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Anisotropic deformation of polystyrene particles by MeV Au ion irradiation

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Abstract

MeV Au irradiation leads to a shape change of polystyrene (PS) and SiO_2 particles from spherical to ellipsoidal, with an aspect ratio that can be precisely controlled by the ion fluence. Sub-micrometer PS and SiO_2 particles were deposited on copper substrates and irradiated with Au ions at 230 K, using an ion energy and fluence ranging from 2 to 10 MeV and 1×10^{14} ions/cm^2 to 1×10^{15} ions/cm^2. The mechanisms of anisotropic deformation of PS and SiO_2 particles are different because of their distinct physical and chemical properties. At the start of irradiation, the volume of PS particles decrease, then the aspect ratio increases with fluence, whereas for SiO_2 particles the volume remains constant.

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Keywords: Anisotropic deformation; Ion irradiation; Polystyrene

1. Introduction

A bottom–up approach has been extensively employed for the fabrication of nanostructured materials. As structure-building units, sub-micrometer-sized colloidal particles have been used in the synthesis of photonic crystals [1], biological sensors [2], nanomachining [3] and templates for the fabrication of porous materials [4] or as masks for lithographic patterning [5,6]. Although the synthesis of colloidal particles with a spherical shape has been previously studied [7,8], the synthesis of non-spherical particles is still a big challenge. A photonic crystal usually possesses fcc or hcc close-packing structure through self-assembly of spherical colloidal particles by sedimentation or convective capillary flow. Photonic crystal building from non-spherical particles can make a breakthrough in the realization of a 3D photonic band gap [9], which is impossible for a close-packing structure. Though production of non-spherical particles has been reported [10], it is difficult to aggregate them into a well-ordered crystal structure by self-assembly. Ion-irradiation-induced anisotropic deformation is a useful method and has been investigated recently [11–14]. The method can deform the lattice of entire assembled structures. According to the thermal spike model [15], the high electronic energy deposition and a low directional straggle in the ion trajectory causes a cylindrically shaped narrow liquefaction region around the ion track. Plastic relaxation of the local shear stress induced by thermal expansion of this hot cylindrical region can result in plastic deformation perpendicular to the cylindrical axis. The diameter perpendicular to the ion track increases and the diameter parallel to it decreases, making the spheres into oblates. However, these studies were limited to inorganic substances such as SiO_2 and ZnO and the deformation of organic substances has not been reported up to now.

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Organic material has unique physical and chemical properties compared with inorganic material. In the fabrication of inverse opal photonic crystals, colloidal particle assembly was used as template and is removed after filling the voids with high refractive index inorganic materials (for example, TiO_2 with a refractive index of 2.6) [16,17]. In such cases, a polymer template is usually employed because it can be easily removed by an organic solvent or burned off in an oven without damage to the inorganic skeleton [16–19].

In this paper, PS particles were bombarded with MeV Au ions and a large deformation successfully obtained. The irradiation-induced deformation mechanism for colloidal polymer spheres is discussed.

2. Experiment

PS particles with diameters of 1000 ± 45 nm and 670 ± 25 nm and SiO_2 particles with a diameter of 450 ± 20 nm were dispersed in ethanol. Droplets were dripped onto a clean surface of a Cu foil and dried naturally in air for 24 h. The experiments were carried out with Au ions produced by a 1.7 MV tandem accelerator, with a vacuum below 1×10^{-4} Pa. The samples were irradiated at 230 K, the Au ion energy was varied between 2 and 10 MeV and fluences ranged from 1×10^{14} to 1×10^{15} ions/cm^2. The Au ion beam was at an angle of 45°with respect to the sample surface.

The morphology of the irradiated and non-irradiated particles was probed by scanning electron microscopy. Images were recorded in the direction perpendicular to the irradiation beam to give optimum observation of the deformation of the spherical particles, as shown in Fig. 1(a).

3. Results and discussion

Fig. 1(b) shows a SEM image of the 670 nm diameter PS irradiated by 10 MeV Au ions with a fluence of 2×10^{14} ions/cm^2. It clearly shows that anisotropic deformation of the particles occurred after irradiation. The spheres were deformed into oblate ellipsoids. Different kinds of colloidal particle deformation extent could be qualitatively evaluated from the aspect ratio defined as the transverse

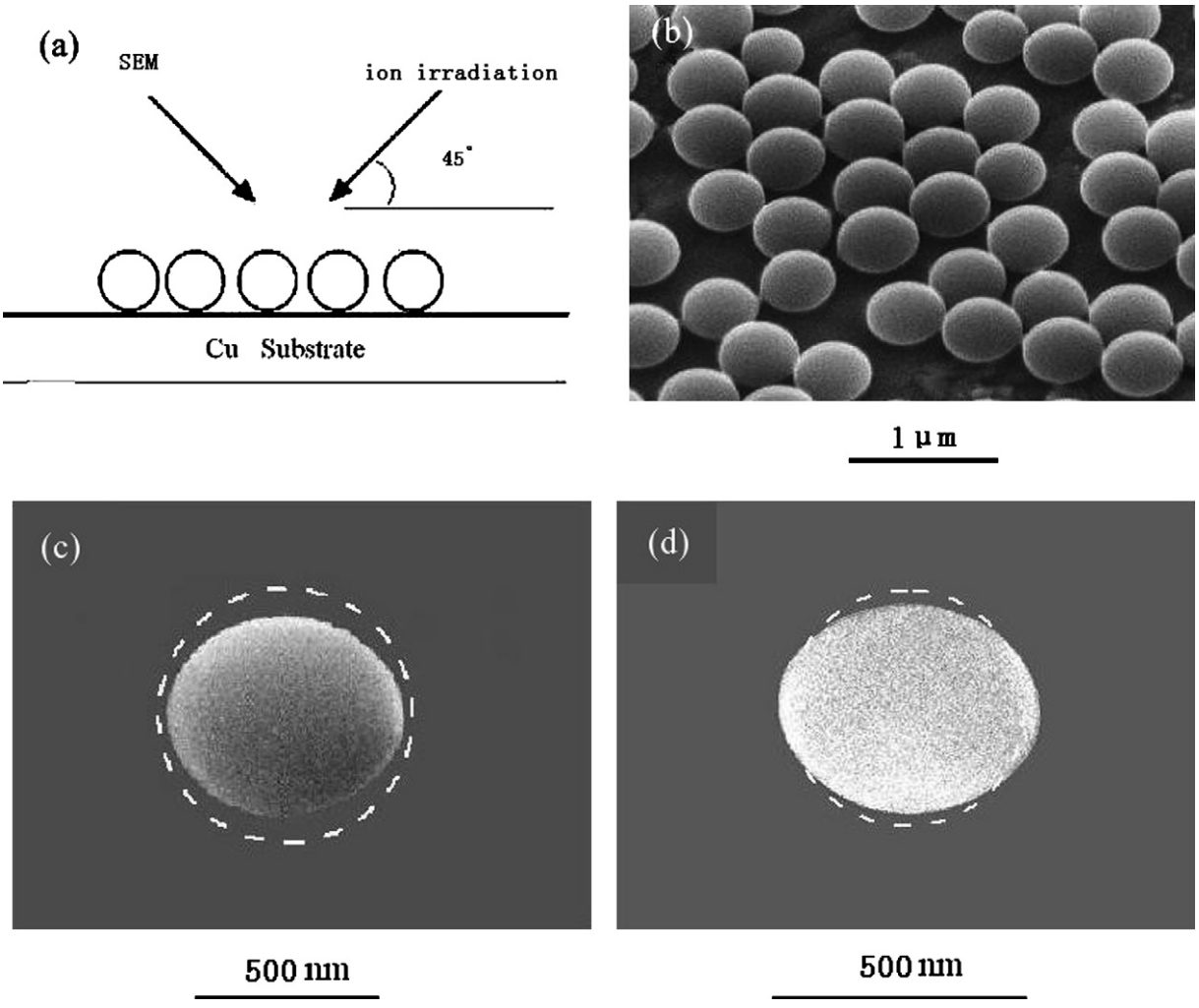

Fig. 1. (a) Irradiation geometry. (b)–(d) SEM images of the samples after 10 MeV irradiation to a fluence of 2×10^{14}/cm^2; (b) 670 nm PS particles; (c) single 670 nm PS, the dashed circle represents the original spherical size before irradiation; (d) single 450 nm SiO_2 particle, the dashed circle represents the original spherical size.

diameter divided by the longitudinal diameter of the oblate ellipsoids, as listed in Table 1. Fig. 1(c) and (d) shows the change of 670 nm PS and 450 nm SiO_2 irradiated with 6 MeV Au ions to a fluence of 2×10^{14} ions/cm^2. From Fig. 1 and Table 1, it can be seen that the volume of PS particles decreases whereas the volume of SiO_2 is almost unchanged after irradiation.

Table 1
Diameter and aspect ratio of different colloidal particles irradiated by 10 MeV Au ions with a fluence of 2×1014/cm^2

Sample (nm)	Transverse diameter (nm)	Longitudinal diameter (nm)	Aspect ratio
1000 PS	938 ± 42	760 ± 35	1.23
670 PS	635 ± 23	510 ± 18	1.25
450 SiO_2	504 ± 18	405 ± 16	1.24

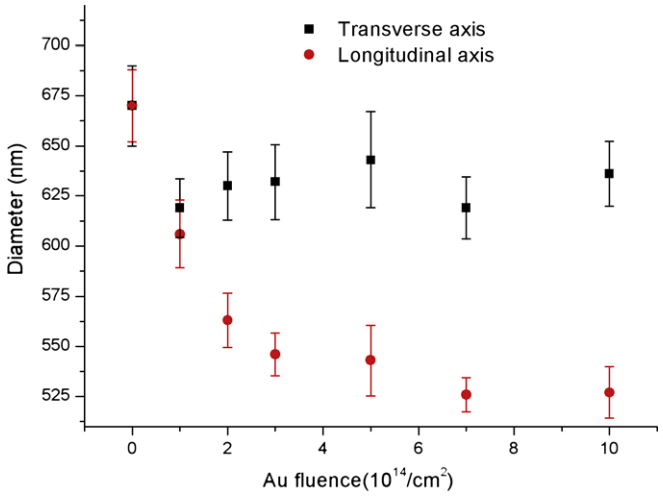

Fig. 2. Change in diameter as a function of 6 MeV Au ion influence.

In order to measure the deformation rate with fluence, the 670 nm PS particles were irradiated with 6 MeV Au ions from 1×10^{14} ions/cm^2 to 1×10^{15} ions/cm^2. Because organic and inorganic materials have totally different physical and chemical properties, the deformation mechanism of PS particles under irradiation cannot be deduced from that of SiO_2 [15]. Changes in the longitudinal and transverse diameter of the 670 nm PS particles as a function of fluence are shown in Fig. 2. The PS particles become smaller with increasing fluence, while no volume changes were found for SiO_2 particles, as shown in [11]. The shrinking process took place inhomogeneously, being larger at the initial stage and approaching a constant rate at the final stage. The high electronic energy deposition causes a high temperature region around the ion track. Polymerization contraction occurs at high temperature for the cross-linking [20]. In PS, the formation of hydroxyl (–OH), alkene (C=C) and alkyne (C–C) groups has been observed with MeV heavy ion bombardment [21], so the chemical change has to be considered besides the thermal spike model [15].

The shrinkage of PS particles is beneficial from some points of view. The volume of inorganic particles does not change after irradiation which causes the transverse diameter of irradiated oblates to be longer than the diameter of the original spheres. The crystal lattice of

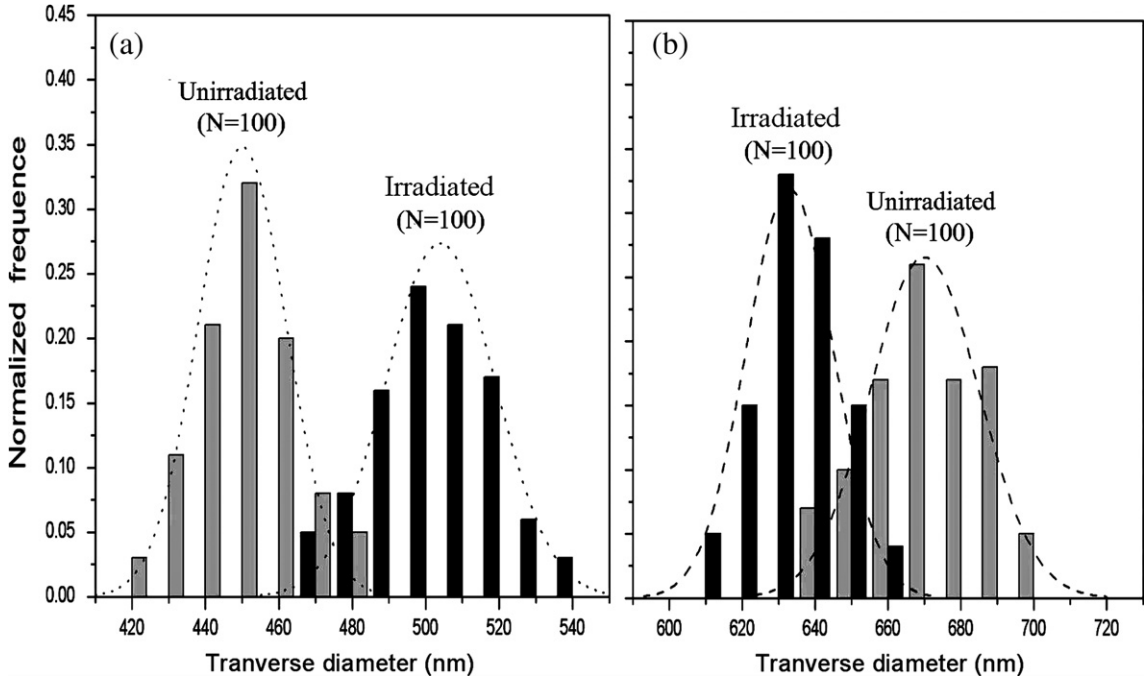

Fig. 3. Histogram of the transverse diameter size distribution of non-irradiated and irradiated particles with 10 MeV Au ions to a fluence of 2×10^{14}/cm^2 (a) SiO_2 particles (Gaussian distributions with standard deviations of $\sigma = 20$ nm (unirradiated) and $\sigma = 18$ nm (irradiated are indicated by the dashed lines); (b) PS particles (Gaussian distributions with standard deviations of $\sigma = 25$ nm (unirradiated) and $\sigma = 23$ nm (irradiated are indicated by the dashed lines).

self-assembled multilayer photonic crystal is either fcc or hcp. Deformation of the particles may produce tensile stress with the surrounding particles leading to a decrease of lattice integrity. For the PS particles we observed that the transverse diameter is smaller than the diameter of the original spheres in Fig. 2. Hence the deformation of PS particles does not cause interaction between the oblate spheres after irradiation, so the crystal lattice is undisturbed.

Fig. 3 shows the size distribution of the transverse diameter of 670 nm PS and 450 nm SiO_2 particles before (gray histogram) and after (black histogram) irradiation. The transverse diameters of the SiO_2 and PS particles change in a different manner, one becomes large and one becomes small. It also proved that the volume of the PS becomes small after irradiation and the volume of SiO_2 almost does not change.

Anisotropic deformation of PS particles is due to electronic energy loss deposition and its relaxation process. According to the thermal spike model [15,22] the anisotropic deformation per unit of deposited energy density can be represented as $\partial A/\partial S_e \propto \alpha/\rho C$ at the same irradiation fluence, where α is the thermal volume expansion coefficient, ρ is the mass density and C is the specific heat per unit mass. Thus the deformation of PS is larger than for SiO_2 by almost two orders of magnitude [23]. To compare the deformation rate as a function of the electronic energy loss, we measured the longest axis d_1 and shortest axis d_2 of the oblate ellipsoids, such that the aspect ratio of the oblate $\kappa = d_1/d_2$. Fig. 4 shows the aspect ratio change of the 670 ± 25 nm PS and 450 ± 20 nm SiO_2 oblates as a function of the average electronic energy loss of Au ions with a fixed fluence. The PS aspect ratio change is larger than that of SiO_2 at the same electronic energy loss. However, the deformation rate of PS is not two orders of magnitude larger than that of SiO_2 [23]. During Au ion bombardment of PS, α, ρ and C change greatly, with α increasing and ρ and C decreasing. Prolonging the line, it can be deduced that there is an electronic energy loss threshold for the deformation, even if such a threshold was not reported in [14]. The reason for the difference may be the irradiation temperature. In [13] the irradiation temperature was 77 K, far lower than that used here. A lower irradiation temperature can induce a larger deformation rate, as proved in [14]. The electronic energy loss threshold is 1.25 keV/nm and 1.33 keV/nm for PS and SiO_2, respectively at 230 K in our experiments.

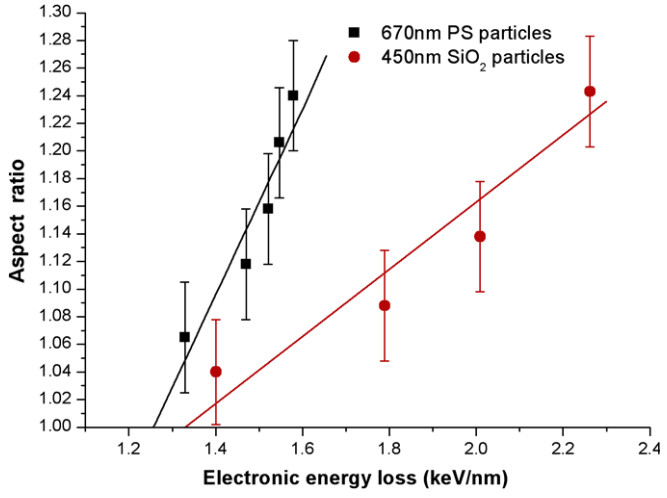

Fig. 4. Aspect ratio of SiO_2 and PS oblates at a fixed fluence of 2×10^{14} ions/cm^2 as a function of the average electronic energy loss at 230 K.

4. Conclusions

A combination of chemical synthesis, self-assembly and ion irradiation makes it possible to fabricate colloidal ellipsoids with a continuously tunable shape. Although irradiation-induced anisotropic plastic deformation of colloidal inorganic particles has been previously investigated, deformation of organic particles has not been reported until now. Here, MeV Au ions were used to bombard PS and SiO_2 particles, leading to a shape change from spherical to ellipsoidal, with an aspect ratio that can be precisely controlled by the ion fluence. The same deformation rate of PS particles needs less electronic energy loss than that of SiO_2 and the electronic energy loss threshold for PS deformation is less than that of SiO_2. Deformation of PS is important because it possesses obvious advantages compared with inorganic particles. As a template material, deformed PS colloidal particles can be easily removed from the host material and deformation leaves undisturbed the integrity of the material lattice, so deformed PS colloidal particles could have more widespread applications.

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