Communication

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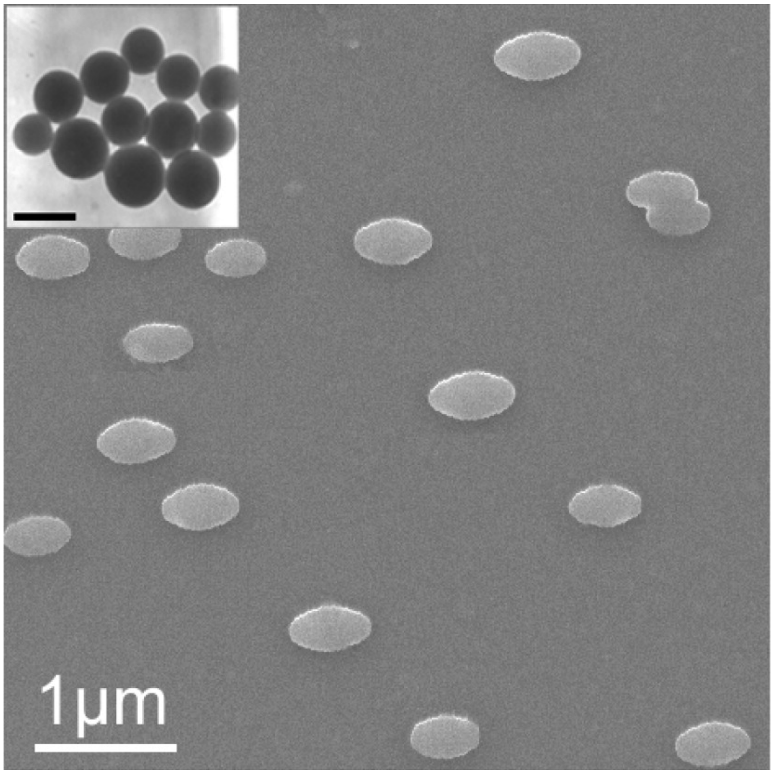

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Photoinduced Deformation of Amphiphilic Azo Polymer Colloidal Spheres

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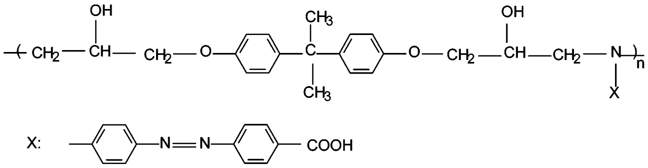
Photoinduced reversible surface deformation on films of azo polymers (polymers containing azobenzene-type chromophores) has attracted considerable attention since the effect was first reported by Natansohn et al. and Tripathy et al. in 1995.[1,2] When these films are irradiated with an interference pattern of coherent Ar^+ laser beams, surface relief gratings (SRGs) can be formed on the film surfaces at temperatures well below the glass transition temperatures (T_gs) of the polymers. The SRGs formed are stable below the T_gs of those polymers and can be removed by heating samples to temperatures above their T_gs or erased optically even below the T_gs. Experiments indicated that the SRG formation is neither a thermally driven process nor the ablation in the irradiation regions at low or middle light intensity.[3−6] The process is believed to be the effect of the repeated trans−cis isomerization cycles caused by photoexcitation of azobenzene chromophores. The large-scale surface deformation has been attributed to internal pressure gradients caused by an isomerization-driven free volume expansion in the bulk,[3] the force based on the dipolar interaction of the azo chromophores with the optically induced electric field gradient,[4] a translational wormlike diffusion caused by the photoisomerization of the azobenzene chromophores,[5] and a mean-field force caused by the molecule alignment.[6] The grating formation process implies that the effect of light irradiation should be able to cause deformation of other types of azo polymer substances within micrometer scale. However, evidence pointing to such discovery is still lacking.

Colloidal particles, which have been widely applied in many industrial products, have at least one dimension within the nanometer to micrometer range.[7] Colloidal particles formed from azo polymers can be used as a relatively simple material to demonstrate the photoinduced deformation effect. Spherical colloids have played a predominant role in the colloid science and technological endeavors for many years.[8] Recently, the effort to produce nonspherical colloids from spherical colloids, such as by mechanically stretching spherical colloids embedded in polymeric matrixes,[9] has started to arouse significant interest due to potential applications in photonic band gap (PBG) crystals.[10] In such applications, fabrication based on a light-driven process can show some obvious advantages. Here, we communicate the observation that significant shape deformation was photoinduced for colloidal spheres made of an amphiphilic azo polymer. By this process, nonspherical colloids can be controllably photofabricated from spherical colloids.

The chemical structure of the polymer (BP-AZ-CA) is given as



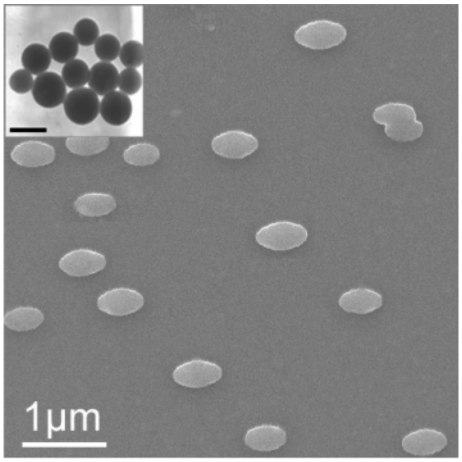


Figure 1. SEM image of prolates obtained from the colloidal spheres of the azo polymer after being exposed to interfering polarized Ar^+ laser beams for 10 min. Insert: TEM image of the spherical colloids before irradiation. The average size of the spheres is 295 nm, and the scale bar in the TEM picture is 300 nm.

The preparation and characterization of the polymer have been reported elsewhere.[11] BP-AZ-CA is covalently bonded with the pseudo-stylbene-type azo chromophores[12] and has been known as an SRG-forming polymer.[11] The number average molecular weight of the polymer was estimated to be 41 000 with the polydispersity index of 2.2.

The colloidal spheres were prepared by a method similar to those used to obtain micelles and other self-assembled aggregates of amphiphilic polymers.[13] In the process, BP-AZ-CA was first dissolved in tetrahydrofuran (THF), a good solvent for the polymer, and then a suitable amount of Milli-Q water was added dropwise into the THF solution. When the water content reached a critical value,[14] uniform colloidal spheres were obtained. Then an excessive amount of water was added to quench the structure formed, and the suspension was dialyzed against water for 72 h to remove THF. The sizes of the colloidal spheres were detected by Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS).[15] When the initial concentration of BP-AZ-CA in THF changed from 0.1 to 1.0 mg/mL, the average size of the spheres could be adjusted in a range from 160 to 310 nm.

The water suspension of the colloidal spheres (2 mg/mL) was transferred to the surface of a silicon wafer, which formed a thin layer by solution casting under gravity. An Ar^+ laser beam at 488 nm with an intensity of about 150 mW/cm^2 was used as the light source (Figure S1 in the Supporting Information). The colloidal spheres were exposed to the interfering p-polarized Ar^+ laser beam for different time periods. A typical Scanning Electron Microscopy (SEM) image of the colloidal spheres after the laser irradiation for 10 min is given in Figure 1.[16] A TEM image of the spheres before the laser irradiation is shown as an insert in the same figure for comparison. It can be seen that before exposure to the laser beam,

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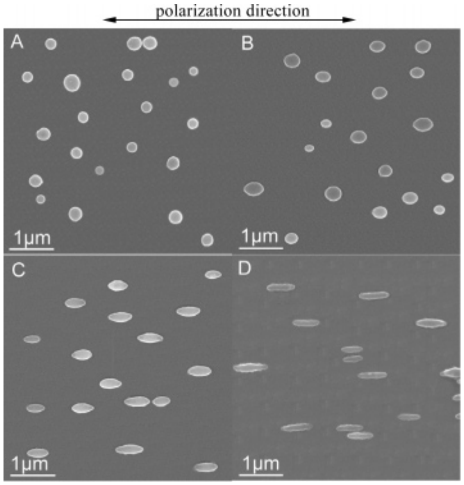

Figure 2. SEM images of colloidal spheres before irradiation (A) and after irradiation for different times: (B) 5 min, $l/d = 1.31$; (C) 12 min, $l/d = 2.03$; (D) 15 min, $l/d = 2.35$.

the colloids were typical spheres. After the irradiation, the spheres were deformed to ellipsoids, which was confirmed also by AFM and TEM (Figures S2 and S3 in the Supporting Information). The elongated direction of the spheres is perpendicular to the casting direction and is the same as the polarization direction of the laser beam, which has been proposed as the gradient force direction induced by the interfering polarized laser beams.[4]

The average major-to-minor axis ratio (l/d) of the colloids can be used to express the deformation degree of the colloids, which can be controlled by the exposure time of the colloidal spheres. Figure 2 shows the SEM images of colloidal particles observed before irradiation and after irradiation for different times. After 5 min irradiation, obvious change in the shape can be observed. The morphology of colloidal spheres changes to prolates (i.e., "rugby-balls"). The average major-to-minor ratio is about 1.31 (as shown in Figure 2B). When the irradiation time increases, the elongation ratio also gradually increases. The average major-to-minor ratios after 12 and 15 min irradiation are 2.03 and 2.35, respectively (as shown in Figure 2C,D). The morphology of colloids changes to "spindles", and finally even to "rods". When irradiated for a longer time (30 min), the colloids continue to deform, but the shape of the particles becomes less regular (Figure S4 in the Supporting Information).

The relationship of the average major-to-minor ratio (estimated statistically from SEM images of 100 colloidal particles) and the irradiation time is given in Figure 3. It can be found that the major-to-minor ratio increases almost linearly with the irradiation time in this range. It indicates that the colloidal particles with different major-to-minor ratios can be prepared by simply adjusting the irradiation time.

The exact mechanism that caused the colloidal sphere deformation is not clear to us at this current stage. The gradient force model, proposed by Kumar et al. to explain the SRG formation,[4] appears to agree with the observation. However, the possibility that other mechanisms may also play a role in the process cannot be ruled out. It is believed that the deformation effect demonstrated in this article will shed new light on the general understanding of the photoinduced deformation nature and can be used as a new way to prepare nonspherical colloids from colloidal spheres.

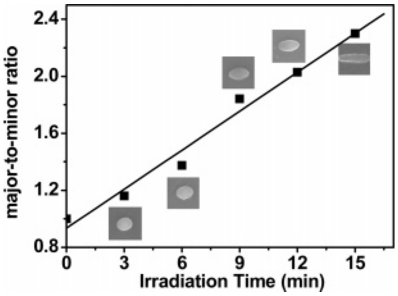

Figure 3. Relationship between the average major-to-minor ratio of the colloidal particles and the irradiation time.

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Supporting Information Available: Experimental setup for laser light irradiation, AFM and TEM images of the ellipsoids, and SEM images of the colloids after irradiated for 30 min. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) The critical water content depended on the initial concentration of BP-AZ-CA in THF. The critical H_2O/THF ratios were in a range from 0.2 to 0.3 (v/v) under current conditions.
(15) A Hitachi H-800 transmission electron microscope with the accelerating voltage of 150 kV was used to observe the spheres. The size and size distribution of the colloidal spheres were also measured with a Marvern Zetasizer 3000 dynamic light scattering instrument equipped with a multi-τdigital time correlation, a 632 nm solid-state laser light source. The scattering angle used for the measurement was 90°, and the temperature was controlled at 25 °C.
(16) The Scanning Electron Microscopy (SEM) measurement was performed on a field emission microscope JEOL JSM-6301F, which was operated with an accelerating voltage of 5 kV. All of the samples prepared for SEM studies were coated with thin layers of carbon (∼5 nm in thickness) before the measurement.

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