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Controlled Synthesis of 2D Ordered Structures by Electron Irradiation and Subsequent Heating Decomposition

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1. Introduction

Two-dimensionally (2D) ordered structures have recently attracted much interest due to their unique properties and applications in catalysts [1], gas sensors or biosensors [2], photonic crystal [3], surface enhanced Raman scattering [4], microfluidic devices [5] and so on. These properties strongly depend on the morphology and unit size of ordered structures. Therefore the morphology-controlled synthesis of 2D ordered structures has attracted attentions increasingly and various methods have been developed. Here, we present a novel route to fabricate 2D ordered structures with different morphologies based on the electron irradiation of polystyrene (PS) colloidal monolayer and subsequent heating decompostion.

2. Methods and Results

2.1. Sample preparation

Silicon wafer with the size of 2 cm x 2 cm was ultrasonically cleaned in acetone and subsequently in ethanol for 1 h, and finally cleaned in Piranha solution (70% H_2SO_4 + 30% H_2O_2) for 1 h followed by triple rinsing in distilled water. Colloid solution of monodispersed PS sphere powder with the diameter of 1.3 μm (Soken, Chemisnow, Japan) were prepared with the concentration of 3.0 wt% by dispersing in pure water using sonication. Large-scale monolayer colloidal crystals were prepared on the cleaned silicon substrate by spin-coating.

2.2. Electron irradiation and heating experiment

The PS colloidal monolayer with its substrate was put into vacuum chamber and irradiated with an electron beam generated from a thermionic electron gun. The irradiating process was carried out at ambient temperature in a vacuum chamber under a pressure of less than 2 x 10^{-5} torr. The energy of the electron beam irradiating the samples was fixed at 50 keV and the current density of electron beam was changed from 5 μA to 50 μA. The electron beam diameter was 20 mm and the total electron fluence was varied from 1 x 10^{16} cm^{-2} to 5 x 10^{18} cm^{-2}. Water-cooling system was used in order to removing a heat produced during the electron irradiation. After irradiation, the samples were heated at 360 ^oC with different temperature.

2.3. Morphology study

Morphologies of the samples were characterized by a field-emission scanning electron microscope (FESEM, FEI XL30). Figure 1a is the FESEM image of PS colloidal monolayer with the size of 1.3 μm after the electron irradiation at the electron fluence of 1.2×10^{17} cm^{-2} without heating. Hexagonal close-packed arrangement, whose morphology is similar to the pristine PS colloidal monolayer, is shown in Figure 1a. Interestingly, after heating at 360 ^oC for different time, the morphologies of electron-irradiated samples were evolved to the network-like ordered array (Figure 1b), star/tortoise array (Figure 1c), hexagonal non-close-packed microsphere array (Figure 1d), respectively. In these ordered structures, each unit was still located at original place of PS sphere in colloidal monolayer after irradiation and its volume gradually decreased with increasing heating time. The network-like ordered array, composed of smaller spheres and necks between neighbor spheres, was formed after heating at 360 ^oC for 3h and had almost six necks on each sphere linked with its six neighbor spheres, as shown in Figure 1b. If the heating time was increased to 4h, isolated spheres with six legs were formed (Figure 1c). If the heating time was further increased to 5h, the hexagonal non-packed-closed microsphere array was obtained, as shown in Figure 1d.

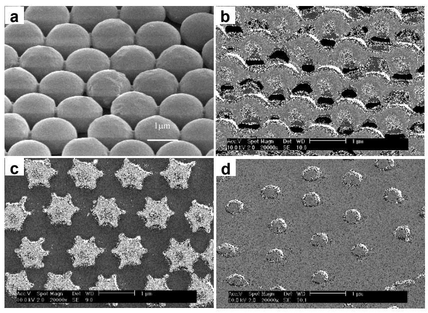
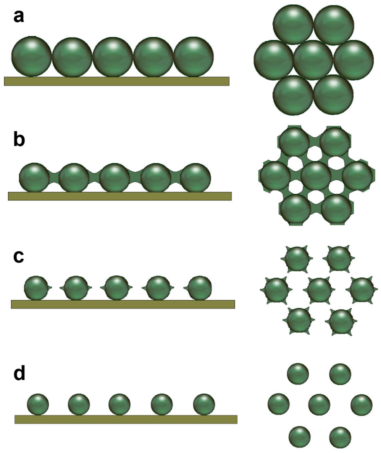


Figure 1. FESEM image of 2D ordered structures from the PS colloidal monolayer with PS sphere size of 1.3 μm after electron irradiation at the electron fluence of 1.2×10^{17} cm^{-2} and subsequent heating a) after electron irradiation without heating; b), c), and d) after electron irradiation and subsequent heating at 360 ^oC for 3h, 4h, and 5h, respectively.

The morphological evolution induced by electron irradiation and subsequent heating can be described as Scheme 1. A network-like array, combined structure of sphere array and necks between neighbor spheres, is firstly obtained by heating for 3h. With increasing heating time, it seems that the necks between each pair of neighbor sphere are decomposed and tortoise-like (or star-like) particle array is formed. If heating time is further increased, the hexagonal non-close-packed sphere array is evolved from the tortoise-like one due to disappearing of tortoise legs and unit size in ordered array is further reduced.



Scheme 1. Formation of ordered structures with different morphologies by electron irradiation and subsequent heating with increasing time from a) to d).

3. Conclusion

We present a novel method to fabricate 2D ordered structures with different morphologies by electron irradiation and subsequent heating decomposition. In this method, by changing electron fluence and heating time, 2D ordered structures with various morphologies could be fabricated. The method has the following features: (1) Good repeatability - These ordered arrays can be well-repeated with the same irradiation and heating condition. (2) Tunable periodicities - Periodicities of such ordered structures could be easily tuned in a large range from hundreds of nm to several μm by changing the PS sphere size of colloidal monolayer. (3) Useful templates or masks- our results indicate such 2D ordered structures could be used as templates or masks for lithography to create other ordered arrays. (4) Maskless and low cost - The method presented here utilizes the intrinsic orderliness of monolayer colloidal crystal and masks are not required. Hence this method has an advantage of relatively low cost.

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