

Polymer nanosphere lithography: fabrication of an ordered trigonal polymeric nanostructure†

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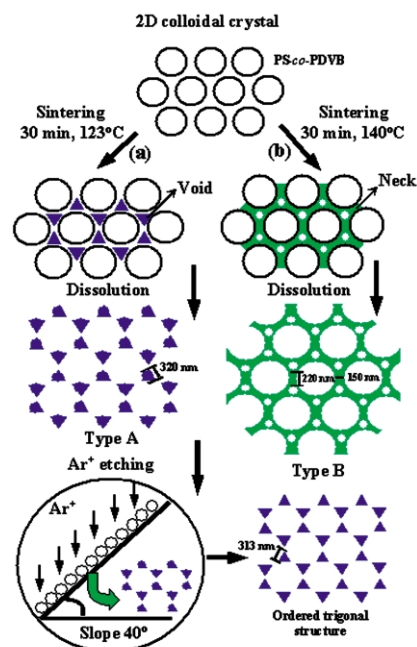
A combination of nanosphere lithography, sintering rheology and selective dissolution of self-assembled colloidal arrays was used to fabricate a novel trigonal polymeric nanostructure whose trigonal structure became more evident after Ar⁺ ion etching.

Ordered polymeric micro- and nano-structures have attracted much attention because of their potential uses in sensors,¹ electronic devices,² cell culture,³ photonic crystals,⁴ and templates for novel materials.⁵ Numerous approaches have been used to prepare polymeric micro- and nano-structures, including soft lithography,⁶ laser interference,⁷ water-in-oil emulsions,⁸ block copolymers,⁹ holographic lithography,¹⁰ and colloidal self assembly.¹¹ Here, we focus on the colloidal self-assembly method. Most attempts to use colloidal self-assembly to create polymeric micro- and nano-structures have employed spherical colloids as building blocks; the spherical shape is inevitable because it gives the lowest interfacial energy during common emulsion polymeric colloid growth processes. Although spherical polymeric colloidal nanoblocks have been successfully used as photonic band gap materials,⁴ templates of carbon nanotubes,¹² and etching masks for nanohole arrays,¹³ potential advantages of non-spherical colloids have led to the production of polymeric spheroids¹⁴ and polygonal aggregates.¹⁵

One important application of colloidal self-assembly is nanosphere lithography.¹⁶ Two dimensional (2D) self-assembly of spherical colloids usually forms a close-packed structure with triangular void spaces enclosed by three neighbouring colloidal particles. These regularly ordered void spaces have been used as deposition sites for vaporized inorganic materials. Ordered inorganic nanostructures have been made *via* this method. Recently, we fabricated a macroporous polymer structure using a method that combines sintering rheology and selective dissolution.¹⁷ This approach can be combined with nanosphere lithography to fabricate ordered non-spherical polymeric nanostructures. Here, we report on the novel process of ordered trigonal polymer nanostructuring. Our results suggest that self-assembled close-packed spherical colloids can be converted into down-sized, ordered trigonal nanostructures.

Scheme 1 depicts the overall procedure followed in our experiments. First, a 2D colloidal monolayer with hexagonal order was formed by convective crystallization¹⁸ on a flat film of an azo-functionalized polymer that firmly holds the colloidal particles, thereby maintaining the hexagonal structure during subsequent experimental steps. The colloidal particles (*diameter* 500 nm) consist of crosslinked polydivinyl benzene (PDVB) as the insoluble portion and polystyrene (PS) as the portion soluble in cyclohexane.¹⁹ Colloidal arrays were sintered for 30 min either at 123 °C, the glass transition temperature (T_g) of the colloids (Scheme 1(a)), or at 140 °C (Scheme 1(b)). Sintering at 140 °C caused the formation of necks, denoted by green rods in Scheme 1(b), due to active polymer chain mobility: migration of the uncrosslinked fraction of colloids would be dominant.

† Electronic supplementary information (ESI) available: detailed explanations of Fig. 2, AFM image of trigonal shape after etching and scheme of conventional nanosphere lithography. See <http://www.rsc.org/suppdata/cc/b3/b300638g/>



Scheme 1 First, PS-*co*-PDVB colloidal particles were assembled into a 2D monolayer. The resulting colloidal array was then sintered at (a) 123 °C or (b) 140 °C for 30 min. Sintering at 140 °C caused the formation of necks (green rods in (b)). These necks were converted into rods during dissolution in cyclohexane, where each rod has four neighbours (type B). In contrast, sintering at 123 °C did not produce necks. Dissolution in cyclohexane of the colloidal array sintered at 123 °C gave rise to an ordered array of trigonal shapes (blue dots in (a)), where each trigonal shape has three neighbours (type A). Subsequent Ar⁺ ion etching produced well-defined ordered trigonal arrays.

Scanning electron microscopy (SEM) images of the sintered colloidal arrays show that necks formed when sintering was performed at 140 °C (Fig. 1(b)) but not when it was performed at 123 °C (Fig. 1(a)). Next, the sintered colloids were selectively dissolved in cyclohexane at 40 °C for 2 h. SEM imaging showed that the colloids sintered under different conditions gave distinct ordered polymeric nanostructures after selective dissolution. Selective dissolution of the colloidal array sintered at 123 °C gives rise to an ordered array of spheres of *diameter* 320 ± 55 nm, in which each sphere has three nearest neighbours (Fig. 2(a)), whereas selective dissolution of the array sintered at 140 °C gives an ordered array of rods in which each rod (*width* 150 ± 6 nm, *length* 220 ± 16 nm) has four nearest neighbours (Fig. 2(b)). Hereafter, these structures are referred to as types A and B, respectively.

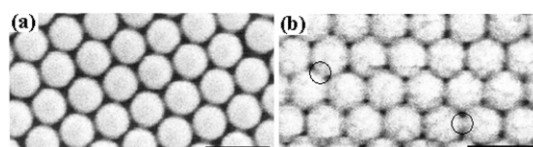


Fig. 1 SEM images of colloidal assembly after sintering at 123 °C (a) or 140 °C (b). Neck is clear (circles in (b)). Scale bar 1 μm.

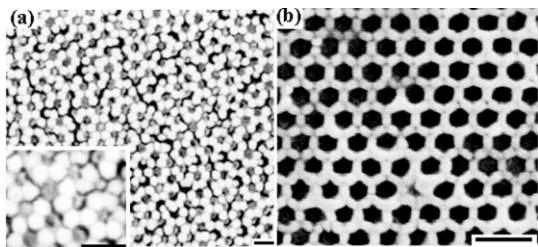


Fig. 2 SEM images of (a) type A and (b) type B patterns. Inset is enlarged view. Scale bar 1 μm .

Sintering rheology has been used to create neck between neighboring colloids, and the neck aids to make stable and continuous structures such as pearl necklace,²⁰ and colloidosomes.²¹ Polymer sintering plays a key role in this experiment. The formation of the type A structure can be explained as follows. The colloids sintered at T_g have no necks between colloids and, consequently, as the dissolution proceeds, insoluble PDVBs are trapped in the triangular void spaces among the neighboring colloidal particles.

Therefore, the selective dissolution results in spherical nanostructures due to the symmetry of the triangular voids (Scheme 1(a), blue dots). The resulting structure is similar to that produced by the nanosphere lithography process in which the triangular voids function as adsorption sites and the colloids function as masks.¹⁶ However, in this experiment, the colloidal particles function not only as masks preventing adsorption but also as the source of the resulting ordered spheres.

The formation of the type B structure during selective dissolution is greatly influenced by the well-developed necks that formed during sintering. As cyclohexane dissolves the colloids, the insoluble PDVBs move and are adsorbed on the necks where relatively strong physical crosslinks of polymer chains could exist, and PDVBs are intermingled with the necks.^{17,22} As a result of this process, the necks are converted into rods during selective dissolution (Scheme 1(b), green rods). These rods lie in an ordered array that reflects the ordering of the necks in the sintered colloidal assembly.

The present results show that two distinctive polymeric nanostructures with different array symmetries are obtained under different sintering conditions. Although further study is required to evaluate the effects of factors such as dissolution period and the PDVB content in the colloids on the final nanostructures, the sintering effect is clear in the present study.

To obtain ordered trigonal nanoarrays, we focused on the type A nanostructure. The type A was etched by exposure to Ar^+ ions at 10 w for 300 s, where the pressure was 100 mPa and the sample was placed on a slope of 40° in the Ar^+ ion chamber (Scheme 1(a), circled illustration). Topographical analysis by atomic force microscopy (AFM) in contact mode (Auto Probe CP) showed that the type A structure before etching (Fig. 3) is comprised of pseudo-trigonal features with an average height of about 100 nm, and not the spheres indicated by the SEM micrograph (Fig. 2(a)). These trigonal features became clearer and separated from one another after etching with Ar^+ ions. This is evident in the SEM image of the etched type A structure shown in Fig. 4, which shows well developed trigonal shapes with no evidence of spherical features. The sides of these trigonal shapes have lengths of 313 ± 35 nm. Given that the mean side length is similar to the diameter of spheres before

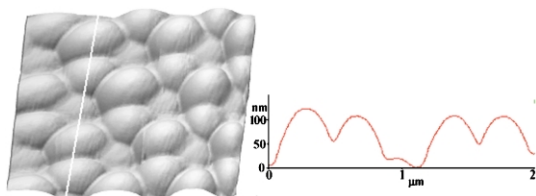


Fig. 3 AFM image and a height profile of type A pattern.

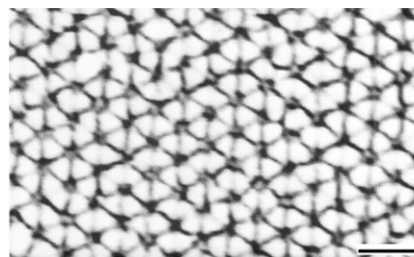


Fig. 4 SEM image of type A after Ar^+ ion etching. Scale bar 1 μm .

etching, it can be assumed that the Ar^+ ion etching mainly affected the shape rather than the size of the nanostructure. AFM analysis shows that the trigonal shapes after etching have flattened surfaces and that the average height of these features decreased to about 60 nm (see ESI†). In conclusion, ordered polymeric trigonal nanostructures were fabricated with downsizing of about 37%²³ in comparison to the initial colloid diameter. Sintering rheology and Ar^+ ion etching functioned to control the resulting nanostructures.

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- 37%; (Original colloid diameter – the side of the resulting trigonal shape)/(Original colloid diameter) = (500 – 313)/500.