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Highly Ordered Arrays of Nanoparticles in Large Areas from Diblock Copolymer Micelles in Hexagonal Self-Assembly

Sang-Hyun Yun,[†] Seong Il Yoo,[†] Jin Chul Jung,[†]
Wang-Cheol Zin,[†] and Byeong-Hyeok Sohn*[,‡]

Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang 790-784, Korea, and Department of Chemistry, NANO Systems Institute, Seoul National University, Seoul 151-747, Korea

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Synthesis of metal, semiconductor, and oxide nanoparticles is an interesting and important research area because of their potential for use in electronic, photonic, chemical, and biological applications.[1−4] In solution-phase synthesis, various nanoparticles have been efficiently produced in a controlled way in terms of their size and dispersity.[5−7] For example, monodisperse magnetic nanoparticles in large quantity were synthesized by stabilizing them with appropriate capping agents under relatively mild synthetic conditions.[5] To fabricate an ideal array for a single registry on each nanoparticle, it is necessary to deposit nanoparticles in perfect two-dimensional order on the solid substrate from the solution of nanoparticles. However, a perfect array of nanoparticles is rarely achieved, particularly over an extended area, because of uncontrolled formation of defects in the self-assembling process of the nanoparticles induced by the solvent evaporation.[8,9] Even with absolutely identical particles, for example, atoms, formation of defects cannot be avoidable in their self-assembly, as in atomic crystals.[10] Defect formation can be minimized by lowering the speed of the self-assembling process, as in atomic layer deposition.[11] In another way, defects can be relieved by the annealing process that can heal defects in the self-assembly, for example, zone refining for pure silicon wafers.[12] However, both methods of reducing defects in self-assemblies would not work effectively in the formation of a two-dimensional array of nanoparticles in long-range order from their solutions.

Alternatively, effective fabrication of a two-dimensional array of nanoparticles on solid substrates was demonstrated by the utilization of a single-layered film of diblock copolymer micelles in a self-assembled arrangement.[13−18] Diblock copolymer micelles containing precursors of nanoparticles were coated onto the substrate to form a two-dimensional array of micelles. Then, an array of nanoparticles was fabricated in situ on the substrate by plasma treatment without deteriorating the original arrangement of micelles. Since the plasma treatment removed the copolymers completely, a pure array of nanoparticles was fabricated. This method was successfully applied to arrays of various nanoparticles including Au,[13−15] Fe_2O_3,[16] ZnO,[17] and TiO_2.[18] However, the arrays were also far from having perfect order due to the inherent size distribution of the diblock copolymer micelles. Instead of micelles, thin films of diblock copolymers themselves were also employed to fabricate a perfect two-dimensional order of their spherical[19−21] or cylindrical[22,23] nanodomains over an extended area by topological pre-patterning,[19,20,23] shearing,[21] or solvent anealing.[22] However, the defect-free arrangement of nanodomains and synthesis of nanoparticles from the ordered nanodomains were limited.

In this communication, a near-perfect hexagonal array of diblock copolymer micelles was created by solvent annealing directly on a single layer of micelles, which equilibrated the size and positional order of the micelles by redistributing the copolymer chains per micelle in the solid state. Then, the hexagonal self-assembly of the diblock copolymer micelles was employed as a template to synthesize a highly ordered two-dimensional array of Au nanoparticles on large areas.

Polystyrene-*block*-poly(4-vinylpyridine) (PS−P4VP) copolymers assemble into spherical micelles of a PS corona and a P4VP core in toluene, a strongly selective solvent for

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[*] To whom correspondence should be addressed. E-mail: bhsohn@snu.ac.kr.
[†] Pohang University of Science and Technology.
[‡] Seoul National University.

(1) Hutter, E.; Fendler, J. H. *Adv. Mater.* **2004**, *16*, 1685.
(2) Adams, D. M.; Brus, L.; Chidsey, C. E. D.; Creager, S.; Creutz, C.; Kagan, C. R.; Kamat, P. V.; Lieberman, M.; Lindsay, S.; Marcus, R. A.; Metzger, R. M.; Michel-Beyerle, M. E.; Miller, J. R.; Newton, M. D.; Rolison, D. R.; Sankey, O.; Schanze, K. S.; Yardley, J.; Zhu, X. *J. Phys. Chem. B* **2003**, *107*, 6668.
(3) Parak, W. J.; Gerion, D.; Pellegrino, T.; Zanchet, D.; Micheel, C.; Williams, S. C.; Boudreau, R.; Le Gros, M. A.; Larabell, C. A.; Alivisatos, A. P. *Nanotechnology* **2003**, *14*, R15.
(4) Shipway, A. N.; Katz, E.; Willner, I. *ChemPhysChem* **2000**, *1*, 18.
(5) Hyeon, T. *Chem. Commun.* **2003**, 927.
(6) Puntes, V. F.; Krishnan, K. M.; Alivisatos, A. P. *Science* **2001**, *291*, 2115.
(7) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545.
(8) Santhanam, V.; Andres, R. P. *Nano Lett.* **2004**, *4*, 41.
(9) Rabani, E.; Reichman, D. R.; Geissler, P. L.; Brus, L. E. *Nature* **2003**, *426*, 271.
(10) Hull, D.; Bacon, D. J. *Introduction to dislocations*; Butterworth-Heinemann: Boston, 2001.
(11) Leskalä, M.; Ritala, M. In *Handbook of Thin Film Materials*; Nalwa, H. S., Ed.; Academic Press: New York, 2002; Vol. 1, p 103.
(12) Zulehner, W. *Mater. Sci. Eng. B* **2000**, *B73*, 7.
(13) Förster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195.
(14) Spatz, J. P.; Herzog, T.; Mössmer, S.; Ziemann, P.; Möller, M. *Adv. Mater.* **1999**, *11*, 149.
(15) Spatz, J. P.; Mössmer, S.; Hartmann, C.; Möller, M.; Herzog, T.; Krieger, M.; Boyen, H.-G.; Ziemann, P.; Kabius, B. *Langmuir* **2000**, *16*, 407.
(16) Sohn, B. H.; Choi, J. M.; Yoo, S. I.; Yun, S. H.; Zin, W. C.; Jung, J. C.; Kanehara, M.; Hirata, T.; Teranishi, T. *J. Am. Chem. Soc.* **2003**, *125*, 6368.
(17) Yoo, S. I.; Sohn, B. H.; Zin, W. C.; An, S. J.; Yi, G. C. *Chem. Commun.* **2004**, 2850.
(18) Li, X.; Lau, K. H. A.; Kim, D. H.; Knoll, W. *Langmuir* **2005**, *21*, 5212.
(19) Cheng, J. Y.; Ross, C. A.; Thomas, E. L.; Smith, H. I.; Vancso, G. J. *Appl. Phys. Lett.* **2002**, *81*, 3657.
(20) Segalman, R. A.; Hexemer, A.; Hayward, R. C.; Kramer, E. J. *Macromolecules* **2003**, *36*, 3272.
(21) Angelescu, D. E.; Waller, J. H.; Register, R. A.; Chaikin, P. M. *Adv. Mater.* **2005**, *17*, 1878.
(22) Kim, S. H.; Misner, M. J.; Xu, T.; Kimura, M.; Russell, T. P. *Adv. Mater.* **2004**, *16*, 226.
(23) Xiao, S.; Yang, X. M.; Edwards, E. W.; La, Y. H.; Nealey, P. F. *Nanotechnology* **2005**, *16*, S324.

10.1021/cm0618953 CCC: $33.50

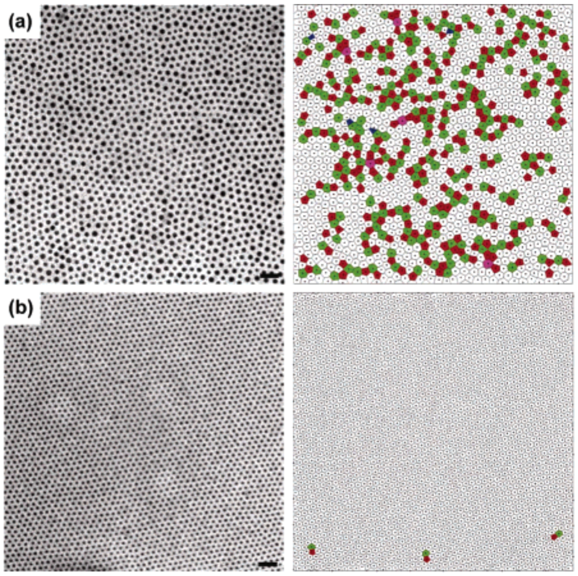

Figure 1. TEM images (left) and Voronoi diagrams (right) of single-layered films of PS−P4VP micelles (a) before and (b) after THF annealing. In the TEM images, P4VP cores were selectively stained with I_2. The scale bars are 100 nm. In the Voronoi diagrams, P4VP cores having four, five, seven, and eight nearest neighbors are marked in blue, red, green, and pink, respectively.

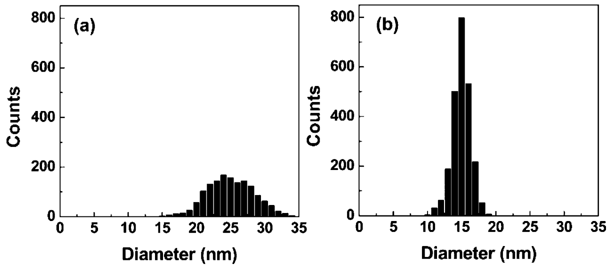

Figure 2. Size distribution of the cores of PS−P4VP micelles (a) before and (b) after THF annealing shown in Figure 1. The actual counts were obtained from larger areas than the images of Figure 1.

the PS block. Figure 1a shows a typical transmission electron microscopy (TEM) image of a single layer of micelles, which was spin-coated on cleaned silicon wafers or freshly cleaved mica substrates at 2000 rpm from a 0.5 wt % toluene solution of PS−P4VP ($M_n^{PS} = 47\,600$ g/mol, $M_n^{P4VP} = 20\,600$ g/mol, polydispersity index = 1.14, Polymer Source, Inc.).

P4VP cores were selectively stained by I_2 and appeared as dark spheres. No overlapping of P4VP cores confirmed a single layer of PS−P4VP micelles, which was evenly coated over the entire substrate (1.5 cm × 1.5 cm) except the edges. However, the hexagonal order of the micelles was only in the short range, which is represented in the Voronoi diagram in Figure 1a. The P4VP cores (represented as points in the Voronoi diagram) having six nearest neighbors are not colored, and those with four, five, seven, and eight nearest neighbors are marked in blue, red, green, and pink, respectively. Many defects (colored non-hexagons) exist in the Voronoi diagram of Figure 1a, which closely matches up with the boundaries between the areas of hexagonally ordered micelles in the TEM image. The short-range hexagonal order of PS−P4VP micelles is associated with the broad size distribution of the PS−P4VP micelles. The diameter distribution of the cores of the PS−P4VP micelles (Figure 2a) was evaluated from larger areas than the TEM image of Figure 1a, assuming that the size distribution of micelles is not much different from that of the cores. The average diameter of the cores was 24.0 nm with a relatively large standard deviation of 3.9 nm (16.3%). Therefore, as demonstrated in the previous reports,[16,17] nanoparticles synthesized from the template shown in Figure 1a were arranged in short-range hexagonal order with a relatively broad size distribution.

When the single layer of micelles shown in Figure 1a was solvent-annealed by a saturated vapor of tetrahydrofuran (THF), the regularity of hexagonal order of PS−P4VP micelles was much improved. After 30 min of annealing (Figure 1b), there were only six defects (three red pentagons and three green heptagons) out of 2592 hexagonal arrays of micelles (hexagons). By the Voronoi analysis on larger areas than the image of Figure 1b, the average percent of defects in hexagonal order was only 0.5%, indicating a near-perfect hexagonal array. By longer annealing than 30 min, some parts of the micellar film were dewetted without further improvement of the hexagonal order. The size distribution of micelles also became narrower by the solvent annealing. After 30 min of annealing, the standard deviation of the diameter of the cores was only 8.5%, a half the value of that before annealing. The average diameter of the cores after annealing (13.0 nm) also became smaller than that before annealing.

Since the solubility of P4VP in toluene is extremely poor, a PS−P4VP copolymer chain with a high fraction of P4VP hardly exists as a single chain (unimer) in toluene.[13,24] Thus, exchanging of unimers between micelles could be limited in a toluene solution of PS−P4VP. However, the exchange is necessary to obtain an equal number of copolymer chains per micelle for the same size of micelles. Fusion or fission of micelles can be the other way to reach an equal size of micelles.[13] But the glassy nature of P4VP at temperatures below the glass transition temperature of P4VP (138 °C) cannot allow fusion or fission of micelles.[13] Therefore, the PS−P4VP micelles formed in toluene had a relatively broad size distribution, resulting in a short-range hexagonal order as shown in Figure 1a. However, when the array of micelles formed from the toluene solution was exposed to THF that has a better solvating power for P4VP than toluene but is still a non-solvent for P4VP,[24] the PS−P4VP chains could be reorganized on the substrate to attain an equilibrium state of micelles. It can be also validated that THF is a non-solvent for P4VP but has a slightly better solvating power to P4VP than toluene by comparing the values of solubility parameters of toluene,[25] THF,[25] and P4VP,[26] which are 18.2, 18.6, and 22.5 $(J/cm^3)^{1/2}$, respectively. The rearrangement of copolymer chains between micelles could result in an equal number of copolymer chains per micelle, which could narrow down the size distribution and improve the hexagonal order. The reduced diameter of PS−P4VP micelles after THF annealing can be associated with the general tendency that the

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(24) Antonietti, M.; Heinz, S.; Schmidt, M.; Rosenauer, C. *Macromolecules* **1994**, *27*, 3276.

(25) Grulke, E. A. In *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; Wiley-Interscience: New York, 1999.

(26) Yang, J.-M.; Hsiue, G.-H. *J. Biomed. Mater. Res.* **1996**, *31*, 282.

aggregation number of copolymer chains per micelle decreases as the solubility of cores to the solvent improves.[13,24] Arrangement of PS−P4VP micelles can be achieved from a THF solution instead of a toluene solution. However, the hexagonal order of micelles was not as good as that in Figure 1b, although the diameter of the micelles was similar to that in Figure 1b. Furthermore, irregularly shaped micelles were observed, presumably because of aggregation of unimers, which exist in THF, by fast evaporation of solvent during spin coating. However, a long-range hexagonal order of micelles like Figure 1b was attained again by THF annealing directly on the spin-coated micelles. Thus, the THF annealing on the micellar array was a compulsory healing step to obtain a near-perfect hexagonal order of micelles.

To synthesize a highly ordered two-dimensional array of nanoparticles, a hexagonal array of PS−P4VP micelles after THF annealing was employed as a template. Although a variety of nanoparticles can be synthesized with PS−P4VP micelles,[13] Au nanoparticles were selected as a model case. A single layer of PS−P4VP micelles after THF annealing (Figure 1b) was immersed into an ethanol solution of $HAuCl_4$, a precursor of Au nanoparticles, which was selectively coordinated to the pyridine units of the P4VP core by protonation.[13] Then, by treatment over oxygen plasma, Au nanoparticles on the substrate were synthesized while preserving the order of the micelles. X-ray photoelectron spectroscopy (XPS) results showed that unstable gold oxide was formed by the oxygen plasma but was converted to gold even at room temperature in air (Supporting Information). Since the copolymers were completely removed by the plasma,[15−17] XPS results confirmed that a pure array of Au nanoparticles was obtained. A field-emission scanning electron microscopy (FE-SEM) image in Figure 3a shows a highly ordered hexagonal array of Au nanoparticles that was found all over the substrate. The average diameter of the Au nanoparticles was 11.4 nm with a standard deviation of 1.0 nm (8.8%). By the Voronoi analysis on the image (Figure 3b), there were only six defects (non-hexagons) out of 3162 hexagonal arrays (hexagons). The average percent of defects in hexagonal order over larger areas than the image of Figure 3a (0.6%) was similar to that of the micelles (0.5%), indicating that a near-perfect hexagonal order of micelles was maintained during the synthesis of the Au nanoparticles.

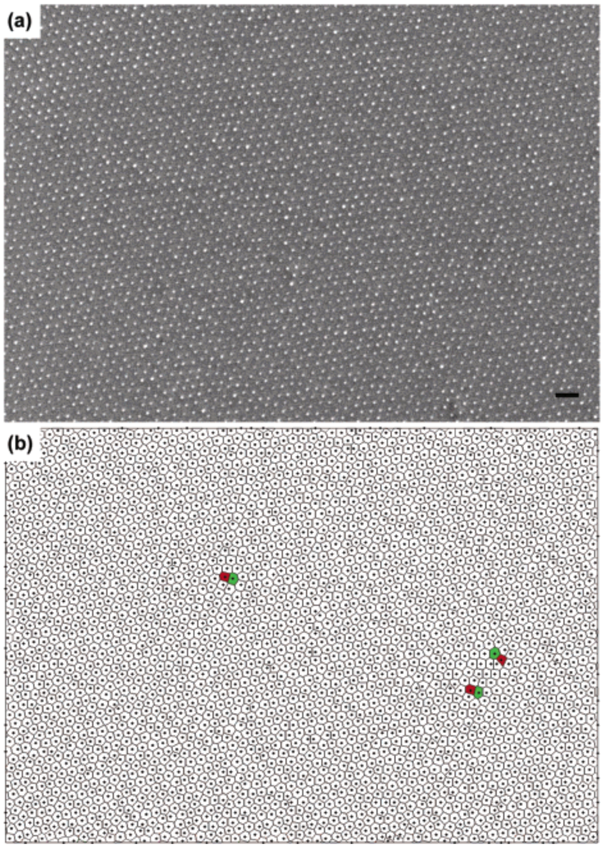

Figure 3. (a) FE-SEM image and (b) Voronoi diagram of a long-range hexagonal array of Au nanoparticles synthesized from a single-layered film of PS−P4VP micelles. The scale bar is 100 nm. In Voronoi diagram, Au nanoparticles having five and seven nearest neighbors are marked in red and green, respectively.

In conclusion, an array of PS−P4VP micelles in near-perfect hexagonal order over a large area was created by solvent annealing in situ on a single layer of micelles. The solvent annealing process healed defects in the self-assembly of micelles by allowing redistribution of copolymer chains between micelles on the solid substrate. Then, a highly ordered two-dimensional array of Au nanoparticles over an extended area was successfully synthesized from the hexagonal assembly of PS−P4VP micelles, which was not easily obtainable with colloidal solutions of nanoparticles. This well-ordered template of micelles essentially eliminates the current limitation of the approach of diblock copolymer micelles to create highly ordered arrays of nanoparticles and can be applied to various nanoparticles such as ZnO, Fe_2O_3, and TiO_2.

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Supporting Information Available: XPS data on an array of nanoparticLes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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