Nano-scale Shaping of Colloidal Building Blocks in Photonic Crystals

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Close packings of a number of colloidal particles has been studied due to its unusual optical properties or highly efficient mass transfer when it is used as catalytic support. In particular, controlling the light with these materials always require the precision in their periodic positions and size uniformity of building blocks at nanometer scale. Therefore, any additional process in photonic crystals should be nano-fabrication, of which uncertainty would be one billionth meter. In this presentation, we will demonstrate the use of dry etching as the highly precise nano-fabrication tool for isotropic shaping colloidal building blocks in self-assembled photonic crystals. In this case, we have controlled shapes of polymeric microspheres in their close-packed structures keeping the lattice constants, which have caused change of their optical property precisely.

The procedure for the fabrication of connected open structures is described schematically in figure 1. Firstly, the colloidal crystal film of 280-nm polystyrene (PS) microspheres on substrates was prepared by a modified vertical deposition method, and was annealed at 100 °C for 12 hours to make the PS spheres sintered and necked. The sintered colloidal crystals were then exposed to HNB (Hyperthermal Neutral Beam) of oxygen gas for the partial etching of PS microspheres. In doing this, the energetic neutral oxygen gas collides with PS microspheres and reacts with the hydrophobic surfaces to generate gaseous H_2O, CO, or CO_2 leaving behind the partially etched particles, each connected with twelve nearest neighbors through very thin cylinders. The etching chamber was operated at 80 mTorr of oxygen pressure for given etching time intervals.

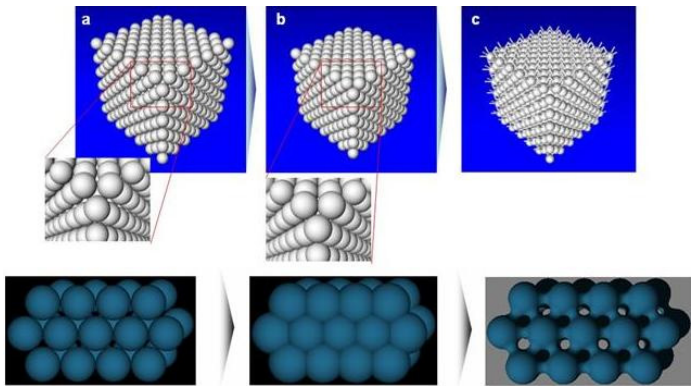

Figure 1. Schematic of the fabrication of non-close-packed artificial opals with interconnecting networks: (a) PS colloidal crystal film, (b) sintered colloidal crystal film, (c) non-close-packed artificial opal

Non-closed packed structure of isolated microspheres with thin connecting networks can be confirmed from the SEM images of various viewing angles in figure 2(a), 2(b) and 2(c), which were

taken after HNB etching for 3 minutes. Our HNB etching shows three important features of colloidal assemblies; firstly, the size of partially etched PS particles was quite uniform except for the top layer, which were bombarded most severely and sacrificed by HNB. Secondly, the spherical morphology of particles was maintained, indicating that the etching was nearly isotropic. The isotropic partial etching of the microspheres is because the impinging gas of HNB onto the colloidal crystal in chamber is charge-neutral so that the oxygen gas molecules or radicals collide uniformly with hydrophobic PS surface. This is an advantageous feature of the present HNB dry etching; conventional reactive ion etching produced the anisotropic morphology of PS microspheres. And, thirdly, the particle surface of our open structure is much smoother than conventionally etched one, which means that damaged rugged surface by anisotropic etching can be prevented by oxygen HNB.

To investigate the effect of HNB etching on the stop band position of colloidal crystal, we measured the reflectance spectra of annealed PS colloidal crystal and its connected open structures . As shown in figure 2(e), the maximum reflectance peaks due to Bragg diffraction were blue-shifted with the etching time since the volume fraction of building blocks was decreased during etching. It is noteworthy that the lattice spacing of fcc structure was maintained due to the presence of robust interconnecting cylindrical networks between microspheres. As noted from figure 2(e), all samples exhibited the Fabry-Perot resonances as minor peaks at wavelengths longer than 650 nm, indicating a good colloidal crystallinity and optical quality. The intensity of the maximum reflectance peak was reduced with the etching time, which was consistent with the evolution of reflectance spectra of polymeric woodpile structures etched by oxygen plasma by Wegener and his colleagues. Consequently, the reduction of volume fraction of polystyrene microspheres with the etching time was responsible for the reduction of peak heights in reflectance spectra. Moreover, the broadening of reflectance peak for the sample with HNB-treatment for 5 minutes was observed, which was caused by the size variation of polystyrene microspheres across the connected open structure film. This result provides a possible route to fine tuning of stop bands (both positions and widths) of colloidal photonic crystals by changing the size of building blocks during the HNB etching procedure.

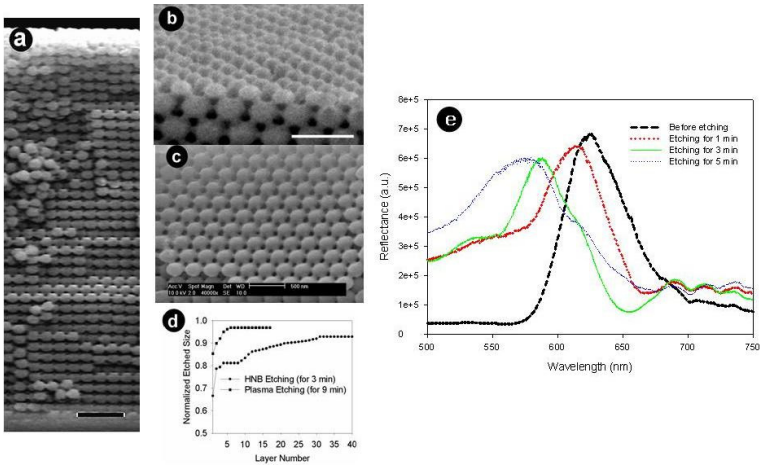

Figure 2. (a-c) Cross-sectional SEM images of non-close-packed PS opals at various viewing angles. The original PS spheres was 280 nm in diameter, sintered at 100 C for 12 hours and oxygen HNB treated for 3 minutes. Scale bars are 1 μm for (a) and 500 nm for both (b) and (c). (d) Variation of the size of HNB-etched PS particles across the 40-layer colloidal film. The PS size was normalized with respect to the initial value of 280 nm. The initial size was 850 nm in the O_2 plasma etching. (e) reflectance spectra of sintered colloidal crystal and non-close-packed opals prepared by HNB etching. HNB treated for 1 to 5 minutes.