A Simple Method for the Production of a Two-Dimensional, Ordered Array of Small Latex Particles

R. Micheletto,* H. Fukuda, and M. Ohtsu†

Ohtsu "photon control" project, Kanagawa Academy of Science and Technology, KSP East Room 408, 3-2-1 Sakado, Takatsu, Kawasaki City, Kanagawa 213, Japan

Received November 18, 1994. In Final Form: May 25, 1995®

We present here a simple technique for depositing wide monolayers of submicron-sized latex particles. The method is straightforward and does not require any special apparatus. We also studied the quality of the arrays formed, giving information on either the large scale structure or the small scale one. With this technique we succeeded to deposit arrays of 42 nm sized latex spheres, as far as we know, the smallest regular monolayer array ever deposited.

Introduction

In order to perform some experiments to study high-density optical storage media, beyond the optical diffraction limit, by a near field optical method,[1,2] we needed a regular two-dimensional array of submicron-sized latex spheres on which a photochromic Langmuir−Blodgett film could be deposited for use as the optical storage medium. This array works to concentrate the evanescent light from the subwavelength aperture within the area equivalent to the sphere diameter. The deposition of such an array became increasingly difficult as the diameter of the particle decreased. Strong Brownian motion and capillary forces create a state of disorder in the system that is difficult to control.[3] Several authors have developed techniques to create such colloidal crystals, but, as far as we know, they did not involve particles smaller than 55 nm and they used special devices to deposit the film.[3−9]

We consider our method a simple and efficient derivation from the various techniques described in refs 3−9. The main differences with respect to other proposed techniques are due to the fact that with our method it is possible to use simple commercial untreated spheres; we do not need salt or surfactant in solution, nor do we need to electrically charge the particles, also, there is no confinement between any boundaries nor surface pressure controls. The introduction of a fine thermal control together with execution of the evaporation in a small volume and under a determined water to particle concentration allow the formation of our monolayers. We obtained rather large crystalline arrays even of very small particles, down to 42 nm diameter, as far as we know the smallest to be deposited in a regular monolayer array.

With the optical technique introduced above, the size of the data bit coincide with the area occupied by one particle. With a 42 nm size, it would be possible to reach the extremely high data density of approximately 200 Gbit per square inch, which is 2 orders of magnitude greater than magneto-optical compact disk medium.

We will give a detailed explanation of the method used and we will show the results and a preliminary analysis of the structure of the films, made by SEM and AFM. We will evaluate quantitatively the quality of the array formed by means of Fourier analysis.

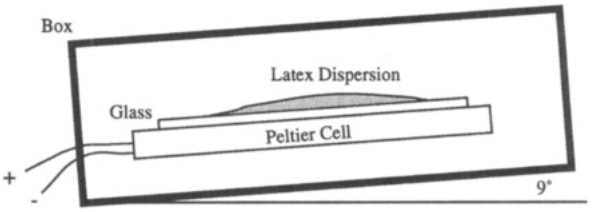


Figure 1. Schematic drawing of the evaporation system.

Experimental Procedure

As is well-known, the production of a latex particle monolayer film is usually realized by the evaporation of a solution on a substrate.[3,4,7,8] We believe that the quality of the results depends strongly on the properties of the substrate as well as on how homogeneous the process of evaporation is. Thus we focused our efforts on obtaining an efficient treatment to clean the substrate and, at the same time, we controlled the temperature and the humidity of the system by means of common tools. We use slide glasses (Matsunami, 18 × 18, thickness 0.15 mm) as substrates. We treated the glasses with pure sulfuric acid for 24 h, to obtain a clean and hydrophilic surface. The glasses were then preserved in ethanol until used.

Polystyrene latex beads (JSR, Stadex/Dynospheres, catalog SC-004-R), with a diameter of 42 nm were used. These particles did not have any surface treatment, were monodisperse (CV = 12.8%), and were originally dispersed in pure water at 1.0 wt %. A droplet of this mixture, with an opportune ratio of water/particles, was deposited on a glass surface. The proper water/particles ratio was calculated depending on the deposition area and on the size of the spheres (refer to the Appendix for details of the easy calculations). We found that the quality of deposition did not depend strongly on the concentration. As the matter of fact, we noticed that if the concentration is 1 or even 2 orders of magnitude higher than the theoretical value, the results were still sufficiently good.

The thin glasses used as substrate were fixed on a Peltier cell (Netsu Denshi, PW-124) for a good thermal stability (0.1 °C). We noticed that the value of the temperature is not as important for the quality of the film as its precise stability. For all the samples presented here, the temperature control of the Peltier cell was set to room temperature (22 °C, known with ±1 °C precision). The whole system was enclosed in a small plastic box (around 300 cm^3). We believe that the small volume helps to slow down the evaporation process, which takes approximately 2 h to take

† Also with Tokyo Institute of Technology, 4259, Nagatsuta-cho, Midori-ku, Yokohama 227, Japan.

® Abstract published in *Advance ACS Abstracts,* August 15, 1995.

(1) Betzig, E.; Trautman, J. K.; Wolfe, R.; Gyorgy, E. M.; Finn, P. L.; Kryder, M. H.; Chang, C. H. *Appl. Phys. Lett.* **1992**, *61* (2), 142.
(2) Jiang, S.; Ichihashi, J.; Monobe, H.; Fujihira, M.; Ohtsu, M. *Optics Commun.* **1994**, *106*, 173.
(3) Denkov, N. D.; Velev, O. D.; Kralchevsky, P. A.; Ivanov, I. B.; Yoshimura, H.; Nagayama, K. *Langmuir* **1992**, *8*, 3183.
(4) Kralchevsky, P. A.; Nagayama, K. *Langmuir* **1994**, *10*, 23.
(5) Pieranski, P.; Strzelecki, L.; Pansu, B. *Phys. Rev. Lett.* **1983**, *50*, 900.
(6) Murray, C. A.; Van Winkle, D. H. *Phys. Rev. Lett.* **1987**, *58*, 1200.
(7) Dimitrov, A. S.; Dushkin, C. D.; Yoshimura, H.; Nagayama, K. *Langmuir* **1994**, *10*, 432.
(8) Van Winkle, D. H.; Murray, C. A. *Phys. Rev. A* **1987**, *34*, 562.
(9) Dushkin, C. D.; Nagayama, K.; Miwa, T.; Kralchevsky, P. A. *Langmuir* **1993**, *9*, 3695.

0743-7463/95/2411-3333$09.00/0

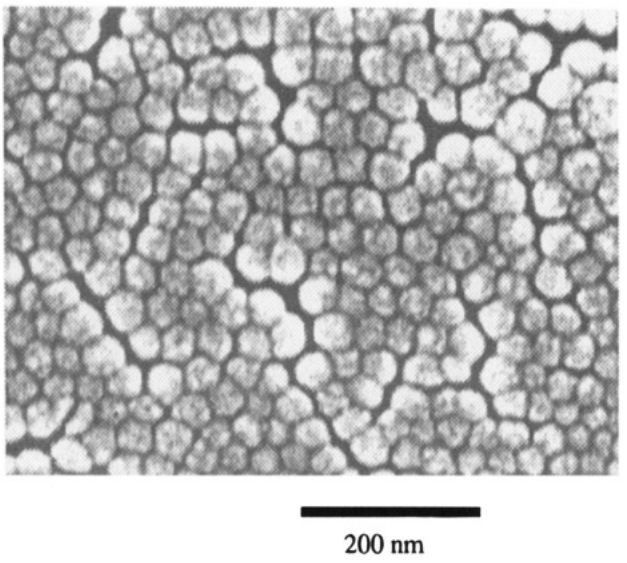


Figure 2. A sequence of SEM images of a latex particle array monolayer deposited with the method described. The picture is taken in the same position at different magnification scales. The particles are JSR Stadex/Dynospheres, catalog SC-004-R, 42 nm in diameter.

place completely. The box also protects the surface from the external air flow, which can disturb it. The whole system was tilted about 9°. In this way the evaporation starts from the top

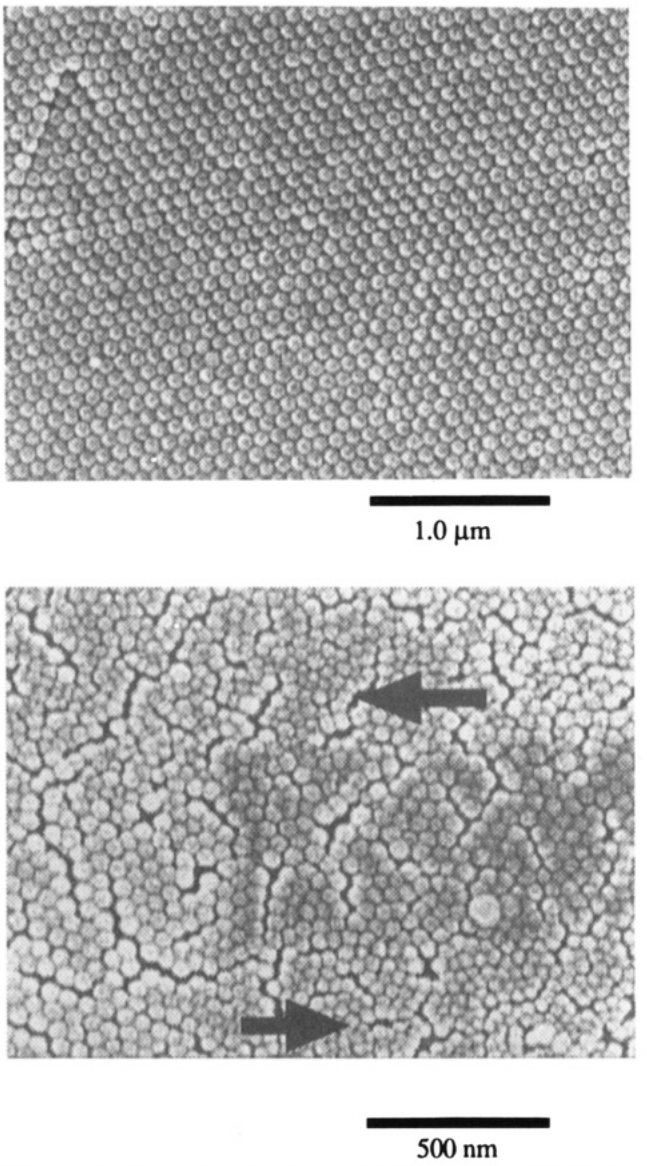


Figure 3. A regular structure of 100 nm CV = 2.6% latex spheres (a, top) compared with CV = 13% spheres (b, bottom). We can see rather irregular regions where not all the spheres have the same radius (top left and bottom right of b).

of the sample on a horizontal border where evaporation takes place. This border moves then to the bottom of the sample until it is completely dry. The speed of evaporation and the quality of the resulting sample depends on this angle; 9° was used on all samples presented here. Refer to Figure 1 for a schematic view of the setup.

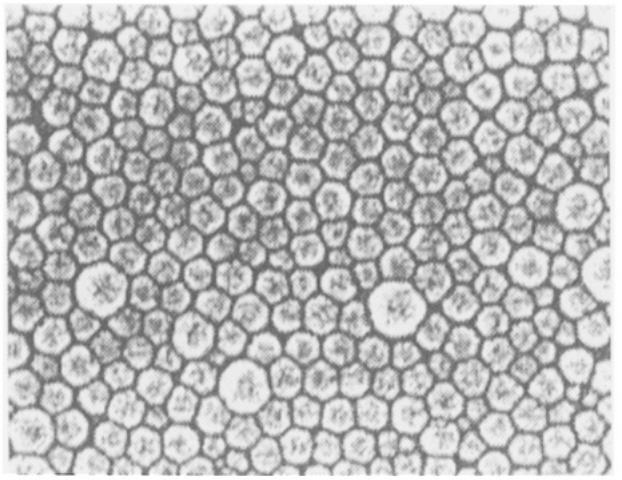
Our depositions covered an area of about 1 cm^2, but in any sample only around half of the area was covered by monolayers. The other half is the one where the evaporation take place at last, at the bottom of the sample. We believe that in such regions the remaining of water concentrates impurities and the excess particles, creating multilayers and clusters.

To analyze the resulted deposition we used an atomic force microscope (SII, SPI-3700) and a scanning electron microscope (Hitachi, S-4500). All the samples were sputtered with a thin layer of gold (around 10 nm thickness) with a Hitachi E-1030 ion sputter machine.

Results and Evaluations

We show in Figure 2a–c a sequence of SEM images taken in the same location but at different magnification scales. The array looks sufficiently regular, for our purposes, in the first image at low scale.

The irregular features in these films are essentially due to the size dispersion. Comparing, for example, parts a and b of Figure 3 provides clues. The first represents



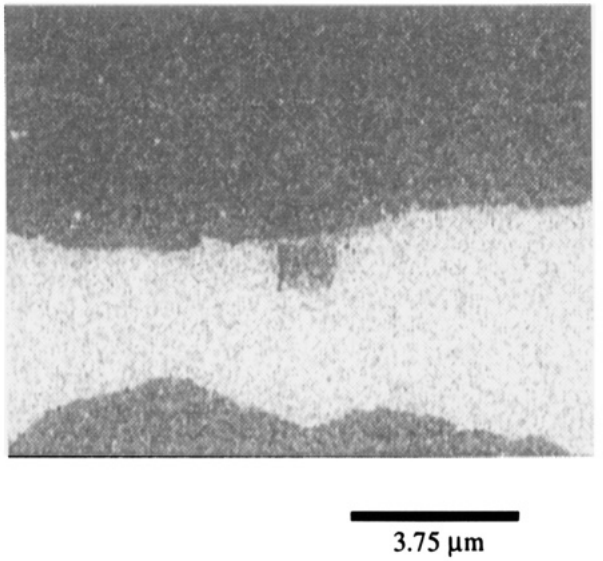


Figure 4. Two SEM image of a monolayer of 56 nm Polyscience carboxylate latex spheres, catalog 16661. In the short scale (a, top) we do not observe shrinkage-associated empty spaces (see the text).

a highly regular structure; in this case the particles are 100 nm in diameter with a rather low size dispersion (2.6%). The second shows 42 nm particles with 13% dispersion. This time we can spot regions where the particles have the same size (central part of the picture), and the array is regular; elsewhere we can notice zones of disorder where the particles present great differences in size (top left and bottom right).

The regular spaces in the two-dimensional array that we noticed on low-scale images has been observed also by other authors and are known to be due to the shrinking of the particles.[7] In spite of this, we propose that this irregularity is due solely to the particle−water−particle forces that acts in the evaporation process. To confirm this, we have chosen some polystyrene surface-treated particles. We deposited, with the same procedure described above, a film of surface-treated 59 nm particles (Polyscience Inc., Polybead, Fluoresbrite Carboxilated Microspheres, monodispersity CV < 5%, originally in pure water at 2.5%). As shown in Figure 4a,b, the large scale behavior is similar, but the small-scale, shrinkage-associated empty spaces do not appear. Since the inner material (polystyrene) and the deposition procedure used are the same, we can claim that the phenomena is due to the collective interactions between the water and the surface of the spheres, not a physical shrinking of the particles.

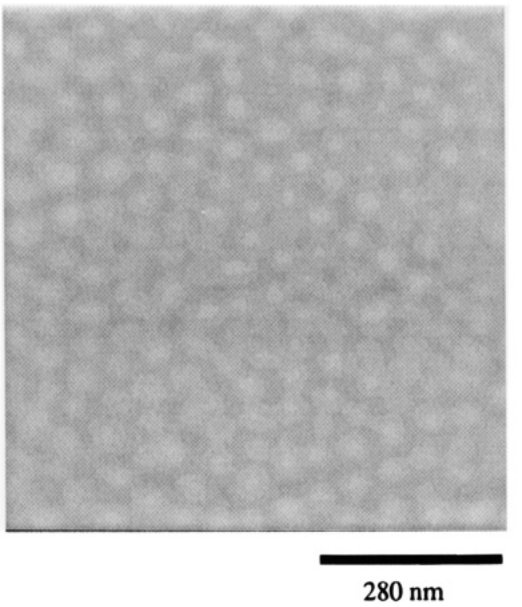


Figure 5. AFM image of an array of 42 nm Stadex latex particles. The image has been filtered for measurements.

At large scales the structure appear to be a grid of long stripes (Figure 2c). These stripes are 10−20 μm wide and several millimeters long. We tried to understand their nature and to avoid the formation of them. Our strategy was mainly to reduce the temperature because in some of our preliminary experiments we noticed that the macroscopic stripes got wider at lower temperatures; however, the nature of these macrostripes is not clear and is under investigation.

To evaluate the quality of the produced two-dimensional array, we used Fourier analysis. In Figure 5 is shown the original AFM scan of 42 nm particles on a 780 × 780 nm area. Notice that the image has been band-pass filtered to emphasize the center of the spheres.

In Figure 6a we show its one-dimensional spatial Fourier spectrum, averaged on about 10 rows of particles, as shown by the rectangular area in Figure 6b. Figure 6c is the space-amplitude representation of the same Fourier spectrum; the 42 nm period can be clearly seen.

The regularity of the array is given by the sharpness of the peak indicated in Figure 6a; we claim, for our sample, $\Delta f_x = 14\ \mu m^{-1}$ (width at half-maximum of the spectral shape). To present this value in space unities we simply consider that the center of the peak is located at $f_{x0} = 24\ \mu m^{-1}$ ($x_0 = 1/24 = 41.7$ nm), then we can conclude that $x_0 \cong 42 \pm 22$ nm (Δx has been estimated as $\Delta x = x_0/f_{x0}\Delta f_x$).

In Figure 7 is shown the two-dimensional Fourier power spectrum calculated on the same pattern shown in Figure 5. The hexagonal structure of the two-dimensional crystal can be easily recognized with the six peaks indicating the three main directions of the array.

Discussion and Conclusions

We succeeded in depositing a highly regular two-dimensional array of small polystyrene latex spheres. The monolayer lay on the glass substrate in the form of long stripes (see Figure 2c or 4b). These stripes are several micrometers large and millimeters long. The area covered by the monolayer is approximately 50% of the total deposition area. We have still not performed a complete optical storage experiment, but we claim that the samples realized can be used to investigate our optical medium systems[2,10] and it is possible to obtain a very high data

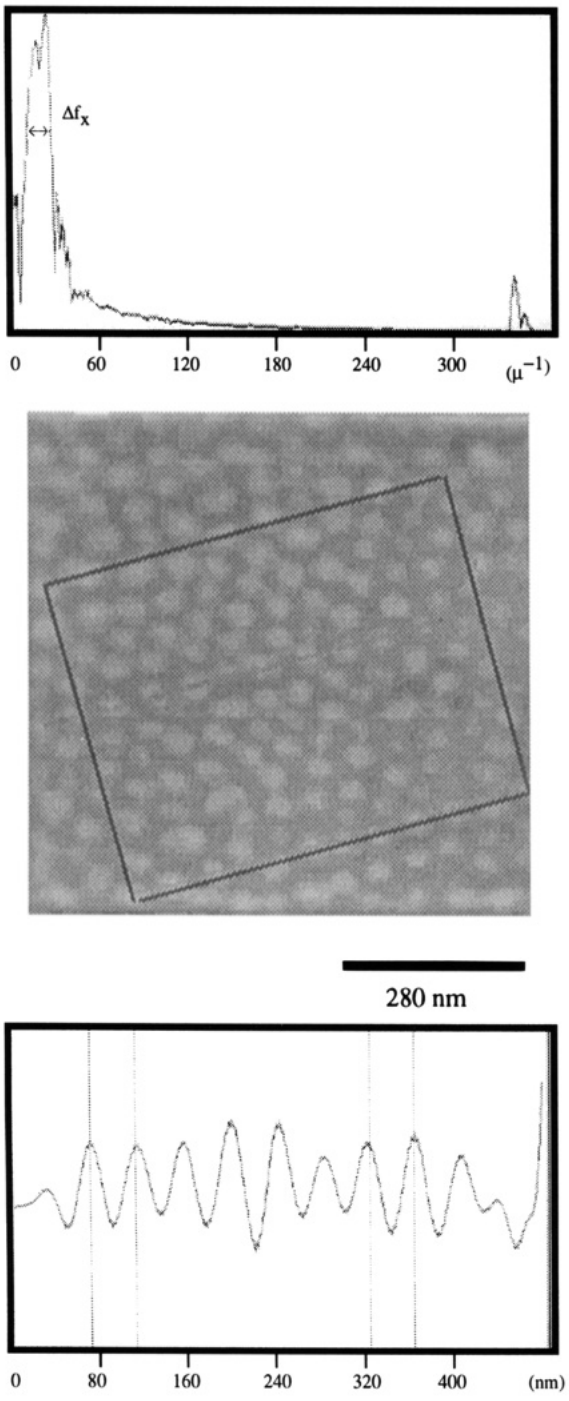


Figure 6. (a, top) Fourier one-dimensional spectrum, averaged on the region showed in part b. (b, middle) The region in which measurement has been calculated. (c, bottom) Space-amplitude representation of the Fourier spectrum in b. The 42 nm period can be clearly seen.

density. In fact, the dimension of the bit, for 42 nm particles, would be $2.8e^{-12}$ in.^{2}, which, considering that the covering of the monolayer is 50%, yields around 200 Gbit per inch. This figure is 2 orders of magnitude greater than the most advanced optical storage devices.

The samples obtained are easy to reproduce and require no particular skill or precise instruments. The quality of the formed arrays has been quantitatively evaluated through Fourier analysis.

On the basis of what we have experienced, we think that improvement in the thermal and humidity control

(10) Fukuda, H.; Micheletto, R.; Ohtsu, M. Proceeding of the Near Field Optics 3, EOS Topical Meeting, Brno, Czech Republic, May 1995, p 183.

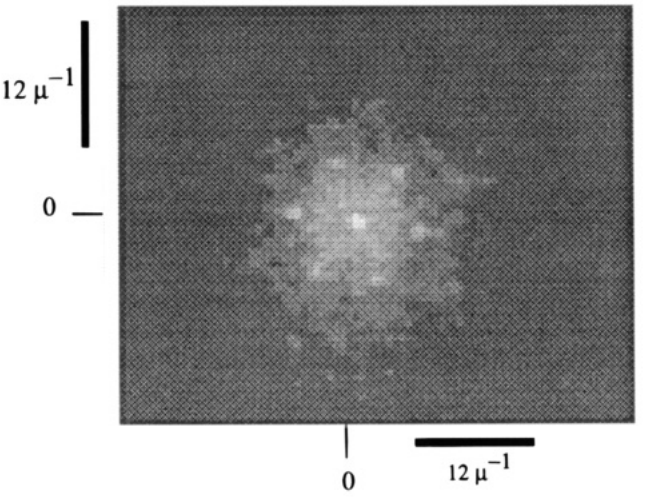


Figure 7. Two-dimensional spectrum of the array in Figure 5. The hexagonal structure of the crystal is visible.

can increase the quality of the samples. The deposition process can be carried out at lower temperatures, such as 4 °C, for example, to obtain better results. We have found problems in doing so, due to water condensation on the sample at such temperatures. We believe that improving humidity control can overcome this and lead to more regular depositions and higher coverage with the monolayer. Many other different applications may be found.

Appendix

We calculated the latex/water proportion simply by imposing that a monolayer of spheres should cover evenly the area of deposition. We choose, for example, an area $A = 1$ cm^2; we suppose that a droplet of $C = 10\ \mu$L of water will dry in such area. Usually the company which produces the particles will give the original concentration of the particles as

$$\eta = 6\omega/(\pi\varrho\phi^3) \times 10^{12} \text{ particles mL}$$

where ω is the percentage of solid latex, ϱ is the density of polymer, and ϕ is the diameter of the spheres in microns. For 42 nm Dinosphere, we apply that formula using $\omega = 0.01$ (1 wt %), $\varrho = 1.05$ (polystyrene), and $\phi = 0.042$, which yields

$$\eta = 2.45 \times 10^{14} \text{ particles/mL}$$

This is the original concentration we start with. Now we determine what concentration we should have to obtain one monolayer over the area A. Firstly we calculate the number of particles that will cover evenly such an area (N_p). Since a particle of 42 nm diameter will occupy an area $A_p = \pi/(\phi/2)^2$, we have

$$N_p = A/A_p = 7.2 \times 10^{10} \text{ particles}$$

then we divide this by the amount of water we need, 10 μL, and we have the concentration:

$$\eta^* = N_p/C = 7.2 \times 10^{12} \text{ particles/mL}$$

Acknowledgment. We wish to thank Antony S. Dimitrov of Nagayama Proj. (ERATO, Tsukuba, Japan), Prof. Vladimir I. Troitsky of Technobiochip (Marciana, Italy), and Prof. Atsushi Ikai of T.I.T. (Tokyo, Japan) for their keen support and suggestions. This work has been partially supported by S.T.A. Fellowship of Japan.

LA940921L