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Patterned structures self-assembled from nanoparticle-polymer mixtures confined in square-pillar arrays

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HIGHLIGHTS

- The effect of the nanoparticle volume fraction is investigated.
- The influence of the sizes of the system and the pillars is explored.
- Various highly-ordered patterned structures are found.
- The hidden competition relationship is revealed.
- The results play an important role in understanding array confinement.
- It is helpful for designing the functionally useful microstructures.

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ABSTRACT

Using the hybrid self-consistent field and density functional theories, we investigate the self-assembling behavior of nanoparticle-polymer mixtures confined in square-pillar arrays. By varying the volume fraction of nanoparticles and the sizes of the system and the pillar, various patterned structures are achieved. The predicted structures can be reasonably comprehended by the competition between entropy and enthalpy of nanoparticles and polymers. The results play an important role in understanding array confinement and provide a helpful guidance for designing the functionally useful microstructures.

1. Introduction

Confinement is an efficient method to control the self-assembly of soft matter [1,2]. The confinement surface breaks the symmetry of the bulk. The bulk phase behavior is restrained by the interface energy and confinement-induced entropy. In the past decades, the material quality of confinement surface has developed from hard surfaces to soft surfaces [3–8]. The geometrical structure of confinement surface has changed from a flat surface to cylindrical and spherical surfaces [9–13]. Both experiments and theories have proven that the shape and curve of confinement surface can promote the formation of many novel structures which cannot be found in the bulk.

In recent years, pillar arrays have received extensive attention due to their technical applications [14–16]. There has been a growing interest in array confinement, where pillars are proposed to control the self-assembly of soft matter. The

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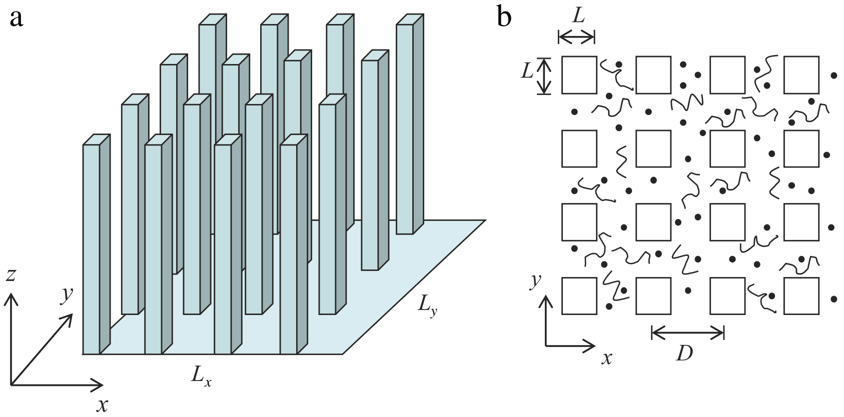

Fig. 1. (a) Schematic representation of periodic square-pillar array. (b) Top-down schematic of square-pillar array with geometric parameters in the x–y plane. Dots represent nanoparticles. Lines represent polymers. D denotes the center-to-center distance between two neighboring square pillars. L is the side length of each square pillar.

self-assembled patterned structures have many important applications in photonic crystal, microsensor and metamaterial. Compared with conventional methods, array confinement increases many factors to influence the self-assembly, such as the shape, size, and surface field of arrays. Obviously, the competition between entropy and enthalpy becomes more complex. How to control these factors and adjust the match between the array period and the melt period of soft matter becomes an important and basic problem to obtain novel patterned structures. Recently, double-cylinder network structure and various lamellar structures including perpendicular lamellae, undulated lamellae, cylindrical lamellae and perforated lamellae of diblock copolymers confined in nanorod arrays have been observed by tuning the surface field and the degree of confinement [17,18]. Further, the various morphologies of diblock copolymers in square-pillar arrays such as parallel and perpendicular lamellar structures, perpendicular cylinders and bicontinuous structures have been reported by varying the geometric parameters of pillars [19,20]. The predicted morphologies have been reasonably comprehended by the period commensurability between the array and the bulk, as well as the symmetry about the surface field.

It is well known that nanoparticle-polymer mixtures are of great significance for fabricating new materials. Composite materials offer a variety of benefits over the single component with the significantly enhanced mechanical, electronic and photonic properties, and can be widely used in biomaterials, ceramics and semiconductors. Both experimental and theoretical methods have been developed to manipulate their self-assembly [21–29]. For example, the earlier work by Ren and Ma have found that the square lattice, hexagonal and cylindrical structures can be formed in nanoparticle-polymer thin films confined between two polymer-grafted plates [6]. Recently, the patterned-directed phase separation of polymer-grafted nanoparticles immersed in a homopolymer matrix have been observed by Zhang et al., where entropy is an effective driving force for microstructure formation [30,31]. As far as we know, a deep understanding on the self-assembling behavior of polymer nanocomposites under array confinement is still lacking.

In the past decades, several theoretical and simulation methods have been developed to study the phase behavior of polymers, including self-consistent field theory (SCFT), coarse-grained Monte-Carlo method (MC), molecular dynamic method (MD), dynamic density functional theory (DDFT), Brownian dynamics simulation (BD) and dissipative particle dynamics (DPD). Combining SCFT for polymers with density functional theory (DFT) for particles, Balazs et al. [32,33] first addressed the self-assembled structures of nanoparticle-copolymer mixtures. Experimental and theoretical comparisons have confirmed that the hybrid SCFT/DFT is quite successful in investigating the equilibrium microstructures of nanoparticle-polymer mixtures. The advantage of this method is that it does not require a prior assumption of the unknown structure. Therefore it is powerful to tackle the problem that the structure is unknown prior. Only starting with an initial random chemical potential field, the mixture can self-associate into ordered structures.

In this work, we used the hybrid SCFT/DFT to predict the self-assembled structures of nanoparticle-polymer mixtures confined in square-pillar arrays. In our model, several new parameters are introduced, such as the length and the volume fraction of polymers, the size and the concentration of nanoparticles, the type and the magnitude of interactions, which may increase the possibility of finding yet undiscovered microstructures. The theoretical understanding of the hidden competition relationship controlling the formation of patterned structures needs to be further explored. In such system, we first choose a suitable polymer length. The statistical length of the polymer is taken as unit length. Then we fix the interaction between nanoparticle and polymer to ensure the phase separation of the mixture. After taking these parameters, we undertake a systematic study by varying the nanoparticle volume fraction and the sizes of the system and the pillar. As expected, a lot of highly-ordered patterned structures are observed. The present study may deepen the understanding of confinement-induced patterned structures for nanoparticle-polymer mixtures and be helpful for structural design.