Optical properties of a photonic crystal of hollow spherical shells

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We report on optical transmission studies of three-dimensionally ordered photonic crystals of close-packed spherical shells. These samples are fabricated using a double-template method, which allows for extensive control over shell thickness. The transmission spectra exhibit an optical stop band, whose spectral position and width depend on the thickness of the shell and on the overlap between adjacent spheres, in a manner consistent with numerical simulations. These parameters can be controlled over a wide range, thus permitting systematic studies of the optical properties, and providing a valuable method for engineering the characteristics of the optical stop band in colloidal photonic media. © *2000 American Institute of Physics.* [S0003-6951(00)01644-2]

Photonic band-gap materials have a periodic modulation of their dielectric function and can inhibit certain frequencies of electromagnetic radiation from propagating through specific crystal orientations. Ever since the discovery that a photonic crystal can exhibit a full photonic band gap, namely, a band of frequencies over which an electromagnetic wave cannot propagate in any direction,[1] there have been numerous attempts to fabricate different structures to observe this phenomenon in the visible regime. One method is to use a chemical self-assembly technique to form a close-packed structure of colloidal spheres.[2–6] Though this photonic crystal does not exhibit a full gap, it has been shown that the inverted structure (that is, a crystal of close-packed air spheres in a dielectric matrix) does, provided the matrix has a refractive index greater than 2.8.[7] Busch and John have shown by numerical simulations that parameters, such as the degree of incomplete filling of the interstitial regions and the linkage between the air spheres, are important for controlling the band-gap characteristics in such a crystal.[8] Recently, Richel and co-workers have noted that the incomplete filling of the interstitial areas in a macroporous oxide film can influence its optical properties.[9] Any method to make photonic crystals that permits control of these parameters is a significant step toward engineering these materials for specific applications.

In this letter, we provide an experimental report on the optical properties of colloidal films where these important morphological parameters are controlled. We have recently developed a synthetic method which permits the formation of close-packed colloidal crystals of hollow spheres, with controllable shell thickness. These materials are topologically very similar to the structures imagined by Busch and John,[8] and they exhibit similar enhancements in the width of the optical stop band. We demonstrate the systematic control of the band-gap characteristics through engineering of the structural parameters of the hollow spherical shells, particularly the shell thickness.

The fabrication of these materials relies on a double-template method. In this method a colloidal crystal of silica spheres is formed using a convective assembly process.[6] Because the colloids used to form this crystal are nearly monodisperse (~5% size dispersion), they form close-packed arrays which are ordered over ~1 cm^2 area, with few crystalline defects or grain boundaries. These are used as a template to form a macroporous polymer, in similar fashion to several other recent reports.[10–13] After removal of the silica spheres, the inner surface of the macroporous polymer is coated with a ceramic via the hydrolysis of titanium alkoxides. The polymer scaffolding is then etched away to leave a close-packed array of hollow spheres. The spheres are highly monodisperse, and are crystallized in a close-packed geometry, effectively replicating the properties of the original colloidal lattice. Figure 1(a) shows a transmission electron micrograph (TEM) of the edge of a film of titania hollow spheres. Figure 1(b) shows a close-up image of a single hollow sphere. The shell is uniform, with controllable thickness over a wide range. Figure 1(c) shows an electron micrograph of a large area on the sample surface, indicating the uniformity and surface quality. Analysis of images such as these supports the assertion that the hollow shells replicate both the size and crystallinity of the spheres in the first template, with only slightly larger size dispersion. Figure 1(d) shows an optical image, demonstrating the excellent optical quality of these films. This fabrication method relies on the fact that each air void in the macroporous polymer template is connected to all of its 12 neighbors by apertures of controllable diameter.[13] In addition to providing the necessary access to the interior surface of the air spheres, these internal windows also serve as the controlling feature for the overlap between

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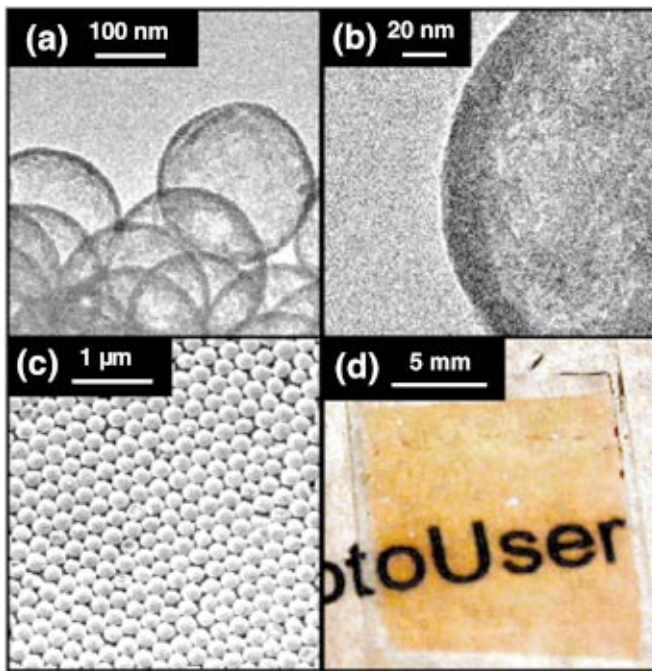[b)]Electronic mail: daniel@rice.edu

FIG. 1. (Color) Images of titania hollow spheres formed using the double-template technique. (a) TEM image of a section of a sample. The average shell thickness is 13 nm. (b) Close-up TEM image of a single titania hollow sphere with an average shell thickness of 26 nm. (c) Scanning electron micrograph showing a top-down view of a crystal of hollow spheres, demonstrating the excellent uniformity in the plane parallel to the substrate. The sphere diameter is 280 nm, with a size dispersion of ~7%. (d) Optical transmission image of a crystal of hollow spheres, showing the high optical quality.
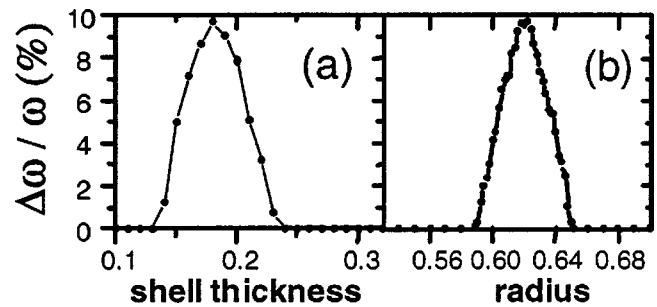

FIG. 2. Results of band-structure calculations for an fcc lattice of hollow spheres, with $\epsilon = 11.9$. (a) Variation in the fractional band gap $\Delta\omega/\omega$ between the eighth and ninth bands with shell thickness (in units of the outer radius) at the optimal sphere overlap of $Z = 0.662A$ (where A is the primitive lattice parameter). (b) Variation in the fractional band gap vs sphere overlap (in units of the lattice parameter) at the optimal shell thickness of $T = 0.18$.

the air spheres, since, because of these windows, the air spheres can be closer to each other than one sphere diameter. Thus, this methodology allows for accurate control over both the shell thickness (which is analogous to the degree of infiltration) and the overlap between spheres (analogous to the sphere connectivity). These are the two parameters identified by Busch and John[8] as key factors in controlling the width of the stop band.

In order to motivate the significance of these two morphological parameters, we have performed band-structure calculations in which the shell thickness or sphere overlap is systematically varied. We find that the maximum fractional gap is more than twice as broad as that found in a fully infiltrated macroporous face-centered-cubic lattice.[8] This optimum structure is achieved with a shell thickness of $T = 0.18$, in units of the outer radius of the hollow sphere. The optimal sphere overlap parameter Z, defined as the outer radius of the sphere in units of the primitive lattice parameter (i.e., the center-to-center distance), is found to be 0.622. Figure 2 shows the variation of the full gap (between the eighth and ninth bands) with each of these parameters, keeping the other one fixed. This shows that both these parameters permit sensitive tuning of the optical properties of the band gap.

To demonstrate that the double-template method provides the ability to tune the band gap using these parameters, we have studied the optical transmission spectra of a series of films. These films were formed using silica colloids of 280 nm diameter, and the number of repeating layers was held constant at ~15. We have recently shown that this is sufficient for the bandwidth to have reached its limiting value, so

that $\Delta\omega$ is not a sensitive function of film thickness.[14] The titania hollow spheres were formed with progressively increasing shell thickness, from ~13 (± 4) nm to ~50 (± 6) nm. With spheres of this diameter, the complete band gap lies in the ultraviolet, where the materials absorb strongly. We, therefore, probe the partial gap, between the second and third bands, that falls in the visible spectrum, using normal-incidence transmission measurements. As with most previous reports on the optics of colloidal crystal-based materials, a small background, monotonically increasing with decreasing wavelength, has been subtracted in order to facilitate analysis of the Bragg peak.

Figure 3 shows transmission spectra for several samples. There is an evident red shift of the stop band as the shell thickness is increased. This is phenomenologically consistent with Bragg's law at normal incidence, $\lambda_{peak} = 2 n_{eff} d$. As the shell thickness is increased, the average index of the film
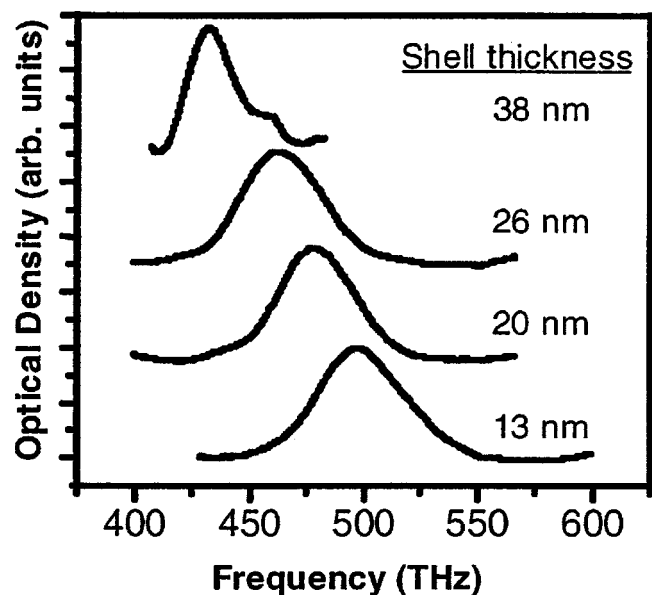

FIG. 3. Transmission spectra of titania hollow spheres for increasing shell thickness. The band gap develops along the (111) direction between the second and third bands. The average sphere diameter (280 nm) and the number of layers (~15) were fixed. The stop band shifts to lower frequency as the shell thickness increases.
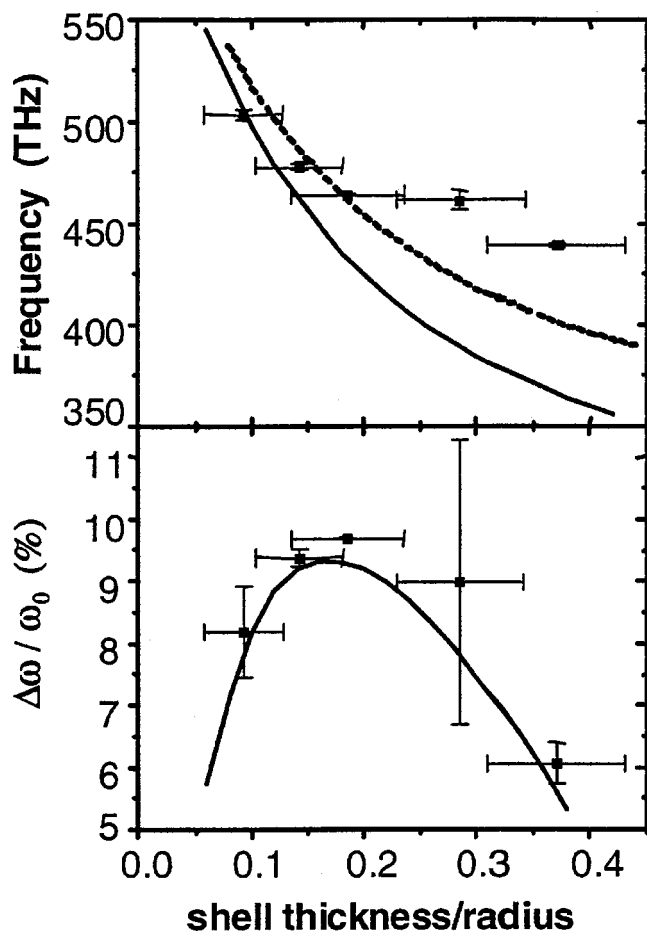
FIG. 4. Transmission spectra analysis of the partial gap along the (111) direction. (a) Central frequency ω_0 of the stop band as a function of the shell thickness. The black squares are the experimental data points, the dashed line is the prediction using a simple Bragg's law analysis and the solid line is the prediction from a full vector calculation. (b) Relative gap as a function of the shell thickness. There is an optimal shell thickness to maximize the gap.

also increases, leading to a red shift. This simple scalar theory, using an effective medium approximation, has been shown to be reasonably accurate for propagation along high-symmetry axes.[15] The dashed line in Fig. 4(a) shows the prediction of Bragg's law, assuming that the titania matrix has a refractive index of 2.

In order to explain the bandwidths, we must resort to a more sophisticated theoretical approach. We calculate the band structure for the hollow sphere system using a full vector numerical technique from which both the spectral position and width of the stop band can be extracted. This method uses a frequency-domain iterative approach to perform a direct computation of the eigenstates and eigenvalues

of Maxwell's equations using a plane-wave basis.[16] The solid lines in Fig. 4 show the results of these calculations. We note that because both the shell thickness and the sphere overlap can be determined from electron microscopy these are not adjustable parameters in the simulations. The only unknown parameter is the refractive index of the titania shells; it is known that the hydrolysis reactions used to form these samples produce oxides with lower indices than those of the bulk materials.[17–19] As with the Bragg's law calculation mentioned above, the simulations shown in Fig. 4 assume a refractive index of 2 for the shell material, consistent with previous reports.[19] The agreement between the data and these simulations is excellent, particularly for the fractional bandwidths.

In conclusion, we have demonstrated that the double-template method affords additional degrees of control over sample morphology, and that these can be used to tune the characteristics of the optical stop band. Because these materials are formed via templating of high-quality colloidal crystals, they are planar with controlled thickness, and contain few defects and no grain boundaries.[6] This makes them excellent candidates for optical transmission studies. With the versatility afforded by the chemical templating methods, these colloidal crystal films should find increasing applications as diffractive optical materials.

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