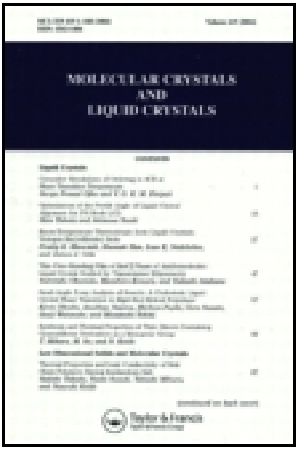

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FLEXIBLE TWO-DIMENSIONAL FINE-PARTICLE ARRAYS AND THEIR PHOTONIC CHARACTERS

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Flexible two-dimensional particle arrays, which are periodic structures in the optical region, were prepared utilized a thermosetting resin. This type of arrays can be bent easily and repeatedly. Beautiful light propagation patterns such as micro-circle or micro-star-like shapes were observed inside of flexible two-dimensional particle arrays from the emission of fluorescent particles in the arrays. This flexible two-dimensional particle array might be changed the general idea of self-assembled structures; which normally exist on solid substrates.

Keywords: periodic structure; photonic crystal; polystyrene particle; self-assembly; two-dimensional array

INTRODUCTION

Forming regular texture of an arbitrary size is the challenge of future technology to produce new types of optical devices (especially for photonic crystals [1–3]), catalytic systems [4], electron emitters [5], bio-interfaces [6], and so on. Among a lot of methods to prepare such regular textures, two-dimensional (2D) particle arrays, in which spherical particles or protein molecules are periodically packed via a self-assembled system [7], have many advantages such as controllability of the number of the layers in a wide range of particle diameter dimensions (from 19 nm to 40 μm) [7].

However, because 2D particle arrays are prepared by means of surface tension and capillary forces at the meniscus, 2D particle arrays can be prepared only on flat solid surfaces or liquid surfaces. In this paper, to widespread 2D particle arrays' applications, preparation of flexible 2D arrays utilized thermosetting resin would be presented.

EXPERIMENTAL

Particle Suspensions

A water suspension of monodisperse polystyrene (PSt) particles ($1.034 \pm 0.020\,\mu m$; Particle-Size Standards, NIST Traceable, Duke Scientific Corp.), 1.0% solids-latex, was used to prepare two-dimensional (2D) particle arrays. The number of the layers particles in the arrays was controlled using methods reported previously [8].

Preparation of Two-Dimensional Particle Arrays

An apparatus for the preparation of the 2D particle arrays was constructed using a small glass cell (Fig. 1a). This cell, which was fabricated using cover glasses, was $25 \times 25\,mm^2$, with a gap width of 0.7 mm. The sprint acts as a device to mechanically decouple the z-axis stage from the cell and the 2D particle array. Approximately 0.2 mL of the suspension was injected into the cell. A glass support plate for the cell was attached vertically to a z-axis stage, and a glass substrate for the preparation of the 2D particle arrays was attached to an x-axis Stage. The movement of these stages can be controlled at rates from 1 to 2500 μm/s. The substrates were non-fluorescent glass slides ("Micro-Slide" glass, Matsunami, Co., Japan).

Initially, the lower edge of the cell was positioned to within 0.1 mm of the substrate using the z-axis stage. Then the suspension was injected, forming a meniscus, as shown in Figure 1a. Next, the substrate was translated several micrometers with the x-axis stage in order to form a broad-based meniscus. Then this stage was translated continuously at a controlled rate. For the preparing monolayer of polystyrene 1 μm particles, the controlled rate is 3 μm/s. The temperature was between 21 and 22°C, and the relative humidity was between 60 and 64%. The coating of particles begins to form within the trailing edge of the meniscus on the substrate. Due to water evaporation and lateral capillary forces (also refereed to as capillary immersion forces), the particles form a 2D particle array. The thickness of the 2D array depends on the angle between the plate and the water surface. The angle between the plate and the water surface can be controlled by the translation speed of the substrate and the height of the meniscus.

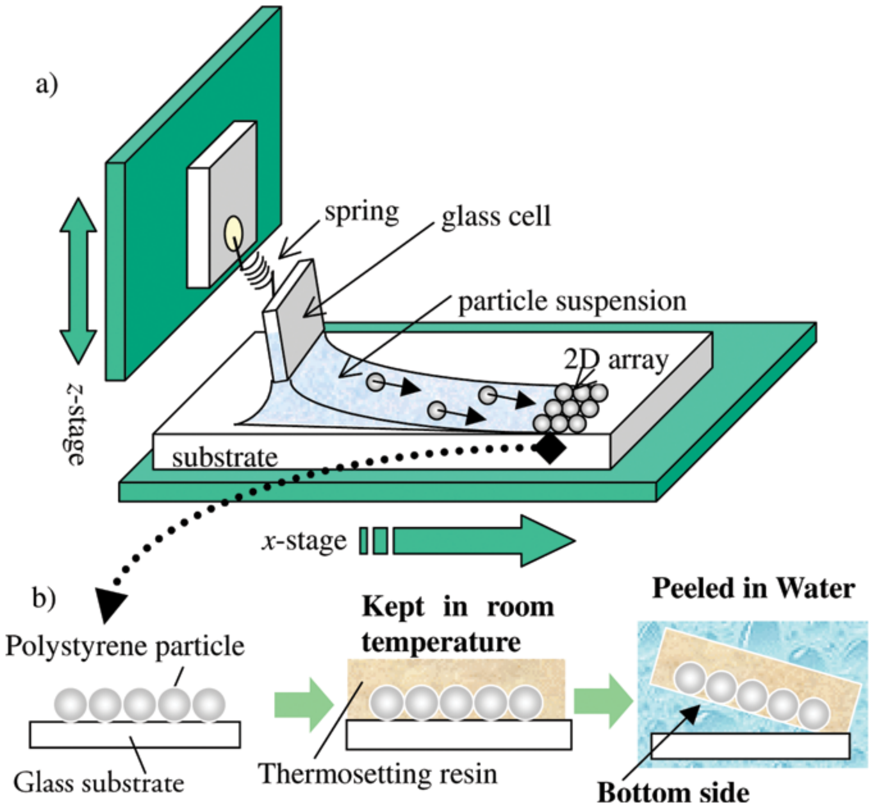

FIGURE 1 Schematic diagrams showing the preparation procedure for 2D particle array on solid substrate (a) and flexible two-dimensional (2D) fine-particle arrays using thermosetting resin (b). (See COLOR PLATE VIII)

Details of the preparation of 2D particle arrays utilizing capillary immersion forces were reported previously [2].

Preparation of Flexible Two-Dimensional Particle Arrays

Thermosetting resin (*Sylgard*® 184 Silicone Elastomer, Dow corning) was dripped on the prepared 2D particle array (Fig. 1b) and kept at room temperature over 48 hours. This combined structure was put in water and peeled off gently from the glass substrate using a tweezers. The resulting material is observed by means of optical microscopy and scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Structures of Flexible Two-Dimensional Particle Arrays

The volume fraction of 2D particle arrays has been calculated [9]: The value of a hexagonal packed monolayer is 0.60. Hence, 2D particle arrays have 40% empty spaces. The basic idea of this paper is putting thermosetting resin in these empty spaces.

The combined structures of 2D particle arrays and thermosetting resin could be peeled off from the glass substrate in water, with no difficulty. Over 90% of 2D particle arrays could be transported in thermosetting resin at the experimental conditions above. The center of polystyrene particles in thermosetting resin can be observed as white area in optical micrographs (Fig. 2a). From this Figure 2a, it is clear that the dripping of thermosetting resin didn't have any important influence on 2D particle arrays' periodicity.

This resulting material can be bent easily and repeatedly. The curvature depends on the thermosetting resin's thickness. Figure 2b is an image of a flexible 2D particle array bending by a needle. The size is 1.5 cm × 2.6 cm. It exhibited beautiful iridescent colors by illumination of white light. The iridescent color is evidence for the highly periodicity in visible-light-wavelength' range.

One of anxieties of our system is whether the thermosetting resin can get in the submicro-spaces between particles. Figure 2c is an SEM image of flexible 2D particle arrays. This observation was done from the bottom side in Figure 1b, which had been contacted with the glass substrate. We can observe that the thermosetting resin could get into the spaces between the polystyrene particles, and covered the bottom of 2D particle arrays. This can also explain the high transported percentage (written above).

Light Propagation Patterns in Flexible 2D Particle Arrays

Matsushita et al. had reported that multilayers of 2D particle arrays, which include some fluorescent particles as light sources, exhibit beautiful light propagation patterns [2]. Those light propagation patterns were born because 2D particle array is a periodic structure of different dielectric materials, polystyrene (dielectric constant, $\varepsilon \approx 2.56$) and air ($\varepsilon \approx 1$). The flexible 2D particle array is a periodic structure of polystyrene and thermosetting resin. Thermosetting resin has a much closer dielectric constant to the one of polystyrene than air has. Hence it can be expected that we could observe different light propagation patterns in flexible 2D particle arrays.

Figure 3 shows the fluorescent optical micrographs of triple layers of a 2D particle array on solid surface (Fig. 3a) and a flexible 2D particle array

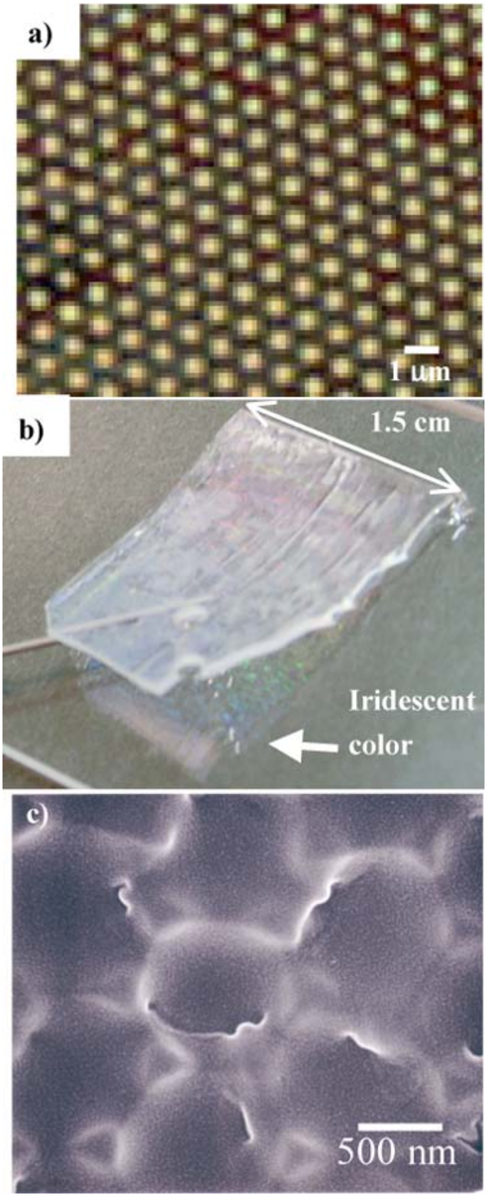

FIGURE 2 An optical microscopic image (a), a digital camera image (b), and a scanning electron microscopic image (c) of flexible two-dimensional fine-particle arrays. The diameter of the latex particle is 1 μm. (See COLOR PLATE IX)

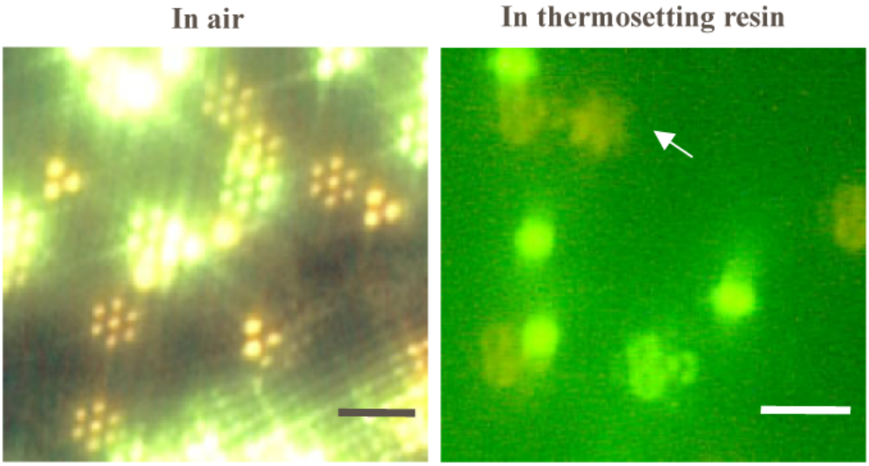

FIGURE 3 Fluorescence micrographs of a 2D particle array on a solid surface (a) and of a flexible 2D particle array. The diameter of the latex particle is 1 μm in both cases. (See COLOR PLATE X)

(Fig. 3b). Both arrays contained green fluorescent particles ($\lambda_{ex}/\lambda_{em}$ 458/540 nm; 0.973 ± 0.028 μm; Fluoresbrite carboxylate microspheres, Polysciences inc.) and red fluorescent particles ($\lambda_{ex}/\lambda_{em}$ 541/612 nm; 1.01 ± 0.05 μm Polymer Microspheres, Red Fluorescing, Duke Scientific Corp.). The number fraction is 1:1:400 (red-green-nonfluorescent). Even with different type of particles, the composite 2D arrays exhibit high-density and highly oriented hexagonal packing.

First, let us explain the observed patterns in a triple layer of a 2D particle array. The observed patterns are classified into several types: (I) when the fluorescent particle is located in the top layer, the top view shows only a single bright spot centered on the fluorescent particle; (II) when the fluorescent particle is located in the middle layer, a triangular pattern is observed; and (III) particularly beautiful patterns are observed when the fluorescent particle is in the bottom layer, i.e., hexagonal arrays composed of seven dots. This hexagonal arrays composed of seven dots is an evidence that this domain is a hexagonal closest packing (hcp). Details of these light propagation patterns were reported previously [2]. It is an important point that those patterns reported previously are composed by only dots.

On the other hand, in a triple layer of a flexible 2D array, the patterns did not composed by dots alone. Figure 3b is a fluorescence optical micrographs of a hcp domain. The observed patterns also can be classified three types: (I) when the fluorescent particle is located in the top layer, a single bright spot is observed as same as in Figure 3a; (II) when the fluorescent particle is located in the middle layer, a triangular pattern is also observed. However, in a flexible 2D particle array, this triangular pattern composed by three circles; and (III) when the fluorescent particle is in the bottom layer, instead of hexagonal arrays composed of seven dots, star-like patterns can be observed (Fig. 3b). These differences can be explained using the difference of dielectric constant.

In the case of 2D particle arrays in air, the light emitted from fluorescent particles can reflect at the boundary between polystyrene particles and air. Hence the fluorescent light propagated inside of the polystyrene particles. However, in the case of flexible 2D particle arrays in thermosetting resin, the light emitted from fluorescent particles can pass through the boundary between polystyrene particle and thermosetting resin because of their close values of dielectric constants. Hence the fluorescent light can be observed the boundary between the polystyrene particle and thermosetting resin, and thus observed as fluorescent circle or star-like patterns.

CONCLUSIONS

In summary, we could succeed to prepare flexible two-dimensional (2D) particle arrays utilized the thermosetting resin. This type of 2D particle arrays can be bent easily and repeatedly. Beautiful micro-circle or micro-star-like light-propagation patterns were observed in the flexible 2D particle arrays from the emission of fluorescent particles in the arrays. This flexible 2D particle array might be changed the general idea of self-assembled structures; which normally exist on solid substrates.

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