

Unconventional Method for Morphology-Controlled Carbonaceous Nanoarrays Based on Electron Irradiation of a Polystyrene Colloidal Monolayer

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ABSTRACT An unconventional and straightforward route to fabricate morphology-controlled 2D ordered carbonaceous nanoarrays is presented. This route is based on the electron irradiation of a polystyrene colloidal monolayer followed by thermal decomposition. This strategy has the advantages of low-cost fabrication and easy manipulation compared to conventional lithography technique and furthermore overcomes the disadvantage of the self-assembly technique that generally has the defect of irregular units in ordered arrays. Various nanoarrays with irregular units, including network-like and star-like ordered arrays as well as hexagonal non-close-packed dot arrays, were fabricated by this novel route. These ordered arrays can be used as templates or masks to fabricate other ordered structures and then can be removed completely by thermal decomposition at a high temperature. Additionally, these arrays are carbonaceous materials that have higher thermal stability and higher refractive index compared with those of the pristine polymer, which are important for real applications such as optical devices. This method might also be used for the fabrication of other unique ordered arrays if different polymer precursor materials are used.

KEYWORDS: carbon nanoarray · non-close-packed array · electron-irradiation · colloidal monolayer · morphology control

Two-dimensional (2D) nanostructured arrays (nanoarrays) have recently attracted much interest due to their various applications in sensors,¹ photonic crystals,² optoelectronic devices,³ surface enhanced Raman scattering,⁴ and microfluidic devices.⁵ Because the properties of nanoarrays strongly depend on the morphology and the size of a unit in the arrays, the development of morphology- and size-controlled synthesis techniques becomes an important issue. Conventional methods for the synthesis of nanoarrays mainly focus on lithographic techniques, such as photolithography, electron beam lithography, and X-ray lithography.^{6,7} Corresponding masks need to be prepared for these methods to fabricate nanoarrays with different morphologies. Although these methods have been well developed, high cost and low throughput still remain un-

solved. Recently, other parallel techniques mainly based on self-assembling routes have been developed. Self-assembly is more suitable for the fabrication of ordered nanoarrays with spherical particles (e.g., 2D colloidal crystals).^{8–11} However, when the shape of the particle becomes nonspherical, it becomes more challenging to create highly ordered arrays by this method.^{12–16} Patterned carbonaceous materials have been intensively researched for several decades because of their excellent properties as field emitters,¹⁷ nanoelectrodes,^{18,19} bionic materials,²⁰ optical devices,²¹ and biological devices.²²

Here, we present a straightforward and novel route to fabricate morphology-controlled 2D ordered carbonaceous nanoarrays with nonspherical units based on the electron irradiation of polystyrene (PS) monolayer colloidal crystals followed by thermal decomposition. In this method, we utilized the intrinsic orderliness of monolayer colloidal crystals and the electron irradiation technique with subsequent heating. As a result, nanoarrays of various morphologies are evolved from the colloidal monolayers at different irradiation and heating conditions. Carbonaceous nanoarrays, including network-like and star-like ordered arrays as well as hexagonal non-close-packed (hnccp) dot arrays are produced. The ordered array of star-like particle is unique and is first reported here. In addition, the periodicity and the size of arrays can be tuned by changing the sizes of PS spheres comprising monolayer colloidal crystals.

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RESULTS AND DISCUSSION

Polystyrene colloidal monolayers with different sphere diameters were prepared on a silicon wafer through the self-assembly of PS nanospheres. The colloidal monolayer with its substrate was placed in a vacuum chamber for the electron-beam irradiation. After the electron irradiation, the sample was heated in ambient air at 360 °C using a furnace. The 2D carbonaceous nanostructured arrays thus were manufactured on the substrate.

Figure 1 shows field-emission scanning electron microscope (FESEM) images of fabricated 2D nanoarrays. Polystyrene colloidal monolayers were prepared with PS spheres 350 nm in diameter. The colloidal monolayer kept its original morphology of hexagonal closed-packed sphere array after electron irradiation (Figure 1A). Interestingly, however, if the irradiated sample was subsequently heated, the morphology of the monolayer evolved into different ordered arrays. When the electron-irradiated sample was heated for 1 h, the size of each sphere was decreased to ~ 275 nm. However, each sphere was still linked with its neighboring spheres by means of “necks”. As a result, the morphology of the monolayer was converted to a network-like array (Figure 1B). When the heating time was increased to 2 h, the particle size was further decreased to ~ 160 nm and the necks were broken. Consequently, the morphology of each particle unit assumed a star-like shape composed of an isolated sphere and six symmetric legs around it (Figure 1C). Further increase in the heating time to 4 h completely removed the necks and reduced the particle size to ~ 80 nm, resulting in hncp dot arrays (Figure 1D). All of these created nanoarrays exhibited a hexagonal arrangement like that of the pristine monolayer with each particle unit being located at the same place of its corresponding PS sphere.

We observed that such ordered arrays shown in Figure 1 could not be fabricated only by heating the pristine PS colloidal monolayer. It is well-known that the glass transition temperature (T_g) of PS is *ca.* 100 °C,^{23,24} and the thermal degradation of PS starts at 310 °C.²⁵ If the PS colloidal crystal is heated at a temperature a little higher than T_g , it will be deformed as a result of the partial melt of the PS spheres (Figure 2B). In addition, if

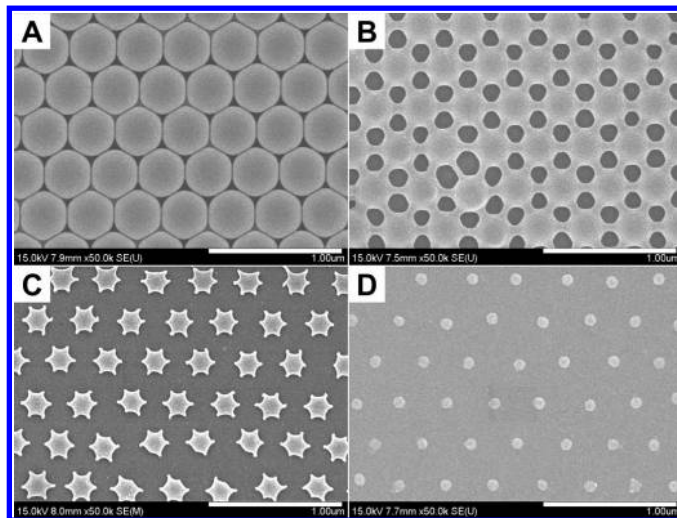


Figure 1. FESEM images of PS colloidal monolayers: (A) after electron irradiation and (B–D) after electron irradiation and subsequent heating at 360 °C for 1, 2, and 4 h, respectively. Scale bars are 1 μ m.

the PS colloidal crystal is heated at a temperature above 310 °C, it will be pyrolyzed. When the pristine PS colloidal monolayers comprising 350 nm spheres were heated at 360 °C for 1 h, they were completely decomposed, and finally nothing was left on the substrate, as shown in Figure 2C. These indicate that electron irradiation is crucial for fabrication of these ordered arrays.

The changes in the chemical structure of PS colloidal monolayers were characterized by Raman spectra to investigate the effect of the electron irradiation and the heating. Pristine PS has several peaks in the Raman spectrum (Figure 3A). However, all of the peaks disappeared after electron irradiation, and instead one broad and asymmetric peak at 1520 cm^{-1} , which can be more clearly seen in Figure 3B, appeared. The broad peak can be decomposed into two Gaussian peaks centered at near 1380 and 1550 cm^{-1} , which correspond to the D and G peaks of disordered graphitic materials, respectively (Supporting Information, Figure S1). In addition, the Raman spectrum of the irradiated PS had a linearly increasing background. These indicate that PS was transformed into hydrogenated amorphous carbon (a-C:H) by the electron irradiation.²⁶ When the irradiated PS monolayers were heated at 360 °C, apparent D and G peaks were seen in the Raman spectra; the posi-

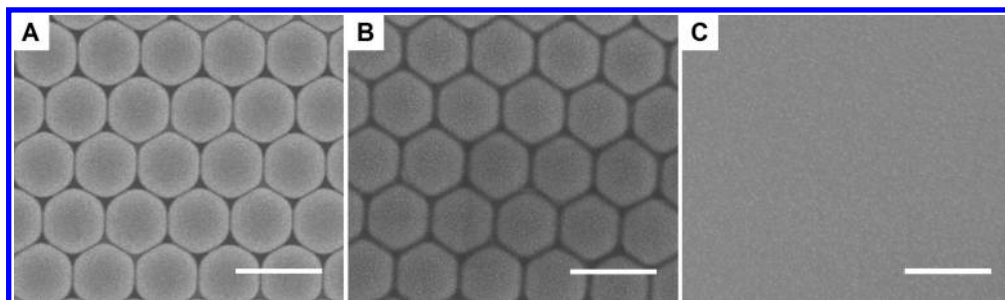


Figure 2. (A) FESEM image of pristine PS colloidal monolayer with sphere size of 350 nm. (B and C) FESEM images of the pristine PS monolayer heated at (B) 120 °C for 6 min and (C) 360 °C for 1 h without electron irradiation. Scale bars are 500 nm.

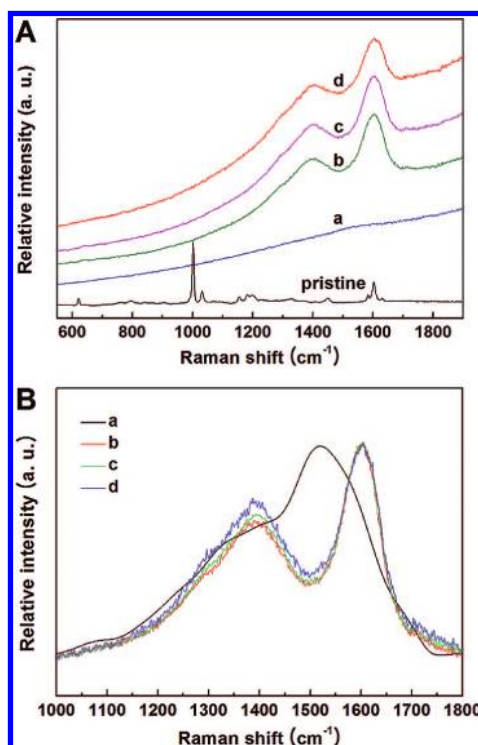


Figure 3. (A) Raman spectra of a pristine PS colloidal monolayer (black) and electron-irradiated PS colloidal monolayers: (a) without heating and after heating at 360 °C for (b) 1, (c) 2, and (d) 4 h, respectively. (B) Background-subtracted Raman spectra of (a–d) in (A).

tion of the D and G peaks shifted to about 1390 and 1600 cm^{-1} , respectively. This upward shift of the D and G peaks represents the reduction of bond angle disorder and growth of aromatic clusters.^{27,28} Furthermore, the intensity ratio of D and G peaks (I_D/I_G) increased while the bandwidth of G peaks decreased compared to those of irradiated PS samples (Supporting Information, Table S1). These indicate that irradiated PS became more carbonaceous material by subsequent heating. One thing to note is that heating time did not greatly change the Raman spectra. According to the report of Schwan et al.²⁶ and on the basis of the measured parameters shown in Table S1 in Supporting Information, we can conclude that the electron irradiation changed PS into a-C:H where aromatic clusters are embedded and the size of the aromatic clusters (<1 nm) were slightly increased by the subsequent heating.²⁹

In our previous report, we showed that hydrocarbon polymer could be transformed into a-C:H.^{30,31} Electron irradiation breaks molecular bonds of polymer followed by abstraction of hydrogen from the polymer, thereby increasing the relative ratio of carbon to hydrogen. Additionally, carbon radicals are created as a result of bond breakage. These radicals bond with each other to form sp^2 and sp^3 carbon atoms, as well as aromatic clusters. Consequently, as the electron dose increases, the polymeric material is gradually transformed to a-C:H with aromatic clusters. Aromatic clusters may

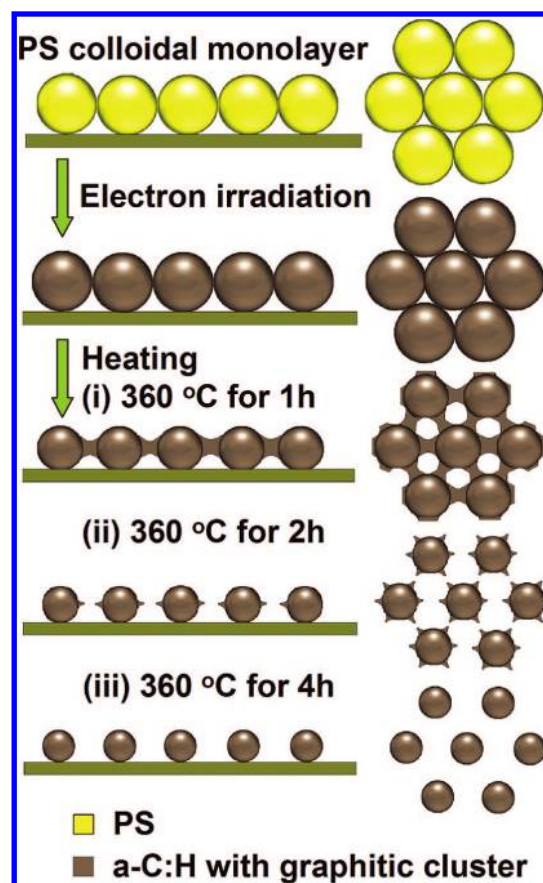


Figure 4. Schematic layout for the formation process of the ordered carbonaceous nanoarrays.

tend to be easily formed by the irradiation because PS has an aromatic ring in a repeating unit.

On the basis of the above analysis, the formation mechanism for these ordered carbonaceous nanoarrays can be easily understood. PS colloidal monolayers are changed to a-C:H sphere arrays after the electron irradiation. Because such a-C:H sphere arrays have a much higher thermal stability than pristine PS spheres, only a small portion of a-C:H spheres are decomposed after heating at 360 °C for 1 h. The size of each sphere decreases as a result of the thermal decomposition while maintaining the spherical shapes. The PS spheres start to be decomposed from outer part of the particles. Since the spheres were originally adhered to each other, slight decomposition of the spheres leaves necks between the neighboring spheres. As a result, network-like arrays are created (i in Figure 4). Further increase in heating time causes the necks to break, resulting in the formation of star-like arrays (ii in Figure 4). Structural changes during the formation of star-like arrays from network-like arrays are shown in Figure 5, which gives clear evidence of morphology evolution of these ordered nanoarrays in the thermal decomposition after electron irradiation. Slightly increasing the heating time causes the central part of the necks to become thinner and eventually break. A further increase in heat-

ing time results in further decomposition of the remaining particles creating hncp dot arrays (iii in Figure 4).

We also observed that ordered nanoarrays with similar morphologies were produced at the same irradiation and heating condition although the PS sphere size was changed from 350 to 750 nm (Supporting Information, Figures S2 and S3). The penetration depth, or range, of a 50 keV electron, is $\sim 42\ \mu\text{m}$, and thus large PS spheres of even a few tens of micrometers in diameter can also be modified by the electron irradiation. The electron range can be further increased by increasing the electron energy (Supporting Information, Figure S4). Therefore, the periodicity and the size of ordered nanoarrays can be easily tuned in a wide range by changing the size of pristine PS spheres. In addition, all the ordered arrays of different morphologies were completely decomposed by heating at $500\ ^\circ\text{C}$ for 4 h. This implies that these ordered arrays can be used as templates or masks to fabricate other ordered structures and then can be removed completely by thermal decomposition.

CONCLUSIONS

A novel and straightforward strategy to fabricate 2D carbonaceous nanoarrays with different morphologies is presented based on electron irradiation of a PS monolayer and subsequent thermal decomposition. Morphologies of ordered arrays can be readily controlled by changing the heating time after an electron irradiation. The periodicity and the size of arrays can be tuned by changing the sizes of PS spheres comprising monolayer colloidal crystals. The presented strategy is

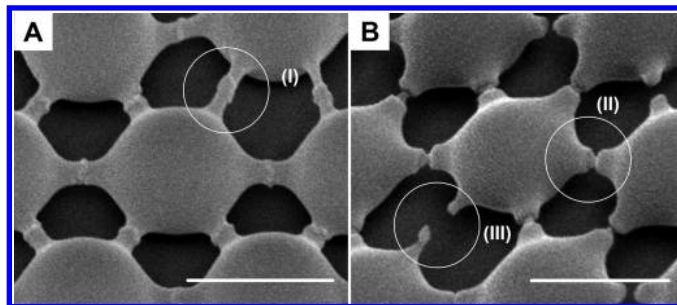


Figure 5. Magnified FESEM images showing the structural change from network-like arrays to star-like arrays. Those structures were fabricated by electron irradiation and subsequent heating at $360\ ^\circ\text{C}$ for (A) 1.25 and (B) 1.5 h, respectively. Scale bars are 300 nm. Area I: a junction on the “neck” in the network-like array, which comes from the original interface contact of two neighboring PS spheres. Areas II and III: the necks begin to be broken from junctions and are finally broken as a result of thermal decomposition.

completely distinguished from electron beam lithography. Electron beam irradiation in this strategy is necessary only to change the polymer to a-C:H with graphitic clusters. In addition, the top-down electron irradiation and the subsequent heating are parallel processes, and moreover a mask is not required in this strategy. Thus, large-area nanoarrays can be readily fabricated with relatively low cost using this strategy. The final products are carbonaceous materials that have higher thermal stability and higher refractive index compared with those of the pristine polymer, which are important for real applications such as optical devices. This strategy may also be used for the fabrication of other unique ordered arrays if different polymer precursor materials are used.

METHODS

Silicon wafers with the size of $1\ \text{cm} \times 1\ \text{cm}$ were ultrasonically cleaned in acetone and subsequently in ethanol for 1 h and finally cleaned in Piranha solution ($70\%\ \text{H}_2\text{SO}_4 + 30\%\ \text{H}_2\text{O}_2$) for 1 h, followed by triple rinsing in distilled water. Monodispersed PS suspensions (2.5 wt % in water, surfactant-free) with diameters of 350 and 750 nm were purchased from Polysciences Inc. The standard deviation in the diameter of the PS spheres is less than 5%. PS colloidal monolayers were prepared on silicon wafer substrates through the self-assembly of PS nanospheres.^{32–37}

The PS colloidal monolayer with its substrate was put into the chamber of an electron beam irradiation device and irradiated with an electron beam that was generated from a thermionic electron gun.^{38,39} The irradiating process was carried out at ambient temperature in a vacuum chamber under a pressure of less than 2×10^{-5} torr. The energy of the electron beam irradiating the samples was fixed at 50 keV, and the current density of electron beam was $45\ \mu\text{A}$. The electron beam diameter was 15 mm, and the total electron fluence was $1.7 \times 10^{18}\ \text{cm}^{-2}$. The water-cooling system was used in order to remove a small quantity of heat produced in the electron beam irradiation process. After the electron irradiation, the samples were put into a furnace for heating in ambient air at $360\ ^\circ\text{C}$. Morphology of the samples was characterized by a field-emission scanning electron microscope (Hitachi, S-4800). Raman spectrum was measured by means of a micro-Raman spectrometer with an Ar ion laser (LabRam HR, Jobin-Yvon).

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Supporting Information Available: Background-subtracted Raman spectrum of electron-irradiated PS colloidal monolayer without heating; FESEM images of ordered arrays from the PS colloidal monolayer with PS sphere size of 750 nm after electron irradiation and subsequent heating with different time; corresponding FESEM image with a tilted angle of 60° ; relationship between electron range and the electron energy; and detailed analysis data of Raman spectra in Figure 2. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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