal crystals. The rough surface will weaken the process of convective assembly. Thus, it is

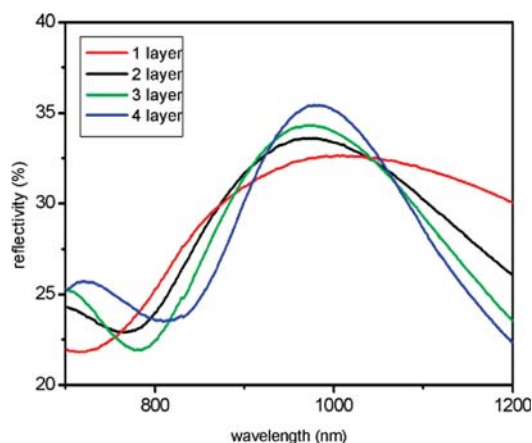


Figure 8. Specular reflectance spectra of ordered arrays of colloidal crystals with certain number of layers, the PSS spheres (diameter is 410 nm). One layer of colloidal crystals (red line), two layers of colloidal crystals (black line), three layers of colloidal crystals (green line), and four layers of colloidal crystals (blue line).

difficult to fabricate large scale ordered arrays of colloidal crystals.^{29–32} Because the degree of roughness of the nonplanar silicon substrate is higher than that of the planar silicon substrate, which prevents the moving of the PSS nanospheres in the self-assembly process, thus the degree of ordering is reduced. Applying the method above, the 2D ordered arrays of colloidal crystals can also be obtained on this substrate. However, it is found that the degree of ordering reduced further; it is believed that the degree of ordering of the 2D colloidal crystals obtained is related to the roughness of the substrate. At the same time, the result proves that the proposed method can be used to prepare the 2D ordered arrays of colloidal crystals on the nonplanar substrate.

LBL Assembly of 2D Colloidal Crystals. The LBL strategy was employed to fabricate ordered arrays of 3D colloidal crystals with certain number of layers. An additional PMA-*co*-PDDA film was prepared on the surface of 2D ordered arrays of colloidal crystals substrate. As obtained above, the 3D self-assembly of the PSS colloidal crystals is fabricated in the ethanol system. Then two-layer ordered arrays of colloidal crystals were obtained after the 3D colloidal crystals are dispersed in the water, rinsed repeatedly with deionized water, and dried with nitrogen gas. In such a cycle, 3D ordered arrays of colloidal crystals with three layers, four layers, and even more layers were obtained. Parts a, b, c, and d of Figure 7 are the one-layer, two-layer, three-layer, and four-layer colloidal crystals, respectively. The FTIR spectrum test of the different layers of colloidal crystal is shown in Figure S4. The stretching vibration of the methyl group of PMA-*co*-PDDA was observed around 2923 and 2852 cm^{-1} , while the stretching vibration of the sulfonic group of PSS nanospheres was observed around 1492 and 1452 cm^{-1} . And it is noteworthy that the intensity of the stretching vibrations increase with the layers of electrostatic self-assembled PMA-*co*-PDDA and PSS nanospheres.

The SEM characterization of 3D ordered arrays of colloidal crystals structures fabricated on the substrate were highly ordered (Figure 7). The SEM images confirm that the crystal exhibits excellent short- and long-range periodicity. Reflectance spectroscopy can be used to identify photonic stop bands, which occur when the structure exhibits a highly periodic variation in refractive index. The theoretical value of λ is 982 nm.^{51,52} As shown in the UV–vis–NIR spectrum test of the different layers of colloidal crystal (Figure 8), it is found that the width of photonic stop bands decreased and the height of photonic stop band increases with the increasing of the layers and its photonic stop bands is 978 nm, conforming to the theoretical value. The result indicated that the ordered arrays of 3D colloidal crystals with the certain number of layers are lattice matched. The above experimental data prove that such a method can be used to realize the preparation of the 3D ordered arrays of colloidal crystals with controllable layers.

Conclusions

We combined 3D self-assembly of colloidal crystals with electrostatic LBL assembly techniques to fabricate 2D ordered arrays of the colloidal crystals. In this process, the 3D self-assembly of the colloidal crystals process and the electrostatic adsorption process were taken in different liquid-phase systems. We obtained 2D ordered arrays of the colloidal crystals on planar silicon substrate, patterned silicon substrate, and nonplanar pattern silicon structure. In addition, the 2D ordered arrays of the colloidal crystals on the planar substrate were extended to fabricate adequate large area of 3D ordered colloidal crystals with certain number of layers. This method provides new routes for the large-area fabrication of highly ordered colloidal crystals in both the bulk and area-specific form, which is believed to be an advance toward the incorporation of colloidal crystals in a range of technologically relevant applications, including smart textiles, large-area and low-energy reflective displays, chemical sensing, and low-cost photovoltaic devices.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Grants 21074048, 20874039, and 20921003), the National Basic Research Program of China (2007CB936402), and MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Zhejiang University (2010MSF04).

Supporting Information Available: Zeta potential of PSS sphere and PMA-*co*-PDDA in different liquid-phase system; the SEM image of self-assembly colloidal PSS nanospheres in water; the AFM height image of patterned PMA-*co*-PDDA on silicon substrate; the FTIR spectrum test of the different layers of colloidal crystals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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