Optical properties of PMMA inverse opal structures with anisotropic geometries by stretching

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Abstract

The fabrication of three-dimensional periodic microstructures with strong anisotropic geometries is important for nanophotonic devices including photonic crystals and hyperbolic metamaterials. In this study, a simple method using self-organizing colloidal inverse opals of PMMA with directional tensile deformation by stretching was successfully constructed in the temperature range 100 °C–115 °C. Reflection spectroscopy was used for investigating the photonic bandgap of the PMMA inverse opal with anisotropic geometries in anisotropic different extents. The wavelengths of the photonic bandgap were related to both the length of the pores in long-axis and short-axis of pores of the inverse opals. The wavelength changes of the photonic band gap significantly affected by the length variation in the short-axis. The anisotropic optical properties were also observed when Ag and Pt were deposited onto the top surface or conformally coated onto the interior interfaces of the anisotropic inverse opals. The structures with higher anisotropic ratios showed stronger variations in the wavelengths of the reflection valleys according to the surface plasmonic polarizations and cut-off frequencies with varying polarization angles of incident light. Moreover, the PMMA inverse opals conformally coated with metals presented indefinite dielectric properties in the visible or near-infrared wavelength region.

1. Introduction

The development of convenient fabrication method for advanced photonic structures including photonic crystals and metamaterials via colloidal crystals [1, 2] and their templating method is significant for future photonic applications [3]. Colloidal self-assembly and templating method provided successful route for three-dimensional photonic crystals [4, 5], and many photonic devices including anti-counterfeiting [6, 7], controlled optical filter [8, 9], and large-angle monochromatic light reflector [7] were built according to these colloidal photonic crystal structures [10, 11]. However, the structural anisotropies of these structures were not as desired, thus limiting their applications relying on the anisotropic photonic achievement. Metamaterials are artificial electromagnetic media with unique and exotic physical properties and have significant implications for sensing [12], imaging [13], and energy harvesting [14–17]. However, the formation of metamaterials highly relies on the complex subwavelength microstructures [18]. The microstructures of metamaterials have developed from double-split ring, single-split ring, and u-shaped ring to fishnet and double bars. Hyperbolic metamaterials are one of the nanophotonic structures relying on the indefinite permittivity, which is a specific high anisotropic dielectric properties [19–23]. They also have several advantages such as low loss, wider response angle, and frequency range. Therefore, the further development of method towards the colloidal structures with anisotropic geometries may provide both solutions for the fabrication colloidal photonic crystals with enriched symmetries and potential hyperbolic metamaterials.

PMMA inverse opals undergo deformation performed by stretching at approximately 80 °C were reported [24] owing to the malleability of polymers. The relationship between the extent of deformation of PMMA inverse opals and the stretching process including the temperature was not well discussed yet. In addition, in situ
polymerization method using methyl methacrylate (MMA) was used instead of solution based filling of inverse opals here for increasing the filling ratios for enhancing the optical properties of the PMMA inverse opals. The stretching temperature dependent anisotropies and related optical properties were also discussed. The indefinite dielectric properties for hyperbolic materials were also discussed based on these anisotropic inverse opals.

2. Results and discussion

The 3D photonic crystals with anisotropic geometries used here were fabricated using PMMA inverse opal film based on colloidal crystals. Colloidal crystal templates were obtained by vertical deposition of silica microspheres (234 nm). MMA was filled into the silica opal template before in situ thermal polymerization inside the opal templates. Then, the silica in the PMMA inverse opal film was removed. Because PMMA is a polymer material with high transparency and ductility, anisotropic PMMA inverse opal films were obtained by slowly stretching the films. Figure 1(a) presents the monodisperse silica opals obtained by the hydrolysis of ethyl orthosilicate with ammonia water. The particle size of silica microspheres was controlled by tailoring the concentration of ammonia and ethyl orthosilicate. Figures 1(b), (c) show the scanning electron microscopy (SEM) image of the PMMA inverse opal structures. The surface of the PMMA inverse opal structure is arranged in hexagonal pore geometries. As shown in figure 1(d), the PMMA inverse opal structure has a reflection peak at 407 nm. The reflection peak is induced from the photonic band gap. The simulated reflection spectrum of PMMA inverse opal structure with same periodicity is also presented in figure 1(d). The simulated reflection peak at 410 nm was basically consistent with the experimental result.

PMMA softens at temperatures >80 °C and can deform directionally under applied stretching force. At <100 °C, PMMA inverse opal structures did not deform into geometries with a high tensile extent before they were broken. The pores in the surface were still in near spherical shapes. There were several pores deformed into elliptical shapes on the top surface; however, the ovality of the pores was quite low and the orientations were still random. Therefore, the geometries of the PMMA inverse opals after stretching at 100 °C were nearly isotropic. The stretching of the film made the spherical pores deform into an elliptical shape, as shown in figures 2(b), (c). The pore periodicities of the PMMA inverse opal films were not destroyed after stretching, and the hexagonal arrangement of the ellipsoid pore arrangement remained. After stretching at 115 °C, the surface of the pores even turned into rod shapes (figure 2(c)). The main axis of the ellipse was parallel to the extension direction of the stretch, while the axis perpendicular to the stretching direction became shorter. The tensile ratio of PMMA inverse opal films was approximately 1:1.2 at 100 °C. The tensile ratios of PMMA inverse opal film were approximately 1:2.3 and 1:3.2 at 110 °C and 115 °C, respectively. The tensile ratio of PMMA inverse opal film was partly tailored by controlling the stretching temperature, until they were broken. The tensile extent increased with increasing temperature; however, PMMA inverse opal film melted at >120 °C. At 120 °C, structural periodicity was not preserved in the PMMA structures (figure 2(d)).

Figure 3(a) presents the reflection spectra of the PMMA inverse opal films stretched at 100 °C. The spectra are almost the same as that of the unstretched ones; however, the PMMA inverse opal films stretched at 110 °C and 115 °C show reflection peaks at approximately 350 nm. As the PMMA inverse opal films were deformed into
isotropic structures, the reflection peak shifted blue. Figure 3(b) shows the simulated reflection spectra of the deformed PMMA inverse opals with pores in different short and long axis lengths. When PMMA was stretched at 110 °C, the tensile ratios between the long and short axes increased to about 2.3, resulting in shifting the reflection peak to approximately 340 nm for the simulated PMMA samples as shown in figure 3(b) with 400 nm in long axis and 180 nm in short axis. The simulated and experimental reflection peaks are basically in accordance to each other. According to simulation, when the short axis length of the pores in PMMA inverse opals was similar, the reflection peaks red shifted with increasing length in long-axis. In the same way, the reflection peaks also red shifted with increasing the length in short-axis when fixing the long-axis length. When the lengths of the pores in long-axis and short-axis were changed simultaneously, the movement of the reflection peaks was affected by both variations in the length. The peak movement relied on variation in the short-axis length more strongly. Therefore, the reflection peaks at normal incident of the deformed PMMA inverse opal film shifted to shorter wavelength and turned broader after they were stretched with increasing length of long axis and the reduction of short axis of elliptical pores. The surface of PMMA might deform different from its interior structures, thus the simulated reflection peak using the surface measurement shifted slightly when compared with experimental peak.

The production of anisotropic geometries of the 3D dielectric porous structures provided possible way for preparing 3D anisotropic photonic crystals. Because metal structures can support surface plasmonic polarizations (SPPs) in which light couples to propagating electromagnetic surface waves at a metal-dielectric interface [25–29], these anisotropic structures coated with metals were also studied. Metals were deposited on the stretched PMMA inverse opal stretched films in two fashions. Gold was sputtered onto the top surface of the PMMA inverse opal films. Because the gold was only deposited on the top surface of the porous structures, no cut-off frequencies were observed in the reflection spectra according to these structures. However, SPP modes were observed on the surface of the metal structures and should be strongly dependent on their direction of propagation [25, 27, 29]. Therefore, the SPP modes were related to the anisotropic surface geometries of the
stretched PMMA inverse opal structures. The reflection spectra at a normal incident angle with different polarization directions are presented in figures 4(a)–(c). The reflection valley is induced from the synergies of the SPP modes and interferences of films. The polarization direction parallel to the direction of the tensile axis is considered as 0°. The deeper reflection valleys should be induced from the SPP of the metal surface on the stretched PMMA inverse opal films. The deeper reflection valley of the stretched PMMA inverse opal film at 115 °C is observed at 558 nm, when the polarization direction of the light was parallel to the elongation direction of the film. The reflection valley changes with the polarizations monotonously. When the polarization direction of the light is perpendicular to the stretching axis of the film, the position of the reflection valley changes to 590 nm, with a significant red shift. Similarly, the reflection valley of the PMMA inverse opal structure stretched at 100 and 110 °C also shifted to longer wavelength with increasing polarization angle of the incident light to the elongation direction. The specific variation of these data is shown in figure 4(d). Because PMMA stretched at higher temperature presented anisotropic geometries in higher extent, the wavelength variations of the corresponding reflection valleys increased more significantly.

The inner surfaces of the PMMA inverse opal film were electroless deposited with platinum. Figure 4(e) shows the reflection spectra with different polarization directions. Because the metal was filled inside the 3D porous structures, cut-off frequencies were observed in the range 600–700 nm. When the polarization of the light changed from parallel towards perpendicular to the elongation direction of PMMA, the wavelength of the related reflection valley changed from 648 nm to 673 nm. The cut-off frequencies red shifted with the change in polarization angle, due to the change in the periodicities along different directions. In addition to the anisotropic reflection spectra, the anisotropic geometries of the metal-dielectric hybrid structures may provide an indefinite dielectric constant, which is the basic property of hyperbolic metamaterials [30–32]. The stretched porous PMMA structure with anisotropic geometries coated with metals was simulated by the S-parameter method. Figures 5(a)–(c) show the related permittivity of the stretched PMMA inverse opals coated with different metals including silver, copper, and platinum according to two polarization orientations, the vertical and parallel directions to the elongation of PMMA. The PMMA inverse opal structures with long-axis length of 160 nm and short axis-length of 80 nm coated with 10 nm thickness silver, copper, and platinum were studied. The permittivity of these structures with polarization vertical to elongation of PMMA was always lower, and its values changed from positive to negative earlier with increasing wavelength when compared to the ones with perpendicular polarization. Therefore, indefinite intervals existed in these stretched PMMA inverse opals when they were conformally coated with metals. The hyperbolic behaviour of the effective medium of the anisotropic
PMMA porous structure coated with 10 nm silver, copper, and platinum were in the ranges 1163–1371 nm, 1225–1458 nm, and 728–778 nm, respectively. Figure 5(d) presents the dielectric constant diagrams of the PMMA inverse opals with anisotropic geometries coated with 15 nm platinum using the experimental periodicities of inverse opals (351 nm in long-axis length and 200 nm short-axis length). The hyperbolic behaviour of the effective medium in the range 759–805 nm was presented.

3. Experimental

Monodisperse silica microspheres were prepared by the hydrolysis of ethyl orthosilicate with ethanol, ammonia, and deionized water. The glass substrates (20 × 20 mm²) were vertically placed in the silica solution until the solution completely evaporated. Colloidal templates of silica microspheres were obtained by vertical deposition self-assembly. MMA and 2,2-azobisisobutyronitrile were added to the silica opal templates in a certain ratio and then polymerized in a 60 °C oven, affording PMMA filled silica opal templates. HF etched silica were obtained from the PMMA inverse opal films. PMMA inverse opal films were elongated using the self-made stretching devices with uniform stretching velocity in the temperature range 100 °C–120 °C, until they were broken. The samples were placed in vacuum before the Pt deposition to ensure a clean surface of the sample. The sample was placed in an aqueous solution of 0.028 mM H₂PtCl₆ and 6.25 mM CH₃OH. The ratio of CH₃OH to deionized water was kept constant at 1:4. The whole reactions were conducted under simulated solar light (xenon lamp) illumination. A deuterium-halide-combined light source (DH2000) providing light from 190 to 2500 nm was coupled to a Y-type fiber and a fiber coupled spectrometer equipped with a Si detector. Simulations of reflectances and S parameters were performed using the finite difference time domain method with plane wave as the light sources. Plane and point detectors were used for reflections and S-parameters, respectively. The effective dielectric constant of the structures was retrieved from simulated S parameters. The refractive refraction were set as 1.49 for simplicity, and all the metals were set with CRC optical constants.

4. Conclusion

PMMA inverse opal structures with anisotropic geometries in different aspect ratios in the range 1:1.2–1:3.2 were prepared by stretching PMMA in the range 100 °C–115 °C. The reflection spectra of the stretched PMMA inverse opals were related to both the length of the short and long axis periodicity of the structures. The reflection peaks shifted to short wavelength when PMMA inverse opals were stretched. The SPP valleys of the stretched inverse opals coated with metals on the top surfaces and the cut-off frequency of the stretched inverse opal conformally coated with metals shifted to longer wavelength when the polarization orientation deviated from the parallel direction according to the elongation of PMMA. The PMMA inverse opals conformally coated with 10–15 nm metals showed absorption in the visible or near IR wavelength with indefinite dielectric constants.
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