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Influence of substrate on self-assembled photonic crystal

Sachiko I. Matsushita[a] and Masatsugu Shimomura*[ab]

[a] *Dissipative-Hierarchy Structures Laboratory, RIKEN Frontier Research System, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan. E-mail: lease@riken.jp; Fax: 81 48 462 4695; Tel: 81 48 462 1111*

[b] *Nanotechnology Research Center, Research Institute for Electronic Science, Hokkaido University, N21W10, Sapporo 001-0021, Japan. E-mail: shimo@poly.es.hokudai.ac.jp; Fax: 81 11 706 9363; Tel: 81 11 706 9368*

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Freestanding monolayers of two-dimensional particle arrays, in which fine particles are two-dimensionally self-assembled in a highly oriented manner, was prepared to examine the influence of substrate on the transmission spectra of 2D particle array; as a result, the spectrum of the freestanding 2D particle array has less noise than that of the 2D particle array on the substrate, and besides, agree with the theoretical result particularly in the near-field discussion.

Monolayers of monodisperse colloidal particles are formed by self-assembly. Among the many self-assembly techniques,[1,2] two-dimensional (2D) particle arrays, in which fine particles of polystyrene (PSt),[3] silica,[4] or proteins[5] are two-dimensionally packed in a highly dense and oriented manner, have been attracting attention because of their features such as large domains, controllability of the layer number, and easy and fast producibility (it takes less than 30 minutes to prepare one sheet 25 × 30 mm). The 2D particle arrays have been studied as high-density optical memory devices[6,7] and photocatalytic systems.[8] In particular, the 2D particle array has been studied theoretically and experimentally as a quasi-2D photonic crystal from the early days.[9,10]

A theoretical calculation for photonic crystals predicts that freestanding 2D particle arrays have sharper transmission spectra than the spectra of 2D particle arrays on substrates.[10] However, 2D particle arrays are prepared on flat surfaces by a self-assembly process of particle suspension. So far, we cannot ignore the influence of the substrates on the intrinsic characters of 2D arrays.

Matsushita *et al*. fabricated freestanding 2D particle arrays by the photo-cross-linking technique. A photoactive cross-linker connected to the particles.[11] However, the photoactive cross-linker was piled up in arrays; consequently, the original quality of 2D particle arrays had deteriorated after photo-cross-linking. Another method of fabricating freestanding 2D particle arrays is the sintering technique.[12] Sintering processes of inorganic and organic materials[13] are reproducible, controllable processes, and are well known both theoretically[14] and experimentally.[15] In this letter, we report the preparation of freestanding monolayers of 2D polystyrene-particle arrays by the sintering technique and show the difference in the transmission spectra between freestanding monolayers and monolayers on a substrate.

Two-dimensional particle arrays were prepared from water suspensions of commercial monodispersed polystyrene microparticles† (1.034 ± 0.020 μm and 0.491 μm). The self-assembly technique for the preparation of 2D particle arrays was originally proposed by Denkov *et al*.[3] Due to water evaporation and capillary forces, the particles that are suspended in water form 2D arrays on a nonfluorescent glass substrate (Matsunami Co., Japan). Moving the substrate horizontally at rates from 1.0 to 3.0 μm s^{-1} controls the speed of array formation. The particle assembly process was observed using a CCD camera. Well-ordered 2D arrays with typical dimensions of 25 × 30 mm were prepared. Details of the fabrication process have been reported elsewhere.[11]

Two-dimensional particle arrays thus formed were placed into an electric oven and kept at 80 °C for 30 min. Polymers sintered by a viscous flow in the contact zone between particles with tensile capillary forces operating.[13] As the results, particles were connected with each other by the sintering process. The hexagonal closest packing after sintering was examined from the diffraction patterns of the He-Ne laser. The particle array after sintering and a proper holder were placed into a plastic case (5 cm × 5 cm, 2 cm height). As holders, a handmade square shaped grid (5 mm^2 square) made of paper for the digital camera image, a copper grid‡ with 25 μm square halls for the optical microscopic observations, and a SUS mesh§ with 50 μm square halls for the transmission spectra measurement (UV3100, Shimadzu Co.) were used.

Distilled water was carefully poured from the corner of the case. The array was peeled softly and moved from the glass substrate to the holder using Teflon tweezers in water. The fragility of the array depends on the sintering conditions; as the sintering temperature becomes high and the sintering time becomes long, the freestanding monolayer becomes stronger. However, it is better not to excessively sinter the film from the point of view of maintaining the spherical shape of the polystyrene particles. In our system, the sintering at 80 °C for 30 min was preferable. The size of freestanding monolayer which we can get from a 2D particle array is at least over the spot size of the light used for detection (1 mm × 5 mm). The maximum original area of the freestanding 2D particle array is about 10 mm^2. Their iridescent colors clearly show the periodicity of particle packing (Fig. 1). By the optical microscopy, we could confirm that this freestanding array is a monolayer (Fig. 1, inset).

The transmission spectra measurement was carried out at normal incidence. The spot size of the light used for detection was 1 mm × 5 mm. Our UV-Vis-NIR spectroscopy is a double beam system. The references of freestanding 2D particle array and the 2D particle array on a substrate were the SUS mesh and the nonfluorescent glass substrate, respectively. Short-term measurement (≈ 15 min.) is preferable for avoiding exfoliation of the freestanding monolayer from the SUS mesh. The transmission spectra of the freestanding 2D particle array and the 2D particle array on a substrate are shown in Fig. 2. Polystyrene is not supposed to absorb in the near infrared region. This spectrum of the 2D particle array on a substrate was

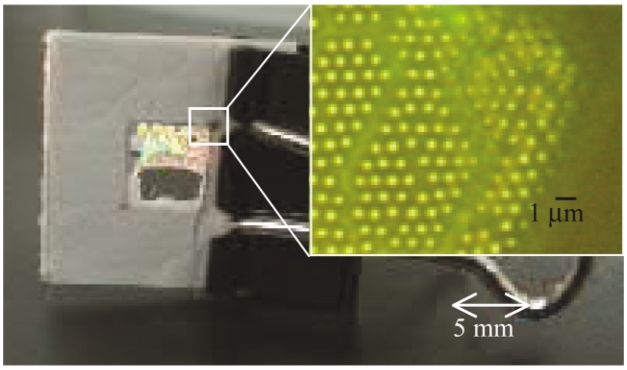

Fig. 1 A digital camera image of a freestanding monolayer of 1 μm diameter polystyrene particles. The optical micrograph is shown in the inset.

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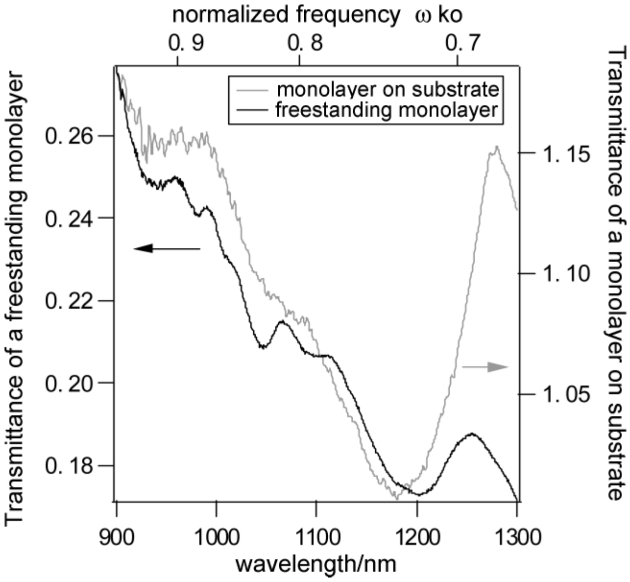

Fig. 2 Experimental results of transmission spectra of a freestanding monolayer (black line) and of a monolayer on substrate (gray line).

obtained after five repetitions of polynomial smoothing. The reproducibility was checked by three freestanding monolayers from the point of view of the amount of noise and the peak position, which are discussed below.

Some extinction peaks were observed in both samples, indicating that high optical quality of millimetre size can be derived by this method. The values of peaks are only a few percent in transmittance. This is because of the thin thickness of the particle monolayer. The extinction peaks at ≈1200 nm, 1050 nm, and 940 nm, are not the Bragg diffraction;[16] in the 1 μm particle's periodicity, the Bragg diffraction at the L-point should be observed around at 2.3 μm.

Miyazaki *et al*. have made calculations for the particle-assembled-type photonic crystal.[10] They used the normalized frequency $\omega_{ko} = (\sqrt{3}/2)(D/\lambda)$; D is the lattice constant. In our work, the lattice constant is 1.034 μm (= particle diameter). Thus, the spectral range from 900 nm to 1300 nm corresponds to ω_{ko} = 0.67–0.96.

The calculation for an isolated sphere of refractive index $n = 1.6$ with a diameter of D shows two marked whispering gallery (WG)-mode resonances of $l = 2$ and $l = 3$ at $\omega_{ko} = 0.70$ and 0.92, respectively.[10,17] The refractive index of 1.6 is that of polystyrene spheres in the visible range. In our system, we can confirm the extinction peaks that are related to the WG modes at $\omega_{ko} = 0.73$ (1180 nm) and $\omega_{ko} = 0.93$ (930 nm) in the spectrum of the 2D particle array on the substrate, and at $\omega_{ko} = 0.72$ (1204 nm) and $\omega_{ko} = 0.92$ (940 nm) in the spectrum of the freestanding 2D particle array. The spectrum of the freestanding 2D particle array has less noise than that of the 2D particle array on the substrate, and agrees with the theoretical result with respect to the peak positions. These effects are unexpected in the calculation.

Apart from these WG modes, other extinction peaks are observed at $\omega_{ko} = 0.88$ (980 nm) and $\omega_{ko} = 0.82$ (1046 nm) in a freestanding monolayer. It was calculated that near-field resonance between particles should be observed at $\omega_{ko} = 0.854$ and 0.870.[17] Now we believe that, even though further quantitative experiments would be required, we could observe the near-field resonance caused by particle alignment without any inhibition from substrates, using freestanding monolayers, as expected in the theoretical calculation.[10]

In summary, freestanding monolayers of photonic crystals are prepared by sintering. The transmission spectra of the freestanding monolayer and the monolayer on a substrate are examined. The transmission spectrum of the freestanding monolayer has less noise than that of the monolayer on the substrate, and besides, agrees with the theoretical result particularly in the near-field discussion.

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Notes and references

† Nanosphere™ Size Standards, NIST Traceable Polystyrene Polymer, Polysciences, Inc.
‡ MICRON GRIDE mesh, NISSHIN EM Co., Ltd.
§ SUS-316, TAIYO WIRE CLOTH Co., Ltd.

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