Plasma-Electron Coirradiation Induced Fabrication of Hexagonal Non-Close-Packed Colloidal Crystal Monolayer

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1. Introduction

Recently, hexagonal non-close-packed (hncp) colloidal crystals attract much interest because of their peculiar optical and surface properties [1]. However, most of current fabrication methods have limitations in controlling the particle size or the period of hncp colloidal crystals, and thus fabrication of hncp colloidal crystals with desired structures is still challenging [2].

Here, we present a novel and systematic approach to controllably fabricate hncp colloidal crystals based on pyrolysis of plasma- and electron-irradiated polystyrene (PS) monolayer colloidal crystals. The particle size and the interparticle distance of the fabricated hncp colloidal crystals can be readily tuned by the approach.

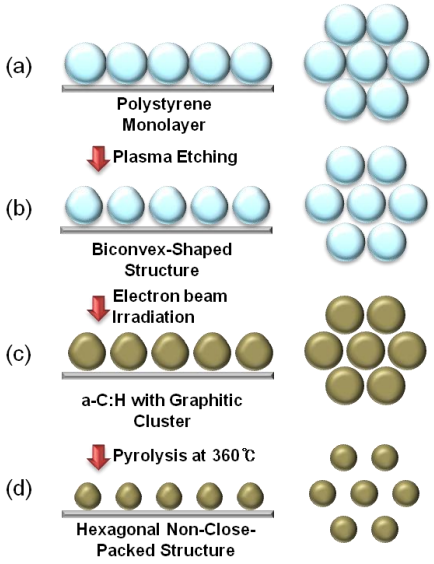
2. Methods and Results

2.1 Experimental

Polished p-type Si (100) substrates (500 μm thickness) with the size of 2 cm × 2 cm were ultrasonically cleaned in acetone and ethanol. Subsequently, the substrates were cleaned in piranha solution to induce hydrophilic surface, followed by triple rinsing in distilled water. Colloidal micro-dispersed PS suspensions (2.5 wt % in water, surfactant-free) with the standard deviation in size less than 5% were purchased from Alfa Aesar. Ethanol was added to PS suspensions to form 1.25 wt % water-ethanol solution. 400 μL of distilled water was then dropped on the treated Si substrate with a pipette, making a flat water film covering the whole substrate area because of its hydrophilic property. By dropping an ethanol-mixed PS solution in this water film, a PS monolayer can be uniformly self-assembled on the whole substrate. After drying it in an ambient condition, a PS colloidal monolayer was prepared on the Si substrate. Fabricated PS monolayer is plasma-etched by a plasma etcher (Samco, RIE 10NR) with an oxygen gas (50 sccm) at a pressure of 7.0 Pa with a power density of 30 W. The etching time was a few min. The PS colloidal monolayer was then irradiated with an electron beam that was generated from a thermionic emitting gun. The irradiating process was carried out in a vacuum chamber under a pressure of less than 2×10^{-5} torr. The energy of the electron beam was fixed at 50 keV, and the current density was ~10 μA cm^{-2}. After the electron irradiation, the samples were put into a furnace for heating in ambient conditions at 360℃ to produce hncp structures consisting of different-sized PS particles by controlling the heating time. Morphologies of all the samples were characterized by a field-emission scanning electron microscope (FESEM, Hitachi, S-4800).

2.2 Schematic Fabrication Procedure

The fabrication procedure of the hncp colloidal crystals is illustrated in Scheme 1. PS spheres dispersed in a water-ethanol mixture solution are drop-casted on a piranha-treated hydrophilic Si substrate and dried in ambient conditions, forming an hcp PS monolayer colloidal crystal via self-assembly. The hcp PS colloidal crystal is slightly plasma-etched to eliminate the interconnecting parts between the spheres. The plasma-etched PS monolayer is further irradiated with an electron beam, followed by pyrolysis in air. The pyrolysis process leads to the size reduction of the PS spheres while the original positions of the PS spheres are unchanged. As a consequence, a regularly-ordered hncp colloidal monolayer is created.



Scheme 1. Schematic illustration for the fabrication procedure of the hncp colloidal crystals and BCCs.

2.3 Control of Hexagonal Non-Close-Packed Colloidal Crystal Monolayer

Figure 1 displays the field-emission scanning electron microscope (FESEM) images of the PS colloidal monolayers at each step shown in Scheme 1. The PS colloidal monolayer prepared by self-assembly of 2 μm PS spheres has regularly-ordered hcp structure as shown in Figure 1a. First the plasma etching induces a size reduction of the PS spheres: the sphere size was decreased from 2 μm to 1.87 μm (Fig. 1b). The following electron irradiation process did not change the sphere size (Fig. 1c). However, when the electron-irradiated PS monolayer was heated at 360 ℃ in air, each PS sphere size was gradually decreased with increasing the heating time, resulting in regularly-ordered hncp colloidal monolayers with variable particle sizes (Figs. 1d-f). The particle sizes were reduced to 1.40, 1.05, and 0.88 μm when the heating time was increased to 3, 60, and 180 min, respectively. This indicates that the particle size comprising a hncp monolayer colloidal crystal can be controlled simply by changing the heating time. Therefore, regularly-ordered hncp colloidal monolayers with different particle sizes and periods can be controllably fabricated by the approach shown in Scheme 1.

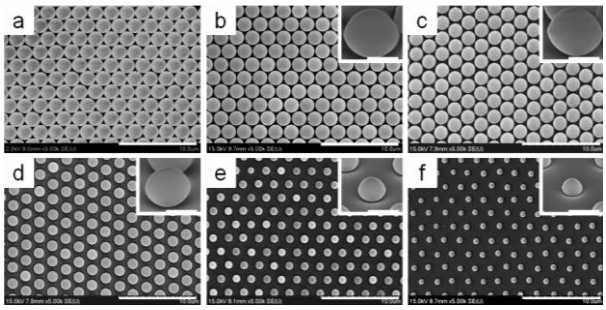


Figure 1. FESEM images of the monolayer colloidal crystals: (a) the pristine, (b) plasma-etched, (c) electron-irradiated, (d~f) hncp colloidal crystals fabricated by the irradiation-assisted pyrolysis after the heating time of 3, 60 and 180 min, respectively. Scale bars are 10 μm.

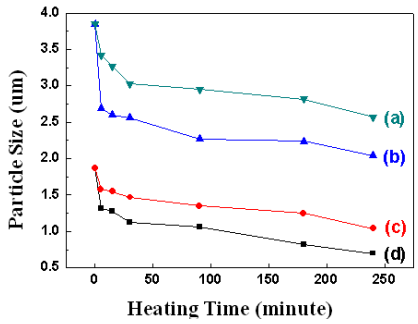


Figure 2. Behavior of particle size as a function of pyrolysis duration and electron fluencies. The particle size and the electron fluence are (a) 4.3 μm, 2.0×10^{18} cm^{-2}, (b) 4.3 μm, 1.0×10^{18} cm^{-2}, (c) 2.0 μm, 2.0×10^{18} cm^{-2}, and (d) 2.0 μm, 1.0×10^{18} cm^{-2}.

2.4 Role of Electron and Plasma Irradiation

For successful fabrication of the well-ordered hncp colloidal monolayers, electron and plasma irradiation processes are indispensable. The necessity of electron irradiation process can be explained by the chemical structure change of electron-irradiated PS. In contrast to pristine PS spheres with glass-transition temperature of 100 ℃, electron-irradiated PS spheres with carbonaceous materials are not melted at the pyrolysis temperature of 360 ℃ but are slowly thermal-decomposed [3]. As a result, the sizes of the PS spheres irradiated at 2×10^{18} cm^{-2} were decreased more slowly than those irradiated at 1×10^{18} cm^{-2} by the pyrolysis process. And proper plasma etching before an electron irradiation process is also crucial for the fabrication of regularly-ordered hncp colloidal crystals. If a PS monolayer colloidal crystal is electron-irradiated and pyrolized without preceding plasma etching, non-regular hncp monolayer was formed. This is attributed to the presence of the materials interconnecting a PS sphere to neighboring PS spheres. Therefore, a plasma etching process to separate PS spheres from neighboring spheres is mandatory for the production of regularly-ordered hncp colloidal crystals. Additionally, if spherical PS particles are exposed to plasma, only the top half surfaces of the spheres are etched away while the bottom half surfaces of the PS spheres are intact. This fact can explain the reason why biconvex-shaped particles shown in Figure 1b were created when the PS spheres were slightly plasma-etched.

3. Conclusions

In summary, we present a novel route to controllably fabricate hncp monolayer colloidal crystals and BCCs based on the pyrolysis of plasma- and electron-irradiated PS colloidal monolayers. The particle size and the periodicity of the 2D hncp colloidal crystals can be controllably changed by differing the pyrolysis duration and the pristine PS sphere sizes, respectively. The approach is very useful to produce hncp colloidal crystals of desired structures and might also be used to fabricate more complex colloidal crystals for various applications including photonics, sensors, and catalysis.

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