

Facile Organization of Colloidal Particles into Large, Perfect One- and Two-Dimensional Arrays by Dry Manual Assembly on Patterned Substrates

Nguyen Nguyen Khanh and Kyung Byung Yoon*

Center for Microcrystal Assembly, Department of Chemistry, and Program of Integrated Biotechnology, Sogang University, Seoul 121-742, Korea

Received July 9, 2009; E-mail: yoonkb@sogang.ac.kr

The organization of colloidal particles into one- (1D) and two-dimensional (2D) arrays on substrates is an important area in modern science and technology.^{1,2} For high precision applications, the 1D and 2D colloidal arrays must be made into large, defect-free, perfect arrays with the precise control of the symmetry and the interparticle distance. The organization process should also be simple and fast, and the qualities of the arrays must be reproducible. However, despite the great efforts directed into this area,^{2–11} the existing methods have not yet met all of the above requirements.

The existing methods commonly begin with the deposition or adsorption of particles from the solution to the substrates. The adhered particles then self-assemble into hexagonally ordered arrays with the help of solvents. However, the two key requirements for the adhered particles to undergo ordering, namely, self-assembly and solvents, have concomitantly served as the anchors that prevent further progress of the field because there are too many factors that sensitively affect the self-assembly process (Supporting Information, **SI-1**). Consequently, the organization of colloidal particles into large (>cm), perfect 1D and 2D arrays based on the self-assembly in solution has been extremely difficult. Thus, novel methods that do not depend on self-assembly and solvents have to be developed.

In relation to the above, organization of dry micro silica beads into three-dimensional (3D) structures on patterned substrates was demonstrated using a microrobot.¹² However, this method is not yet practical. Stemming from our recent finding that rubbing is a highly effective method for the organization of zeolite microparticles into monolayers on flat substrates,¹³ we discovered that rubbing of dry spherical colloidal particles into the patterned nanowell arrays leads to a very fast organization of the spherical colloidal particles into large and perfect 1D and 2D arrays. We refer to this method as ‘dry manual assembly’ and the conventional methods as ‘wet self-assembly’ since they depend on self-assembly in solution.

As for the model spherical colloidal particles, silica beads with the diameters ranging from 20 to 1000 nm were used (Supporting Information, **SI-2**). Glass plates with two different sizes, 2.5 × 2.5 and 15 × 15 cm² and patterned Si wafers with the size 1.0 × 1.0 cm² were used as the substrates. The Si wafers patterned with the square and hexagonal arrays of nanowells (depth = 250 nm) with a diameter/pitch of 200/300, 350/500, and 500/700 (in nm), respectively, were prepared. Positive photoresists (PR, thickness = 350 nm) supported on Si wafers (PR/Si) patterned with nanowells in the square and hexagonal net arrays with 200/300, 350/500, and 500/700 were also prepared. Si wafers patterned with the square net array of

truncated conical silicon pillars with a top diameter/bottom diameter/pitch/length of 200/250/700/250 (in nm) were also prepared. They are denoted according to ‘symmetry/structure/well size or bottom diameter/pitch/material’, where the symmetries are Sq (square) or Hx (hexagonal), structures are W (well) or P (pillar), and the materials are Si or PR/Si (Supporting Information, **SI-3**).

We first tested the possibility of organizing the 20–1000 nm silica beads, respectively, into random monolayers on plain substrates using polyethyleneimine (PEI) as the molecular glue. In fact the organization of silica beads into monolayers by dry manual assembly was expected to be very difficult because the silica beads do not have flat facets unlike zeolite microcrystals and the binding strength between microcrystals and substrates decreases with decreasing the contact area between the solid particle and the substrate.¹⁴ Surprisingly, however, the silica particles readily formed high quality monolayers consisting of small hexagonally packed domains upon rubbing them on PEI-coated flat glass plates for ~1 min (Supporting Information, **SI-4–6**).

Unlike the monolayers produced by wet self-assembly, there was no need to dry the monolayers, and hence, they did not undergo cracking due to the particle shrinkage. Thus, despite the fact that the procedure is extremely simple and fast, the quality of the monolayer was comparable to those produced by the conventional ‘wet self-assembly’ methods. Furthermore, this also worked equally well on a larger substrate, e.g. 15 × 15 cm² (Supporting Information, **SI-7**).

Upon rubbing the 700-nm silica beads on Sq/W/500/700/Si, Hx/W/500/700/Si, and Sq/P/250/700/Si (Figure 1, A–C), each bead precisely positioned itself on each well (Figure 1D,E) or space surrounded by four cones (Figure 1F), giving rise to the perfect orderings of the beads in the square and hexagonal net arrays, respectively, on the entire substrates (Figure 1G,H, Supporting Information, **SI-8**). This method also worked well for the organization of 500- and 300-nm beads (Supporting Information, **SI-9–12**) into perfect arrays on the corresponding patterned substrates. Thus, the above method rapidly yields perfect 2D arrays of silica beads with controlled symmetry and orientation in the centimeter scale.

The method also worked well on patterned PR/Si substrates (Supporting Information, **SI-13**), and the use of patterned PR/Si has also an advantage since the underlying PR layer can be removed after assembly of the arrays by dissolving it with methanol, leading to the production of the perfect 2D arrays on flat substrates (Figure 2A,B).

In fact, pattern-induced organization of colloidal particles into 1D wires, 1D stripes, 2D square net arrays, and 3D colloidal crystals by wet self-assembly methods has received great attention.^{7–10} However, only the substrates patterned with the square net arrays of pillars (not wells) showed some success in organizing the particles into 2D square net arrays.^{8b} Even in this case, the silica beads did not fully occupy all the 500×500 sites, which correspond to 0.1% of those we have used in this report. Furthermore, the pattern-induced self-assembly of the particles into hexagonal net arrays has not been achieved, emphasizing the incomparable superiority of the dry manual assembly to wet self-assembly.

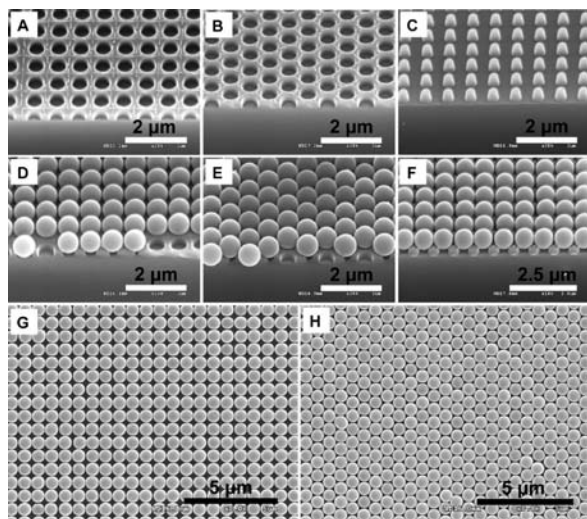


Figure 1. SEM images of Sq/W/500/700/Si (A), Hx/W/500/700/Si (B), and Sq/P/250/700/Si (C); 700-nm sized silica beads fit into the nanowells giving rise to perfect square (D), hexagonal (E), and square (F) net arrays, respectively (tilted views); and the top views of the square (G) and hexagonal (H) net arrays.

The same methodology also worked well for the preparation of perfect 1D wires (Figure 2C) and 1D stripes of square, hexagonal (Supporting Information, SI-14–17), mixed net arrays (Figure 2D), and 2D arrays having both square and hexagonal net array regions (Figure 2E and Supporting Information, SI-18). In fact, the organization of colloidal particles in two different symmetries within a substrate is unprecedented. Although preparations of 1D wires and stripes have also been demonstrated on patterned substrates by wet self-assembly,^{7,9,10b,c,11c} such a lateral ordering of the silica beads between the arrays of 1D structures has not been achieved.

Repetition of the dry manual assembly of silica beads in the square net arrays showed the possibility of producing perfect 3D crystals, as demonstrated with the 700-nm silica beads (Figure 2F). Although not impossible, the multilayer assembly of the same-size silica beads on a larger scale (cm^2) was very difficult (Supporting Information, SI-19) due to the positional instability of the silica beads in the layers higher than the first layer and due to the smaller well (gap) sizes created by the four neighboring silica beads. However, smaller beads such as 300- and 420-nm beads readily fit into the gaps, giving rise to the formation of perfect 2D binary layers of 700/300-nm (Figure 3A) and 700/420-nm (Figure 3B) silica beads in the square net arrays.

The silica beads equal to or smaller than the well size readily entered into the wells giving rise to perfect 2D nonclosely packed

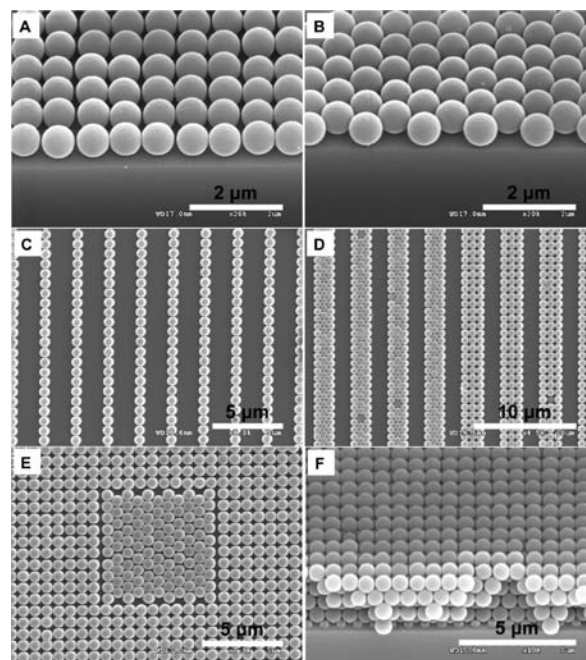


Figure 2. SEM images of 700-nm sized silica beads organized in the square (A) and hexagonal (B) net arrays on flat Si wafers, 1D wires (C); 1D stripes composed of three silica bead rows in both the square and hexagonal net arrays (D); 2D arrays having both square and hexagonal net arrays (E); and five layers of square net arrays assembled on the corresponding patterned Si wafers (F).

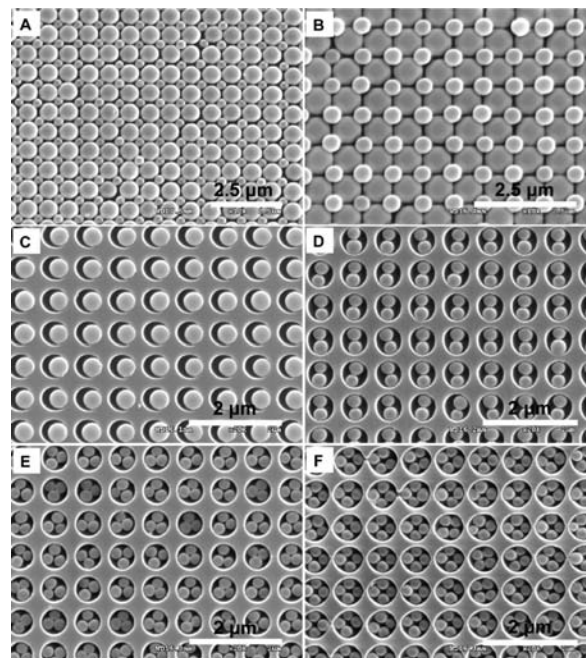


Figure 3. SEM images of the square net arrays of 2D binary silica beads of 700 and 300 nm (A), 700 and 420 nm (B); nonclosely packed 2D arrays of silica beads with the size of 420 nm (C); nonclosely packed square net arrays of two (D), three (E), and four (F) closely packed silica beads with the sizes of 300 (D), 250 (E), and 230 nm (F), respectively, assembled on Sq/W/500/700/Si.

arrays as demonstrated for 500-nm (Supporting Information, SI-20) and 420-nm (Figure 3C) silica beads on Sq/W/500/700/Si. The nonclosely packed 2D arrays have received great attention,¹¹ but nonclosely packed 2D arrays in the square net symmetry have not

been demonstrated. Interestingly, each 420-nm bead could be pushed to the same side of wells by rubbing the silica beads to a uniform direction (Supporting Information, SI-21). When the bead sizes were further reduced, multiple numbers of beads entered into each 500-nm well (Figure 3D–F, Supporting Information, SI-17). Thus, the dry manual assembly is also capable of organizing the colloidal particles into the arrays Xia's group has developed by a wet self-assembly method,^{7a} but much more easily and rapidly.

Unlike wet self-assembly, the strong force applied to the particles during rubbing readily induces even deformation of the silicon wells and silica beads. For instance, the 500-nm circular wells readily deformed into oval-shape wells after accommodation of two 300-nm beads, and the silica beads also deformed into oval shapes. In the case of Figure 3F, it is clear that the well size increased significantly and the walls have become much thinner to accommodate four 230-nm silica beads into each 500-nm well. Thus, even the silica beads with the sizes larger than the well by ~10% can also be inserted into the wells by deformation of the beads and wells, demonstrating the much higher tolerance of the dry manual assembly to the size and shape of the colloidal particles than the wet self-assembly.

We attribute the superiority of the dry manual assembly to the wet self-assembly in terms of simplicity, speed, perfect ordering, and large scale to the following three factors: a much higher tolerance to the size and shape variations of the colloidal particles; the forced rapid movement of the particles on the substrate surface toward the desired direction without being affected by the surface properties such as hydrophilicity, charge, and roughness; and the disuse of solvents.

This method also works well for silica beads with the sizes smaller than 100 nm (data not shown), and we predict that the substrate size can be expanded to an 8-in diameter, which is the limitation of the current lithography. The perfect 1D and 2D arrays will be useful for a variety of applications, and we believe that this methodology will also help develop novel methods to rapidly organize colloidal particles into large and perfect 3D crystals, for which many research groups are working very actively.¹⁵

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Supporting Information Available: Materials, the detailed experimental procedure, additional SEM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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