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Formation of Ordered Mesoporous Films from In situ Structure Inversion of Azo Polymer Colloidal Arrays

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Polymeric porous structures have attracted considerable attention in the past decades because of their possible applications in selective transportation, as catalytic substrates, in biosensors, and as photonic band-gap materials.[1−3] Two-dimensional (2D) and three-dimensional (3D) arrays of colloidal spheres have been widely used as templates to prepare the porous structures with pore sizes in the range from nanometer to micrometer scale.[4,5] In the first step of those template-directed syntheses, the void spaces among the colloidal spheres are fully infiltrated with a liquid precursor, such as a UV or thermally curable prepolymer or an initiator-containing monomer. After solidification of the precursor and removal of the colloidal spheres, highly ordered porous structures can be obtained. Recently, by using block copolymer films or a dual-component (soluble/insoluble) colloid system, the nanoporous or macroporous films have been prepared by selective interaction of solvents with one of the components.[6,7] In this process, the porous structures are formed through a self-assembly process, by which the infiltration step is unnecessary.

Polymers containing aromatic azo chromophores (azo polymers for short) have been extensively investigated in recent years.[8] Azo polymers can show a variety of structure and property variations induced by the trans−cis photoisomerization of the azobenzene units. Those characteristics are promising for applications in photodriven devices.[9,10] Recently, we have reported that photoresponsive colloidal spheres can be prepared from gradual hydrophobic aggregation of amphiphilic azo polymers.[11] The spheres and their arrays show some interesting properties, such as photoinduced deformation and dichroism. As the colloidal spheres possess a core−shell structure with a hydrophobic core and a hydrophilic shell, it can be expected that a treatment with the selective solvent may cause structure inversion.

In this work, it is demonstrated that, when induced by a proper solvent treatment, the ordered mesoporous films can be obtained by in situ sphere−pore inversion of 2D arrays of the azo polymer spheres. The porous structure formation process is schematically described in Figure 1. To our knowledge, this is the first example to show that mesoporous structures can be directly obtained from the colloidal arrays of a homopolymer through local structure inversion. Moreover, by exploiting the photoresponsive properties of the colloidal spheres, films with ordered elliptical pores can be feasibly prepared.

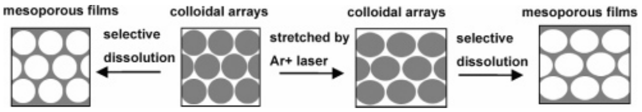
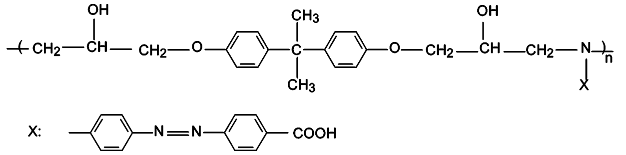


Figure 1. Formation of mesoporous films from the in situ structure inversion of azo polymer colloidal arrays.

The chemical structure of the azo polymer (BP-AZ-CA) used in this work is given as,



which contains both pseudo-stilbene-type azo chromophores and the hydrophilic carboxyl groups.[12] The number average molecular weight of the polymer was estimated to be 41 000, with the polydispersity index of 2.2 by the GPC measurement. The colloidal spheres of the azo polymer were prepared by gradual hydrophobic aggregation of the polymeric chains in $THF-H_2O$ media, induced by a steady increase in the water content.[11] The sizes of the colloidal spheres were estimated by TEM and Dynamic Light Scattering (DLS) measurement. The average hydrodynamic diameter (D_h) of the colloidal spheres used in this study was 223 nm, with the polydispersity index of 0.04 (Figure S1, in the Supporting Information). Two-dimensional arrays of the close-packed colloidal spheres were fabricated by the vertical deposition method.[4,11b] In the process, a silicon wafer was immersed vertically in the colloidal sphere's suspension (about 0.1 mg/mL), and the 2D arrays were obtained by evaporating the dispersion medium at a constant rate (about 0.05 mL/h). The preparation and characterization details for the polymer, colloidal spheres, and 2D arrays can be seen in our previous papers.[11,12]

The mesoporous films were obtained by placing the 2D colloidal sphere arrays in an enclosed chamber for solvent annealing for 6−9 h. The chamber was maintained at 30 °C and filled with THF vapor from the solvent reservoir. The structures formed were dried in a 30 °C vacuum oven for 12 h. A typical SEM image of the mesoporous structure formed by the in situ sphere−pore inversion of the sphere arrays is shown in Figure 2. The SEM image of the sphere arrays before the solvent treatment is shown as an insert in the same figure. Before solvent annealing, the arrays are composed of the hexagonally close-packed spheres. After the solvent treatment, the spheres are transformed to the mesoporous structure directly, which maintains the character of a hexagonal close-packed array. The average pore diameter (150 nm, with a root-mean-squared error of 24 nm), which was estimated from 540 randomly selected pores in SEM images, is smaller than the average sphere size. The distance between the pore centers was estimated to be 250 ± 20 nm. The Atomic Force Microscope (AFM) image of the mesoporous films is given in Figure 3, which further confirms the porous structure observed from the SEM observation. The pore size and the distance between the pore centers were estimated to be 150 and 260 nm from AFM section analysis (Figure S2, in the Supporting Information). The film thickness estimated from the AFM section analysis is about 143 nm.

It can be proved by spectroscopic methods that the porous structures and the colloidal arrays are composed of the same polymer (BP-AZ-CA). Figure S3 (in the Supporting Information)

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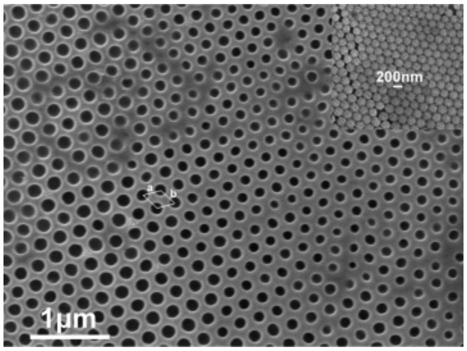

Figure 2. Typical SEM image of the mesoporous structure formed by the in situ sphere−pore inversion of the azo polymer colloidal sphere array, induced by solvent annealing. Inset: SEM image of the colloidal sphere array before the solvent treatment. The pore diameter and the distance between the pore centers were estimated to be 150 ± 24 and 250 ± 20 nm, respectively.

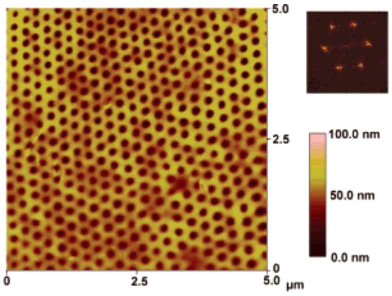

Figure 3. Typical AFM image and fast Fourier transform (FFT) plot of the mesoporous films formed by the in situ sphere−pore inversion.

gives the UV−vis spectra of both the porous structure and colloidal array, which show the same absorption characteristics. The sphere−pore inversion can be further confirmed by the transition of some "isolated" spheres. The SEM images of the isolated spheres and the porous structures obtained by the solvent treatment are shown in Figure S4 (in the Supporting Information). The porous structure can also be obtained by simply dropping THF on the colloidal array surface, although the edges of the pores are less regular (Figure S5, in the Supporting Information). The formation of the mesoporous structures is closely related with the amount of THF dropped. SEM images of the mesoporous films obtained by dropping a different amount of THF are given in Figure S6 (in the Supporting Information). It can be seen that, when the THF amount is small, some pores just begin to form and some spheres can still be seen after the dissolution (Figure S6A). When the THF amount is large, parts of the colloidal sphere array are transformed to a flat film without the porous character (Figure S6B).

The exact mechanism for the sphere−pore inversion is still unclear at the current stage. Due to the preparation method, the colloidal spheres possessed a densely packed hydrophobic core and a loose hydrophilic corona.[11] The sphere−pore inversion could be realized by reversing the colloid formation process, which was caused by the selective dissolution of THF to the different parts of the colloids. The possible scenario is that, in the process, THF swelled the core drastically, and the polymer chains in the corona migrated radially in outward direction and associated with each other to form the porous film. During the inversion process, the character of a hexagonal close-packed array and the periodicity were maintained because of the substrate surface confinement.

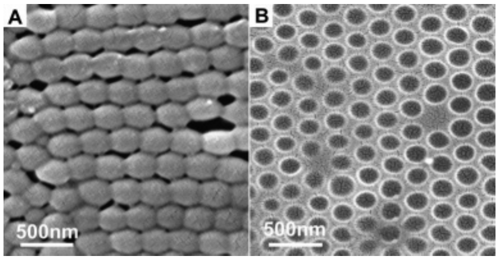

Figure 4. (A) SEM image of an array of the ellipsoidal colloids; (B) SEM image of the mesoporous film with elliptical pores.

The colloidal spheres can be stretched to nonspherical colloids, such as ellipsoidal colloids, by light irradiation.[11a] The SEM images of the array of the ellipsoidal colloids and the corresponding mesoporous film formed from the structure inversion are shown in Figure 4. The array of the ellipsoidal colloids was obtained by the irradiation of a polarized Ar^+ laser beam on the colloidal sphere array for 10 min. After the same annealing treatment, the array of the ellipsoidal colloids is transformed to the structure with elliptical pores. The average axial ratios of the colloids and pores are 1.46 and 1.25. The smaller axial ratio for the pores could be attributed to the stress relaxation occurring in the structure inversion process.

In conclusion, mesoporous polymeric structures with spherical and elliptical pores were obtained by the in situ structure inversion of the azo polymer colloidal arrays, induced by the solvent annealing. This self-assembling approach can be used to fabricate mesoporous structures without the infiltration−removal step. By exploring the photoresponsive properties of the materials, mesoporous films with special pore structures and properties can be expected.

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Supporting Information Available: Experimental conditions for TEM, SEM, AFM, and DLS measurements, and more results obtained from the characterization can be seen. This material is available free of charge via the Internet at http://pubs.acs.org.

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