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Photonic Gaps in Reduced-Order Colloidal Particulate Assemblies

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Colloidal assemblies consisting of monotonic polystyrene microspheres with a controlled degree of ordering were fabricated, and exhibited rich spectral behaviors. Smooth and spike-modulated broad attenuation regions in transmission spectra were observed in highly disordered and partly disordered samples, respectively, in contrast to the narrow peaks observed in well-ordered photonic crystals. These properties are interpreted consistently by analyzing the variation of the volume of closely packed units.

KEYWORDS: colloidal particles, self-organization, disordering, photonic crystal, photonic band gap

1. Introduction

When compared with crystals, amorphous semiconductors exhibit a similar packing of statistically slightly deformed unit cells with variations in the interatomic distances and bond angles.[1)] When a semiconductor is constructed from such deformed unit cells, long-range periodicity is lost, and variability arises in the coordination number. The short-range order of an amorphous semiconductor, however, is similar to the crystalline state of the same material. It is well known that semiconductors such as silicon and amorphous germanium have larger electronic band gaps than their crystalline counterparts. These band gaps are pseudogaps in nature, containing band tails of strongly localized electronic states. That is, the long-range ordering, Bloch theorem and wavefunctions are not fixed properties which are necessary for the formation of electronic energy band gaps in semiconductors.

The photonic analogs of semiconductor crystals are artificial three-dimensional (3D) periodic dielectric structures, so-called photonic crystals (PhCs),[2–9)] in which electromagnetic (EM) modes are organized into photonic bands. Such bands are separated by gaps where propagating states are forbidden. The familiar nomenclature of generic electronic crystals is carried over to the EM cases, meaning that the concepts of reciprocal space, Brillouin zones, dispersion relations, Bloch wavefunctions, Van Hove singularities, and so forth must be applied to photon waves.[10)] Until now, numerous theoretical and experimental studies have focused on PhCs with strictly periodic lattices[11)] because constructive interference phenomena are strongly favored by periodic arrays of multiscatterers. An important problem is the determination of whether there are photonic counterparts of noncrystalline semiconductors with diminished long-range periodic arrays of scatterers but still containing a photonic gap.

Chutinan[12)] and Fan *et al.*[13)] reported a large tolerance of photonic band gaps (PBGs) to lattice distortions. However, the PBG effects were observed to be degraded with increasing perturbations and no new features were found with further increases in the deviation. On the other hand, the issue of the localization of electronic and classical EM waves in disordered media[14,15)] has been studied with increasing interest. The photonic-gap phenomenon in disordered media, although expected, has not been experimentally observed yet.

We have conducted a detailed study of the PBG properties of highly ordered colloidal PhC structures. The motivation for this research is to investigate the photonic-gap phenomenon in less ordered spatial structures. As a first step in this direction, in this paper we report the preparation of polystyrene microparticle assemblies with different ordering degrees. In particular, a broad spectral gap has been observed in disordered samples, and similar broad spectra were modulated by spikes in partially disordered particle assemblies. The occurrence of the observed broad gaps was found to be related to the thickness of the samples and could be preliminarily explained as being due to polycrystalline effects.

2. Preparation of Samples

The samples, which consisted of air/polystyrene microsphere systems, were prepared by the sedimentation of colloidal suspensions, and then decanting/evaporating the supernatant/entrapped water solvent. Compared with other techniques such as electron-beam lithography and laser microfabrication, this method has unique advantages, including: (i) ease of fabrication of the 3D structures with PBGs (if there are any) from the visible to the infrared spectral region, (ii) nearly perfect scatterers (smooth surface, spherical geometry, and polydispersity of less than 5%), making the compacted colloidal suspension an ideal model system for studying disordering effects. Such a system is comparable with noncrystalline silicon consisting of identical Si atoms; (iii) the absorption coefficient for light is extremely small, i.e., linear absorption coefficient $\alpha < 0.00067\,\mathrm{cm}^{-1}$ at 610 nm wavelength,[16)] and the photon scattering are therefore nearly elastic, and (iv) the ordering degree of the microstructures can be easily controlled using different means of sedimentation. This makes it possible to investigate the evolution of the spectral behavior of the structures, from highly ordered to completely disordered.

Colloidal suspensions with a sphere diameter of 270 nm were compacted under different sedimentation conditions: (i) quasiequilibrium evaporation (QEE),[17)] i.e., water was evaporated under controlled high humidity, (ii) natural evaporation (NE),[17)] i.e., water was evaporated under ambient conditions, and (iii) centrifugal sedimentation (CS). In this way, microstructures with different degrees of ordering can be prepared.

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3. Results and Discussion

Typical surfaces of colloidal crystals were characterized by atomic force microscopy (AFM) and shown in Figs. 1(a) and 1(b). The thickness of samples was approximately 50 layers for both ordered and disordered samples. This thickness corresponds to 25 periods for a face-centered-cubic close packed configuration. The transmission spectrum [Fig. 1(c)] at the high-symmetry point of the first Brillouin zone, L, $[(\pi/a)(1,1,1)]$, shows that a transmission valley of -25 dB occurs at 625 nm in the ordered particle assembly [Fig. 1(a)]. The inverse peak position is well fitted by simulation with a simplified transfer matrix technique. This gap can be ascribed to coherent scattering on a parallel set of (111) planes of the crystal. Our previous studies[18] have shown that the peak wavelengths scale well with the diameters of microspheres. These data demonstrate clearly that the observed peaks are due to PBG effects. For disordered structures [Fig. 1(b)], no transmission features appear, as is commonly observed.

The flatness of the surface and the regularity of particle ordering can be transferred to a larger thickness by increasing the volume of the solutions and the sedimentation duration through quasiequilibrium evaporation. A surface morphology similar to that seen in Fig. 1(a) can be observed in a 500-layer sample. For disordered samples, the surface roughness increases with the thickness.

The transmission properties (i.e., the shape of spectral region of the dip) of ordered 3D particulate arrays in thicker samples resemble those observed in thin-layer samples but with a significantly increased intensity attenuation. A dramatic variation is found in disordered structures [Fig. 2(a)].

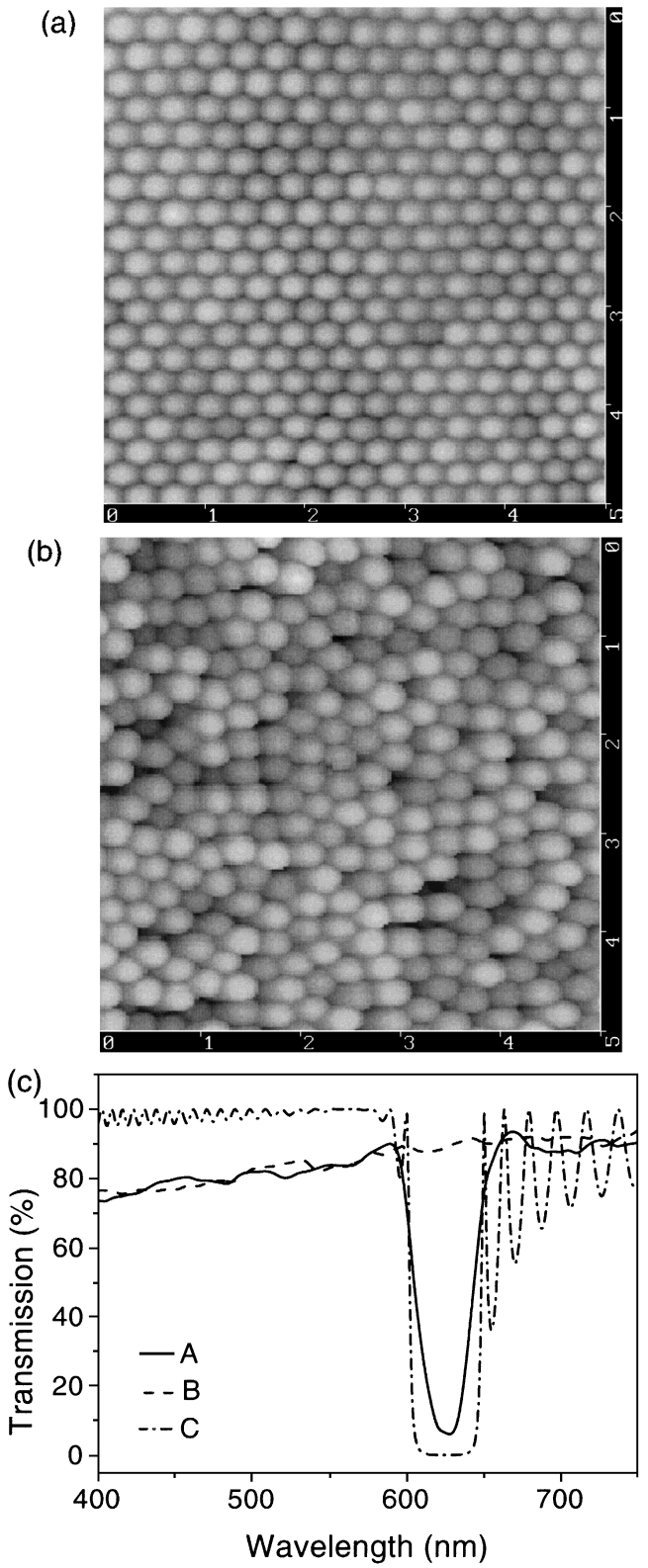

Fig. 1. AFM images of ordered (a) and disordered (b) particle arrays with a thickness of approximately 50 layers. They are prepared by quasiequilibrium evaporation (a) and centrifugal sedimentation (b) techniques, respectively. Solvent water has been removed in both cases. Curves A and B in (c) denote transmission spectra of samples (a) and (b), and curve C represents a simulation.

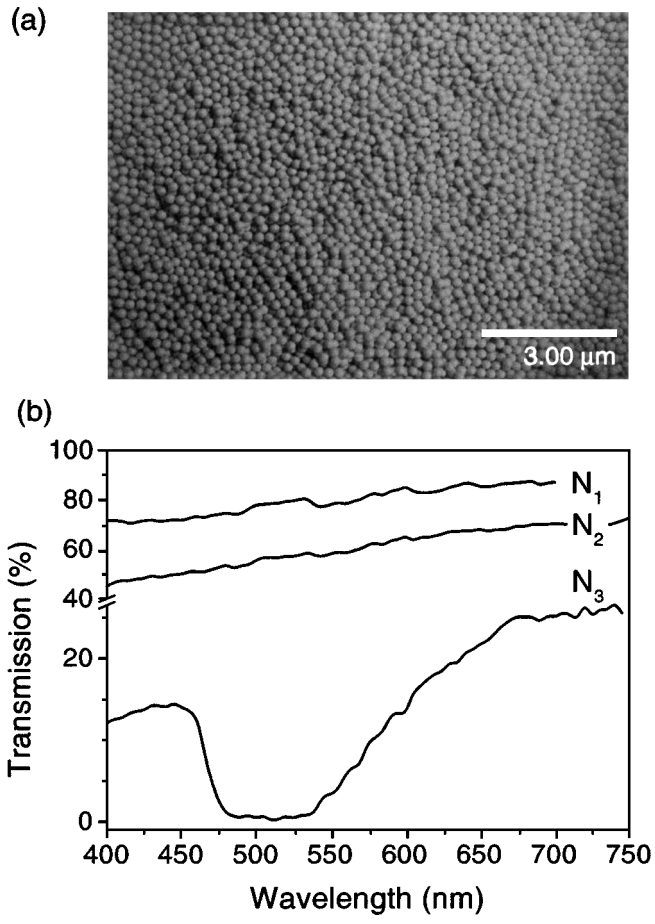

Fig. 2. (a) Typical SEM image of the surface of thick-layer samples, and (b) transmission spectra of $N_1 \sim 50$-, $N_2 \sim 200$-, and $N_3 \sim 500$-layer packing by compelled sedimentation.

A broad peak emerges in the 500-layer sample, as shown in Fig. 2(b). Since polystyrene is optically transparent and no dopants were incorporated to modify the optical absorption, this new feature can only be ascribed to an ordering effect. The origin of such a broad band is intriguing since the disordered spatial distribution of particles is not expected to yield photonic bands due to the lack of long-range periodicity, and therefore is also not expected to yield an optical Brillouin zone. The array order in the disordered samples, similar to that in semiconductor noncrystals, is on the scale of a few intra-atomic spacings, and is disrupted by the presence of "topological" defects. Phenomenologically, the broad photonic gap resulting from the disordered array of monosized particles can be analogous to the "amorphous halo" in the X-ray or electron-beam diffraction of semiconductor noncrystals. However, because the differences between the electrons (fermions) and photons (bosons) (*e.g.*, in mass, charge, spin, their obedience to the Pauli exclusion principle, velocity, dispersion, and wavefunction representation) are fundamental in nature, it is very difficult to make any quantitative analogies between electrons and photons. A new perspective is necessary to investigate the underlying physical origin of the observed photonic-gap effects.

One factor that may be responsible for the generation of the broad attenuation band is the polycrystalline effect. After sedimentation under gravity, the particles are randomly arrayed in the macrodomain, and no long-range periodicity is generated. However, since the pellets are rigid and uniform in diameter, the neighboring spheres still tend to stack in a close-packed geometry. The smallest close-packed unit (CPU) is a tetrahedroid consisting of the four closest neighboring spheres. Such CPUs can expand to several periods, sufficient to fulfill optical functions, *e.g.*, directional Bragg scattering. Due to the small volume, the Bragg effects are very weak. They are not pronounced and observable until the number of CPUs increases to a large value, for example, $>10^3$. The directionally scattered wavelengths are fundamentally determined by the particle diameters but are slightly relaxed by their dependence on CPU orientations. This is just what we observed in the thick samples: the peak position was determined by the particle diameter but was broadened.

In the above hypothesis, the volume of CPUs is small since they are very easily disrupted in a constrained sedimentation. The ordering ranges can be gradually increased by controlling sedimentation conditions. By using a natural evaporation technique, a form intermediate between the highly ordered (by QEE) and disordered (by CS) particulate aggregation forms can be created. Figure 3(a) presents a scanning electron microscope (SEM) image of the partially ordered structure achieved by natural evaporation of the water (500 layers in thickness). Figure 3(b) shows the transmission spectrum of the crystal. The broad band attenuation, similar to that presented in Fig. 2(b), remains but it is modulated by several striding spikes. Based on the previous discussion, the broad absorption band arises from the disordered components of the structures and the sharp peaks are produced by several dominant fully developed CPUs. Since such macroscopic domains with crystalline plane of different orientations are finite in number due to the finite thickness, the peaks appear in isolated spectral positions. One more piece of evidence for the above analysis is that the spikes randomly appear at different

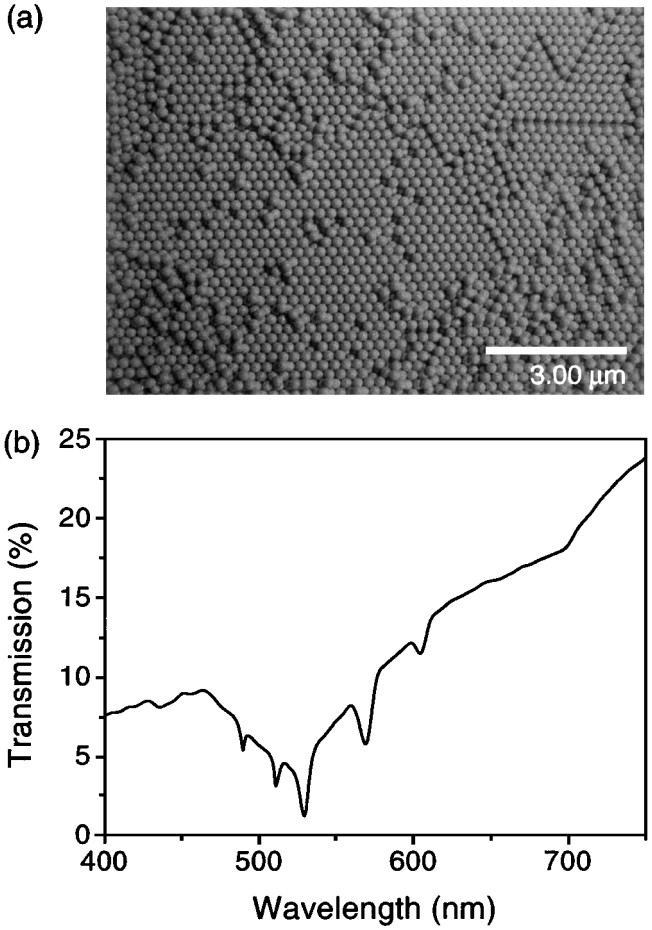

Fig. 3. (a) SEM image of the partially disordered structure prepared by the natural evaporation technique, and (b) the corresponding transmission spectrum.

wavelengths for different samples.

When the sedimentation conditions are further optimized, CPUs grows into a near single crystalline form. The orientations of such enlarged domains are preferentially selected by the substrates, i.e., the (111) planes are packed along the growth direction. That is why relatively narrow (pure) spectra have been achieved with samples prepared by QEE.

Using the concept of the CPU, we have explained all the observed spectral behaviors of different ordering degrees. The interpretation is based on Bragg scattering (conventional notion of PhCs). However, another possibility, light localization, can not be completely ruled out. As a wave phenomenon in disordered systems, Anderson localization[14] is recognized to be common to both quantum particles and classical waves. This strong type of localization pertains to the absence of diffusion in random materials as a result of the constructive interference of all of the scattered waves. A precursor of Anderson localization, known as weak localization,[19,20] which refers to enhanced backscattering in a strongly scattering random medium, was first pointed out for electrons by Abraham *et al.*[21] The related localization for EM waves has also been discussed but has not yet been associated with PBG. In three dimensions, localization due to disorder can only occur when a wave is scattered within a coherence length $l < 1/k$, where l is the transport mean free path and $k = 2\pi/\lambda$ is the wavenumber. This gives the Ioffe-Regel criterion for localizations (classical light and electrons). The light localization effect

is enhanced when the amount of scattering is increased by reducing the particle diameter, or by increasing the refractive index contrast, particle densities and wavelength of light. In the present study, the refractive index contrast rises due to dehydrating from 1.2 (polystyrene/water) to 1.6 (polystyrene/air) and the particle density reaches near 9×10^{18} cm^{-3}, the maximum (a filling ratio of 74% for the close packing of spheres). Weak localization effects have been reported in similar systems in which particles had a diameter of 1091 nm and a density of 0.141×10^{18} cm^{-3}. It is clear that localization is much more liable to occur in our case if the optical connection effect is neglected. Although it is difficult to fully satisfy the requirement of the Ioffe-Regel criterion, the enhanced weak localization effect can strongly depress the light propagation. The problem is whether light localization can provide such a pronounced wavelength dependence (frequency window of localization). Further research is clearly necessary to clarify the mechanism.

4. Conclusions

A strong photonic gap has been observed in a highly disordered monotonic microsphere assembly. This finding may enable the development of very inexpensive and large-scale novel photonic-gap materials, which are promising for both scientific research and technical applications.

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