

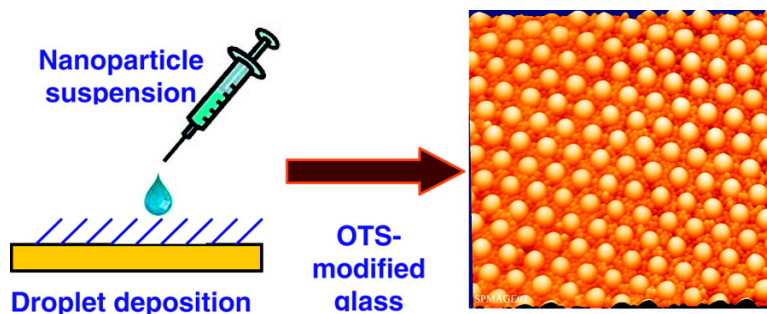
Communication

Ordering of Binary Polymeric Nanoparticles on Hydrophobic Surfaces Assembled from Low Volume Fraction Dispersions

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Ordering of Binary Polymeric Nanoparticles on Hydrophobic Surfaces Assembled from Low Volume Fraction Dispersions

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Nanoparticle (NP) dispersions have been shown to assemble into colloidal crystal arrangements,^{1,2} whose morphology can be tuned with appropriate choice of solution conditions.³ Such materials have great potential as photonic band gap devices,^{4,5} chemical sensors,⁶ data storage,⁷ and capillary columns for chromatography,⁸ to name a few. NPs have also been used to decorate surfaces for use in biological applications such as biosensors^{9,10} and tissue engineering,^{11,12} generated by either colloidal lithography or colloidal templating. Colloidal crystals can be formed on surfaces from monocomponent NP dispersions by gravity sedimentation,¹³ electrophoretic deposition,¹⁴ electrostatic induced self-assembly,¹⁵ magnetic fields,¹⁶ colloidal epitaxy,¹⁷ convective self-assembly,¹⁸ template-assisted self-assembly,¹⁹ spin-coating²⁰ and ink-jet printing.²¹ There are, however, only a few reports of surfaces decorated with crystals from two- or three-component particle systems.^{22–27} Surface patterns of polyelectrolyte templates^{22,23} and Au patterned with hydrophilic/hydrophobic chemistries²⁴ have been used for selective direct assembly of bicomponent NPs without ordering. Mixtures of micron- and nanometer-sized polystyrene (PS) and silica particles can form ordered patterns on hydrophilic glass by convective vertical deposition from particle mixtures in ethanol.²⁶ In addition, a similar method was used to deposit a template of large PS NPs followed by backfilling with small NPs.²⁷

Here we report on a new self-assembly method for generating hexagonally ordered colloidal crystal nanopatterns. Successful ordering requires use of a hydrophobic surface and works for both concentrated and dilute two-component NP suspensions in buffer over a wide pH range (4–10). The patterns are created from drop-casting suspensions of PS NPs of different size ($d = 520–60$ nm) NP ratio, size ratio, and volume fraction. Also, the NP surface chemistry (sulfated, carboxylated, or aminated) does not influence the pattern formation. Two types of hydrophobic surfaces are used, an adhesive carbon tape and octadecyltrichlorosilane (OTS)-modified glass. The two-component ordering was obtained over a range of $10 \times 10 \mu\text{m}$ near the rim of the dried droplets. The ordering is not observed on gold, hydrophilic glass, mica, and highly oriented pyrolytic graphite. The ordered areas were auto-fluorescent when viewed by fluorescent microscopy. In addition, we demonstrate the stability of these two-component patterns to different liquid media, such as ultrapure water (Milli-Q), McIlvaine and PBS buffers. In this case, crystals were generated by a mixture of small PS (70.8 ± 1.0 nm) and large PS NPs (368 ± 2.5 nm), where both were sulfated, having negative ζ potential values (-46.8 ± 1.4 and -83.3 ± 1.6 mV, respectively).

Figure 1A,B shows scanning electron microscopy (SEM) images of the colloidal crystal surface generated by self-assembly from a

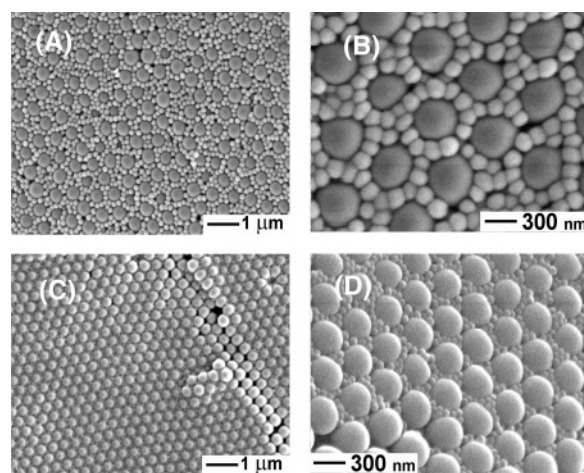


Figure 1. (A) SEM images of 519.8 ± 2.4 nm diameter sulfated PS and 152.1 ± 3.2 nm amino-functionalized PS NPs assembled on carbon tape. NP ratio was 1:200, pH 7. (B) Magnified image showing hexagonal arrangement of large NPs. (C) SEM image of 368 ± 2.5 nm sulfated PS and 59.5 ± 1.4 nm carboxylated PS NP assemblies (ratio 1:50, pH 7). (D) Magnified image of (C) showing hexagonal arrangement of large NPs.

suspension containing 519.8 ± 2.4 nm sulfated PS NPs and 152.1 ± 3.2 nm aminated PS NPs. The hexagonal arrangement of larger NPs with an interdispersed matrix of the smaller NPs is clearly visible. Figure 1C,D (magnified plot) shows similar hexagonal ordering with 368 ± 2.5 nm sulfated PS and 59.5 ± 1.4 nm carboxylated PS NPs. The volume fraction of each NP in this case was 0.0006 and 0.0001, respectively. This observation demonstrates that the surface chemistry of smaller NPs has no influence on the formation of ordered structures.

The role played by substrate chemistry on NP ordering is shown in Figure 2, which shows AFM images of a two-component surface pattern generated from dispersions of 368 ± 2.5 nm sulfated PS and 59.5 ± 1.4 nm carboxylated PS NPs deposited on hydrophobic (Figure 2A) and hydrophilic glass (cleaned by UV–ozone treatment, Figure 2B). Some hexagonal patterns appeared on the hydrophilic glass, but there is less ordering than observed on the OTS-modified glass, which shows patterns over a wide area. Table 1 summarizes the combination of experiments performed in which the hexagonal patterns are created. In a few cases, we attempted to form hexagonal assemblies under quite extreme conditions to challenge the process. At pH 2, the assembly is highly disordered, losing its ability to form hexagonal structures compared to experiments at pH 4, 7, and 10 (see Supporting Information). The most likely explanation

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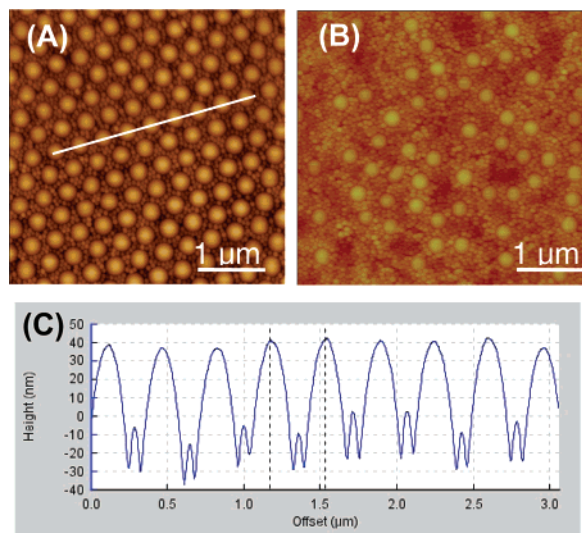


Figure 2. AFM images of NP assemblies. (A) Height image of 368 ± 2.5 nm sulfated PS and 59.5 ± 1.4 nm carboxylated PS NPs (ratio 1:50, pH = 4) on hydrophobic glass. (B) AFM image for deposition on unmodified (hydrophilic) glass. (C) AFM cross-section profile of (A) on hydrophobic glass showing a peak-to-peak distance of 351 nm.

Table 1. Two-Component NP Suspensions Used in This Study

NP combination	NP ratio	vol. fraction (φ)
368 ± 2.5 nm sulfated PS/ 60 nm aminated PS	1:50	0.0006/0.0001
497.1 ± 3.5 nm aminated PS/ 70.8 ± 1.0 nm sulfated PS	1:200	0.052/0.230
519.8 ± 2.4 nm sulfated PS/ 152.1 ± 3.2 nm aminated PS	1:200	0.0137/0.0026
368 ± 2.5 nm sulfated PS/ 59.5 ± 1.4 nm carboxylated PS	1:50	0.0006/0.0001
368 ± 2.5 nm sulfated PS/ 70.8 ± 1.0 nm sulfated PS	1:50	0.0006/0.0001

is aggregation at pH 2 of the smaller particles with lower ζ potentials in suspension prior to assembly. The pH experiments reveal that surface charge has no significant influence on the pattern formation within a certain pH range (4–10) and provided the particles remain in the fluid phase since the surface charge, and hence the ζ potential, changes with pH.²⁷

The results confirm that successful assembly is primarily influenced by the particle size and the substrate chemistry. The detailed mechanisms of formation of these patterns are presently unknown since the assembly takes place over a wide range of particle volume fractions and particle ratios. We observed hexagonal close-packed structural assemblies created from suspensions of very low volume fractions ($\varphi < 0.001$) where the suspension is known to be in the fluid phase, and well below the volume fraction ($\varphi > 0.5$) in which random hexagonally packed structures are known to form.²⁸ Below this volume fraction, similar structures have also been observed when fabricated by convective vertical deposition.²⁶ The mechanism of pattern formation could be entropy-driven, optimizing space, as predicted theoretically²⁹ and experimentally observed for binary inorganic assembly from organic solvents with stabilizing additives.³⁰ In addition, we suggest a capillary flow mechanism to be the cause of such pattern formation.³¹ On hydrophobic surfaces, the convex drop shape has a stronger

evaporating flux and drives the bigger NPs to the droplet perimeter, resulting in hierarchical self-assembly of NPs. Later smaller NPs fill the gap between bigger particles or form a ring around the bigger ones. The ionic strength increases as the solvent evaporates and surface double layers approach zero with drying. Particles of any charge can thus approach each other over time, and unique approach distances exist for each particle combination (large–large, small–small, and small–large) that are different compared to pure water. Thus particles assemble with respect to each other over several distinct scales of time and distance for each particle size during drying.

In summary, ordered binary patterns of NPs with hexagonal arrangements can be created by simple self-assembly on hydrophobic surfaces. The patterns were stable under a number of different liquid media. This allows manipulation of surface structure and chemistry at the nanoscale and provides ideal model systems for studying interfacial phenomena, such as protein adsorption/immobilization, cell/bacterial adhesion, and wetting phenomena for biosensor and medical materials applications.

Supporting Information Available: Additional experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) van Blaaderen, A.; Ruel, R.; Wiltzius, P. *Nature* **1997**, *385*, 321–324.
- (2) Larsen, A. E.; Grier, D. G. *Nature* **1997**, *385*, 230–233.
- (3) Yethiraj, A.; van Blaaderen, A. *Nature* **2003**, *421*, 513–517.
- (4) Tarhan, I. I.; Watson, G. H. *Phys. Rev. Lett.* **1996**, *76*, 315–318.
- (5) Braun, P. V.; Rinne, S. A.; Garcia-Santamaria, F. *Adv. Mater.* **2006**, *18*, 2665–2678 (review paper).
- (6) Holtz, J. H.; Asher, S. A. *Nature* **1997**, *389*, 829–832.
- (7) Gourevich, I.; Pham, H.; Jonkman, J. E. N.; Kumacheva, E. *Chem. Mater.* **2004**, *16*, 1472–1479.
- (8) Kamp, U.; Kitaev, V.; von Freymann, G.; Ozin, G. A.; Mabury, S. A. *Adv. Mater.* **2005**, *17*, 438–443.
- (9) Welsch, W.; Klein, C.; Von Schickfus, M.; Hunklinger, S. *Anal. Chem.* **1996**, *68*, 2000–2004.
- (10) Willner, I.; Katz, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 1180–1218.
- (11) Agheli, H.; Malmstrom, J.; Larsson, E. M.; Textor, M.; Sutherland, D. S. *Nano Lett.* **2006**, *6*, 1165–1171.
- (12) Bhatia, S. N.; Balis, U. J.; Yarmush, M. L.; Toner, M. *FASEB J.* **1999**, *14*, 1883–1900.
- (13) Deng, J. G.; Tao, X.; Li, P.; Zue, P.; Zhang, V.; Sun, X.; Kwan, K. C. *J. Colloid Interface Sci.* **2005**, *286*, 573–578.
- (14) Dziomkina, N. V.; Hempenius, M. A.; Vancso, J. G. *Adv. Mater.* **2005**, *17*, 237–240.
- (15) Cheng, Z.; Russell, W. B.; Chaikin, P. M. *Nature* **1999**, *401*, 893–895.
- (16) Golosovsky, M.; Saado, Y.; Davidov, D. *Appl. Phys. Lett.* **1999**, *75*, 4168–4170.
- (17) van Blaaderen, A.; Wiltzius, P. *Adv. Mater.* **1997**, *9*, 833–835.
- (18) Jiang, P.; Bertone, J. F.; Hwang, K. S.; Colvin, V. L. *Chem. Mater.* **1999**, *11*, 2132–2140s.
- (19) Yin, Y.; Lu, Y.; Gates, B.; Xia, Y. *J. Am. Chem. Soc.* **2001**, *123*, 8718–8729.
- (20) Mihi, A.; Ocana, M.; Miquez, H. *Adv. Mater.* **2006**, *18*, 2244–2249.
- (21) Park, J.; Moon, J.; Shin, V.; Wang, D.; Park, M. *J. Colloid Interface Sci.* **2006**, *298*, 713–719.
- (22) Zheng, H.; Lee, I.; Rubner, M. F.; Hammond, P. T. *Adv. Mater.* **2002**, *14*, 569–572.
- (23) Hua, F.; Shi, J.; Cui, T. *Nano Lett.* **2002**, *2*, 1219–1222.
- (24) Karakurt, I.; Leiderer, P.; Boneberg, J. *Langmuir* **2006**, *22*, 2415–2417.
- (25) Kiely, C. J.; Fink, J.; Brust, M.; Bethell, D.; Schiffrin, D. J. *Nature* **1998**, *396*, 444–446.
- (26) Kitaev, V.; Ozin, G. A. *Adv. Mater.* **2003**, *15*, 75–78.
- (27) Kim, M. H.; Im, S. H.; Park, O. O. *Adv. Mater.* **2005**, *17*, 2501–2505.
- (28) Bartlett, P.; Campbell, A. I. *Phys. Rev. Lett.* **2005**, *95*, 128302.
- (29) Eldridge, M. D.; Madden, P. A.; Frankel, D. *Nature* **1993**, *365*, 35–37.
- (30) Shevchenko, E. V.; Talapin, D. V.; Kotov, N. A.; O'Brien, S.; Murray, C. B. *Nature* **2006**, *439*, 55–59.
- (31) Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. *Nature* **1997**, *389*, 827–829.

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