J|A|C|S
COMMUNICATIONS

One-Dimensional Assembly of Silica Nanospheres Mediated by Block Copolymer in Liquid Phase

Masashi Fukao,[†] Ayae Sugawara,[†,‡] Atsushi Shimojima,[†] Wei Fan,[§]
Manickam Adhimoolam Arunagirinathan,[§] Michael Tsapatsis,[§] and Tatsuya Okubo*[,†]

Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, Center for NanoBio Integration, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, and Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

Received August 19, 2009; E-mail: okubo@chemsys.t.u-tokyo.ac.jp

Colloidal silica spheres and their assembly processes are encountered in nature and numerous technological applications.[1] The controlled organization of silica spheres into ordered arrays could enable uses in optical devices,[2] membrane and other separations,[3] templates for functional porous materials,[4] and functional fluids.[5] Two- or three-dimensional colloidal silica structures have been obtained by various techniques such as sedimentation,[3,6] simple drying,[4] and guided self-assembly.[2] In contrast, fabrication of one-dimensional (1D) arrays remains a challenge because of the fundamental difficulty in organizing isotropic particles into an anisotropic structure. 1D assembly of silica spheres was achieved in V-shaped grooves[2,7] or by electrospinning[8] only for particles over 300 nm in size, where the 'top-down' approach is applicable.

Some examples of 1D assembly of metal, semiconductor, and other nonsiliceous nanoparticles in liquid phases have been reported. They are mostly based on inherent anisotropy of magnetic[9] or electric dipoles,[10] crystal-face specific heterogeneity,[11] and nonuniform distribution of ligands on the surfaces.[12] Templating methods using linear biomacromolecules[13] and carbon nanotubes[14] are straightforward, but they usually need surface functionalization of nanoparticles and are unsuitable for obtaining uniform, closely arranged 1D assembly. Here, we report a novel approach to organize silica nanospheres (SNSs) one-dimensionally in a liquid phase with the aid of a commercially available amphiphilic block copolymer.

Uniform-sized SNSs ca. 15 nm in size are used in this study. They have been synthesized in the emulsion system containing tetraethoxysilane (TEOS), water, and L-lysine as a catalyst.[4a,b,15,16] This method gives monodispersed, colloidally stable SNSs in solution.[4a,b,15−17] Block copolymer Pluronic F127 is used to induce 1D assembly of SNSs in the suspension. F127 is a nonionic triblock copolymer consisting of poly(ethylene oxide) and poly(propylene oxide) (PEO-*b*-PPO-*b*-PEO) with an average molecular weight of 12 600 and 70 wt % PEO content. F127 exhibits amphiphilicity below the cloud point (>100 °C for 10% aqueous solution) and forms micelles or liquid crystals depending on temperature and the concentration.[18] F127 is known to adsorb on a silica surface through hydrogen bonding between the ether oxygens in PEO and the silanol groups.[19] For the preparation of 1D assemblies of SNSs, F127 was added to the above suspension and dissolved with stirring at 60 °C. The weight ratio of SiO_2 to F127 was 1:1. The pH of the suspension was lowered to 7.2−7.5 by using hydrochloric acid. The resultant suspension was incubated at 60 °C for several days without agitation.

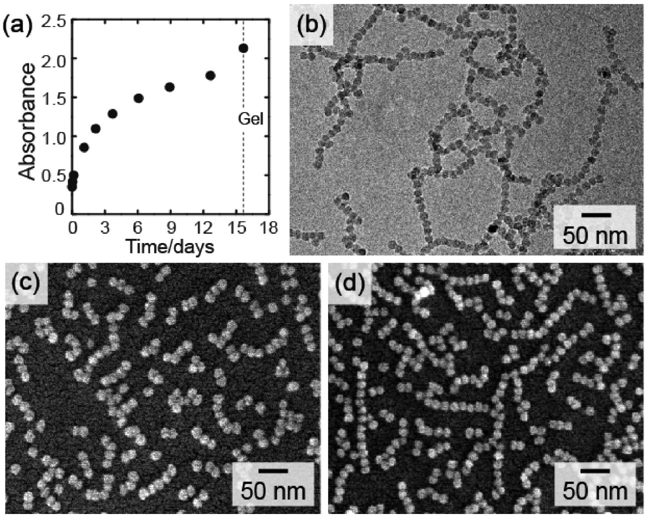

Figure 1. (a) Time-dependent turbidity profile of the SNSs suspension containing F127 (pH 7.5) measured by UV−vis spectroscopy. The absorbance increases across the entire wavelength range of 300 to 800 nm. The representative data at 350 nm are shown here. (b) Cryo-TEM image of the frozen-hydrated sample at pH 7.2, after 8 days of incubation. (c,d) SEM images of 1D chains of SNSs transferred to Si substrates. They were obtained at pH 7.5 after (c) 1 day and (d) 7 days of incubation, respectively. Before SEM observations, the samples on the substrates were irradiated with UV light (172 nm) under an air pressure of 50 Pa to remove organic components[20] and were sputter-coated with Pt.

Figure 1a shows the time-dependent turbidity profile of the suspension after adjusting the pH at 7.5, which was taken by using UV−visible spectroscopy at 350 nm. The turbidity gradually increases over 2 weeks, and the suspension eventually forms a weak gel. This indicates the slow aggregation of SNSs in a liquid phase. The cryogenic transmission electron microscopy (Cryo-TEM) has revealed the formation of 1D chain-like structure of SNSs in the suspension. The typical Cryo-TEM image of the frozen-hydrated sample after 8 days of incubation (pH 7.2) shows the presence of relatively straight 1D chains (Figure 1b and Supporting Information, Figure S1). Each SNS associates closely enough that no gaps are recognized between neighboring particles. The adhesion of particles is apparently strong enough that 1D chains can be transferred to substrates. Figure 1c and d are SEM images of 1D chains of SNSs that were dip-coated on Si substrates. The progress of particle connection is also evident from these images. Two to five SNSs are connected linearly after 1 day of incubation at 60 °C, pH 7.5 (Figure 1c), while longer chains are observed after 7 days of incubation (Figure 1d).

To examine the effect of F127 on particle assembly, SNSs were incubated with different amounts of F127 (SiO_2/F127 = 1:x (w/w), where x = 0−2.0). In the absence of F127, the suspension remains

---

[†] Department of Chemical System Engineering, The University of Tokyo.
[‡] Center for NanoBio Integration, The University of Tokyo.
[§] University of Minnesota.

10.1021/ja907013u CCC: $40.75

transparent for more than 2 weeks at 60 °C, pH 7.2, showing good colloidal stability of SNSs. In contrast, a small amount of F127 ($x = 0.1$) strongly facilitates particle connection; precipitates consisting of highly aggregated SNSs are generated right after the pH adjustment to 7.2 (Figure S2a). The increase in the concentration of F127 results in the formation of networked SNSs at $x = 0.5$ (Figure S2b) and more ordered 1D chains at $x = 0.8-2.0$. Malmsten et al. reported that silica nanoparticles of 15 nm in size aggregated in a dilute aqueous solution of F127,[19] but the formation of the anisotropic assembly has never been reported.

The mode of particle assembly is controlled systematically by changing the pH of the suspension. SNS colloids were mixed with F127 (SiO_2/F127 = 1:1 (w/w)) and incubated at 60 °C for 7 days at various pHs ranging from 8.0 to 6.0. SNSs remain dispersed in the suspension at pH 8.0, and only dispersed SNSs are observed when transferred to a substrate (Figure 2a). In contrast, 1D chains with relatively unbranched, straight structures are formed at pH 7.5 (Figure 1d). Longer, more bent chains with branches are observed at pH 7.0 (Figure 2b). Further lowering of pH to 6.0 gives a more disordered chain-like assembly with increased branching (Figure 2c). The tendency of random assembly at lower pH can be explained by the reduction of electrostatic repulsion between the particles. The decrease in pH increases the number of undissociated silanol groups on the silica surface[1] and consequently reduces the surface charge of SNSs (the zeta potentials of SNSs without F127 are −50.2, −44.2, −40.7, and −29.0 mV at pH 8.0, 7.5, 7.0, and 6.0, respectively). The undissociated silanols also facilitate the interaction of PEO and SNSs through hydrogen bonding,[19] which may affect the adsorption of F127 on silica. The effect of pH on the surface charge of F127 should be negligible since F127 is nonionic at the present pH range.

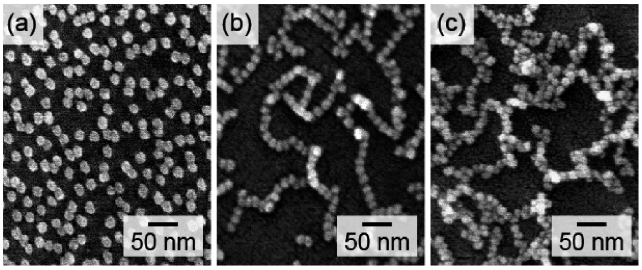

Figure 2. SEM images of SNSs transferred to Si substrate. They were formed in the presence of F127 at pH (a) 8.0, (b) 7.0, and (c) 6.0 after 7 days of incubation.

The balance between electrostatic repulsion and F127-mediated attractive interaction seems to be important for the 1D assembly of SNSs. Instead of adjusting the pH, 1D assembly has also been promoted by the addition of salt to the suspension, which is a common approach to reduce electrostatic repulsion between colloidal particles. SNSs are colloidally stable at 60 °C, pH 8.8 in the presence of F127 (SiO_2/F127 = 1:1 (w/w)). The addition of sodium chloride to the suspension results in the formation of 1D assembly of SNSs at the salt concentration of 0.08 to 0.12 M but induces random aggregation at 0.2 M (Figure S3).

The incubation temperature is also an important parameter. The particle assembly is promoted at higher temperatures, while it is retarded at lower temperatures. More straight 1D chains are formed at lower temperatures (Figure S4).

The origin of the formation of anisotropic particle assembly is unclear at present. Taton et al. reported that Au nanoparticles surrounded by the layer of cross-linked poly(stylene-*block*-acrylic acid) formed 1D chains in the liquid phase.[21] In this case, the formation of 1D chains was induced by the transition from spherical to wormlike micelles of the block copolymer, which also occurred in the absence of Au nanoparticles. However, in our system, only F127 aggregates with an average size of 30 nm can be detected by dynamic light scattering (Figure S5). This size is comparable to that of the typical spherical micelles of F127 reported by others.[22] It appears that a synergistic effect of F127 and silica nanoparticles is contributing to the 1D assembly.

In conclusion, we have demonstrated a facile method to prepare a 1D chain-like structure of silica nanospheres by using an amphiphilic block copolymer. The anisotropy of chain-like assembly can be fine-tuned using various handles like pH, ionic strength, and temperature. This work may lead to new applications for silica colloids and may provide useful ideas for the design of other functional materials. Systematic investigation on the role of polymer additives is now under progress.

Acknowledgment. We thank Prof. Yukio Yamaguchi (The University of Tokyo) for zeta potential and dynamic light scattering measurements. We also gratefully acknowledge support from the National Science Foundation (CMMI-0707610). Cryo-TEM characterization was carried out at the Minnesota Characterization Facility which receives support from the NSF through the National Nanotechnology Infrastructure Network.

Supporting Information Available: Detailed experimental procedures and Figures S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Iler, R. K. *The Chemistry of Silica*; John Wiley & Sons: NY, 1979. (b) Bergna, H. E.; Roberts, W. O. *Colloidal Silica: Fundamentals and Applications*; CRC Taylor & Francis: Boca Raton, FL, 2006.
(2) Ozin, G. A.; Yang, S. M. *Adv. Funct. Mater.* **2001**, *11*, 95.
(3) Gong, M.; Bohn, P. W.; Sweedler, J. V. *Anal. Chem.* **2009**, *81*, 2022.
(4) (a) Yokoi, T.; Sakamoto, Y.; Terasaki, O.; Kubota, Y.; Okubo, T.; Tatsumi, T. *J. Am. Chem. Soc.* **2006**, *128*, 13664. (b) Davis, T. M.; Snyder, M. A.; Krohn, J. E.; Tsapatsis, M. *Chem. Mater.* **2006**, *18*, 5814. (c) Stein, A.; Schroden, R. C. *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 553.
(5) Saito, Y.; Ogura, H.; Otsubo, Y. *Colloid Polym. Sci.* **2008**, *286*, 1537.
(6) Holgado, M.; García-Santamaría, F.; Blanco, A.; Ibisate, M.; Cintas, A.; Míguez, H.; Serna, C. J.; Molpeceres, C.; Requena, J.; Mifsud, A.; Meseguer, F.; López, C. *Langmuir* **1999**, *15*, 4701.
(7) Yin, Y.; Xia, Y. *J. Am. Chem. Soc.* **2003**, *125*, 2048.
(8) Lim, J.-M.; Moon, J. H.; Yi, G.-R.; Heo, C.-J.; Yang, S.-M. *Langmuir* **2006**, *22*, 3445.
(9) (a) Zhang, F.; Wang, C.-C. *J. Phys. Chem. C* **2008**, *112*, 15151. (b) Cheng, G.; Romero, D.; Fraser, G. T.; Hight Walker, A. R. *Langmuir* **2005**, *21*, 12055.
(10) Tang, Z.; Kotov, N. A.; Giersig, M. *Science* **2002**, *297*, 237.
(11) Banfield, J. F.; Welch, S. A.; Zhang, H.; Ebert, T. T.; Penn, R. L. *Science* **2000**, *289*, 751.
(12) (a) DeVries, G. A.; Brunnbauer, M.; Hu, Y.; Jackson, A. M.; Long, B.; Neltner, B. T.; Uzun, O.; Wunsch, B. H.; Stellacci, F. *Science* **2007**, *315*, 358. (b) Lin, S.; Li, M.; Dujardin, E.; Girard, C.; Mann, S. *Adv. Mater.* **2005**, *17*, 2553.
(13) Ofir, Y.; Samanta, B.; Rotello, V. M. *Chem. Soc. Rev.* **2008**, *37*, 1814.
(14) Wildgoose, G. G.; Banks, C. E.; Compton, R. G. *Small* **2006**, *2*, 182.
(15) Yokoi, T.; Wakabayashi, J.; Otsuka, Y.; Fan, W.; Iwama, M.; Watanabe, R.; Aramaki, K.; Shimojima, A.; Tatsumi, T.; Okubo, T. *Chem. Mater.* **2009**, *21*, 3719.
(16) (a) Yokoi, T.; Iwama, M.; Watanabe, R.; Sakamoto, Y.; Terasaki, O.; Kubota, Y.; Kondo, J. N.; Okubo, T.; Tatsumi, T. *Stud. Surf. Sci. Catal.* **2007**, *170B*, 1774. (b) Fan, W.; Snyder, M. A.; Kumar, S.; Lee, P.-S.; Yoo, W. C.; McCormick, A. V.; Penn, R. L.; Stein, A.; Tsapatsis, M. *Nat. Mater.* **2008**, *7*, 984. (c) Snyder, M. A.; Lee, J. A.; Davis, T. M.; Scriven, L. E.; Tsapatsis, M. *Langmuir* **2007**, *23*, 9924.
(17) Hartlen, K. D.; Athanasopoulos, A. P. T.; Kitaev, V. *Langmuir* **2008**, *24*, 1714.
(18) Ivanova, R.; Lindman, B.; Alexandridis, P. *Langmuir* **2000**, *16*, 9058.
(19) Malmsten, M.; Linse, P.; Cosgrove, T. *Macromolecules* **1992**, *25*, 2474.
(20) Hozumi, A.; Yokogawa, Y.; Kameyama, T.; Hiraku, K.; Sugimura, H.; Takai, O.; Okido, M. *Adv. Mater.* **2000**, *12*, 985.
(21) Kang, Y.; Erickson, K. J.; Taton, T. A. *J. Am. Chem. Soc.* **2005**, *127*, 13800.
(22) (a) Malmsten, M.; Lindman, B. *Macromolecules* **1992**, *25*, 5440. (b) Desai, P. R.; Jain, N. J.; Sharma, R. K.; Bahadur, P. *Colloids Surf., A* **2001**, *178*, 57.

JA907013U