

sponse analyzer (EG&G, Model 1025). The complex impedance plots of the samples were recorded in the frequency range from 1 to  $10^5$  Hz. The cationic transference numbers,  $t_+$ , were determined by the steady-state current technique proposed by Bruce and Vincent [28]. The details are given by Reiche et al [29]. Ni was used as a working electrode ( $A=0.5$  cm<sup>2</sup>) and Li as counter and reference electrode for cyclic voltammetry.

**Solid-State NMR:** One-dimensional <sup>7</sup>Li static, <sup>27</sup>Al magic-angle spinning, and <sup>1</sup>H/<sup>29</sup>Si cross-polarization magic-angle spinning experiments were performed on a Bruker ASX500 spectrometer. The <sup>27</sup>Al spectra were recorded using a spinning speed of 8–14 kHz and a small tip angle. The spinning speed for the <sup>1</sup>H/<sup>29</sup>Si cross-polarization magic-angle spinning experiments was 4–5 kHz, and the cross-polarization contact time was 2 ms. The <sup>1</sup>H/<sup>13</sup>C WISE experiments were carried out on a Bruker MSL300 spectrometer with a cross-polarization contact time of 200 μs.

Received: February 24, 2002  
Final version: June 17, 2002

## Monodisperse Micrometer-Scale Spherical Assemblies of Polymer Particles\*\*

By Gi-Ra Yi, Vinothan N. Manoharan, Sascha Klein, Krystyna R. Brzezinska, David J. Pine,\* Frederick F. Lange,\* and Seung-Man Yang

Three-dimensional (3D) assemblies of submicrometer monodisperse colloids have received much attention recently, primarily because of their potential uses as photonic crystals.<sup>[1,2]</sup> Face-centered cubic colloidal crystals, formed spontaneously in monodisperse spherical colloids such as polymer latexes or silica suspensions, are the simplest examples of such assemblies. More complex structures can be made by a variety of clever techniques, such as altering the shape of the colloidal particles,<sup>[3–6]</sup> directing their assembly with patterned surfaces,<sup>[7,8]</sup> or tuning the interactions between particles.<sup>[9–11]</sup> Here we show how to fabricate spherical assemblies of polymer colloids, or “supraballs”, that are essentially colloidal aggregates of controlled shape and size. Although similar spherical assemblies have been prepared,<sup>[12–14]</sup> the preparation of *small* (micrometer scale) and *monodisperse* aggregates is a new development. These aggregates may serve as building blocks for more complex colloidal assemblies, including, perhaps, new types of photonic crystals. More importantly, these supraballs may be used to develop highly efficient scatterers that could be used as light diffusers in a wide variety of applications.

Our supraballs are micrometer-sized 3D colloidal assemblies with narrow size distribution and an ordered internal structure consisting of monodisperse latex particles. They are prepared by generating a monodisperse water-in-oil emulsion using a droplet break-off technique developed by Umbanhowar et al.,<sup>[15]</sup> where the water (droplet) phase of our emulsions contains polymer particles. We produce uniform spherical colloidal assemblies by slowly removing the water from the droplets. As shown in Figure 1, an aqueous monodisperse latex suspension is injected into an ambient fluid through a tapered

- [1] C. A. Vincent, B. Scrosati, *Modern Batteries. An Introduction to Electrochemical Power Sources*, 2nd ed., Arnold, London **1997**.
- [2] B. Scrosati, *Nature* **1995**, 373, 557.
- [3] K. M. Abraham, M. Alamgir, *Solid State Ionics* **1994**, 70/71, 20.
- [4] W. Meyer, *Adv. Mater.* **1998**, 10, 439.
- [5] F. Croce, G. B. Appetecchi, L. Persi, B. Scrosati, *Nature* **1998**, 394, 456.
- [6] E. P. Giannelis, *Adv. Mater.* **1996**, 8, 29.
- [7] F. Croce, B. Scrosati, *Polym. Adv. Technol.* **1993**, 4, 198.
- [8] R. Ulrich, J. W. Zwanziger, S. M. De Paul, R. Richert, U. Wiesner, H. W. Spiess, in *Abstract Paper 217*, American Chemical Society, Washington, DC **1999**, p. 377.
- [9] R. Ulrich, *Morphologien und Eigenschaften Strukturierter Organisch-Anorganischer Hybridmaterialien*, Logos-Verlag, Berlin **2000**.
- [10] L. M. Bronstein, C. Joo, R. Karlinsey, A. Ryder, J. W. Zwanziger, *Chem. Mater.* **2001**, 13, 3678.
- [11] P. P. Soo, B. Y. Huang, Y. I. Jang, Y. M. Chiang, D. R. Sadoway, A. M. Mayes, *J. Electrochem. Soc.* **1999**, 146, 32.
- [12] M. Templin, U. Wiesner, H. W. Spiess, *Adv. Mater.* **1997**, 9, 814.
- [13] M. Templin, A. Franck, A. Du Chesne, H. Leist, Y. Zhang, R. Ulrich, V. Schädler, U. Wiesner, *Science* **1997**, 278, 1795.
- [14] R. Ulrich, A. Du Chesne, M. Templin, U. Wiesner, *Adv. Mater.* **1999**, 11, 141.
- [15] D. F. Shriver, P. G. Bruce, in *Solid State Electrochemistry* (Ed: P. G. Bruce), Cambridge University Press, Cambridge, UK **1997**.
- [16] P. Lightfoot, M. A. Mehta, P. G. Bruce, *Science* **1993**, 262, 883.
- [17] E. Quartarone, P. Mustarelli, A. Magistris, *Solid State Ionics* **1998**, 110, 1.
- [18] J. P. Lemmon, J. Wu, C. Oriakhi, M. M. Lerner, *Electrochim. Acta* **1995**, 40, 2245.
- [19] J. C. Hutchison, R. Bissessur, D. F. Shriver, *Chem. Mater.* **1996**, 8, 1597.
- [20] G. C. Rawsky, T. Fujinami, D. F. Shriver, *Chem. Mater.* **1994**, 6, 2208.
- [21] T. Fujinami, A. Tokimune, M. A. Mehta, D. F. Shriver, G. C. Rawsky, *Chem. Mater.* **1997**, 9, 2236.
- [22] S. M. De Paul, J. W. Zwanziger, R. Ulrich, U. Wiesner, H. W. Spiess, *J. Am. Chem. Soc.* **1999**, 121, 5727.
- [23] P. F. W. Simon, R. Ulrich, H. W. Spiess, U. Wiesner, *Chem. Mater.* **2001**, 13, 3464.
- [24] M. Popall, X.-M. Du, *Electrochim. Acta* **1995**, 40, 2305.
- [25] M.-H. Lee, S. T. Ko, K. S. Lee, S. B. Rhee, *Mol. Cryst. Liq. Cryst.* **1997**, 294, 229.
- [26] G. B. Appetecchi, F. Croce, L. Persi, B. Scrosati, *Electrochim. Acta* **2000**, 45, 1481.
- [27] J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed., John Wiley & Sons Inc., New York **1980**.
- [28] a) P. G. Bruce, C. A. Vincent, *J. Electroanal. Chem.* **1987**, 225, 1. b) P. G. Bruce, M. T. Hardgrave, C. A. Vincent, *J. Electroanal. Chem.* **1989**, 271, 27.
- [29] A. Reiche, J. Tubke, R. Sandner, A. Werther, B. Sandner, G. Fleischer, *Electrochim. Acta* **1998**, 43, 1429.
- [30] K. Schmidt-Rohr, H. W. Spiess, *Multidimensional Solid-State NMR and Polymers*, Academic Press Ltd., London **1994**.
- [31] a) A. C. Finnefrock, R. Ulrich, A. Du Chesne, C. C. Honeker, K. Schumacher, K. K. Unger, S. M. Gruner, U. Wiesner, *Angew. Chem. Int. Ed.* **2001**, 40, 1208; b) *Angew. Chem.* **2001**, 113, 1248.

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[\*\*] This work was supported by NSF Grant No. CTS9871970 and Brain Korea 21 program. SMY was supported by a grant from the “Support for Faculty Abroad” program of Korea Research Foundation.

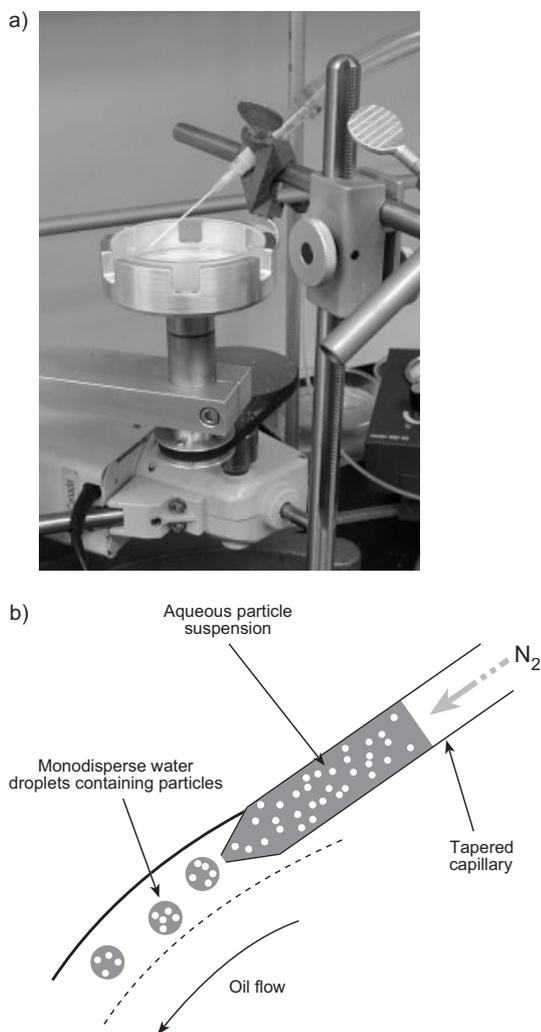


Fig. 1. Experimental setup (a) and schematic diagram (b) for monodisperse suspension emulsion generation.

capillary tube (a micropipette) with inner diameter of 10  $\mu\text{m}$  or 5  $\mu\text{m}$ . Submicrometer polystyrene spheres with hydrophilic surfaces (as prepared by polymerization of styrene with hydrophilic co-monomers) are used as the aqueous latex suspension.

To test our apparatus, we first produced monodisperse water-in-oil emulsions (Fig. 2) by injecting 0.1 M NaCl (used to prevent fast destabilization<sup>[16]</sup>) into mineral oil, using constant gas pressure at the capillary and constant angular velocity for the cup containing the oil. Other groups have already investigated the size, distribution, and shape of droplets detaching from a tip immersed in a co-flowing stream.<sup>[17,18]</sup> When the flow rate in the capillary is low, a force balance between the interfacial tension and the drag force on the droplet at the end of the tip results in a droplet diameter  $d_d$  given by

$$d_d = d_{ti} \left( 1 + \frac{\gamma}{3u\eta_c} \right) \quad (1)$$

where  $d_{ti}$  is the inner diameter of the capillary tip,  $\gamma$  the interfacial tension between the water and oil,  $\eta_c$  the viscosity of

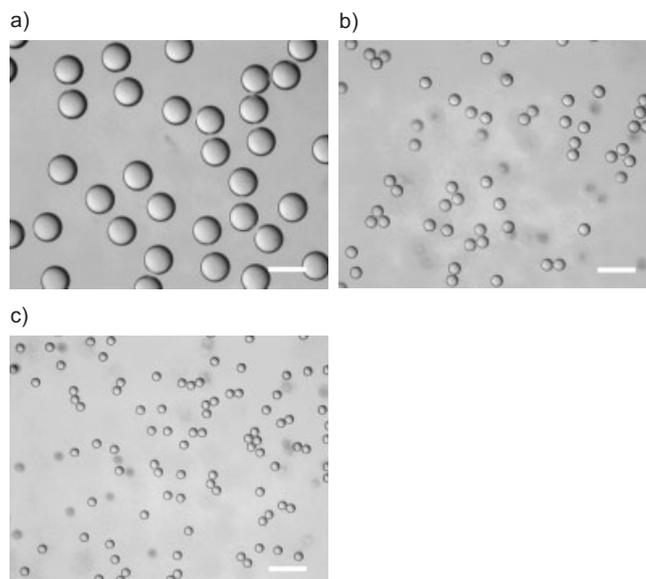
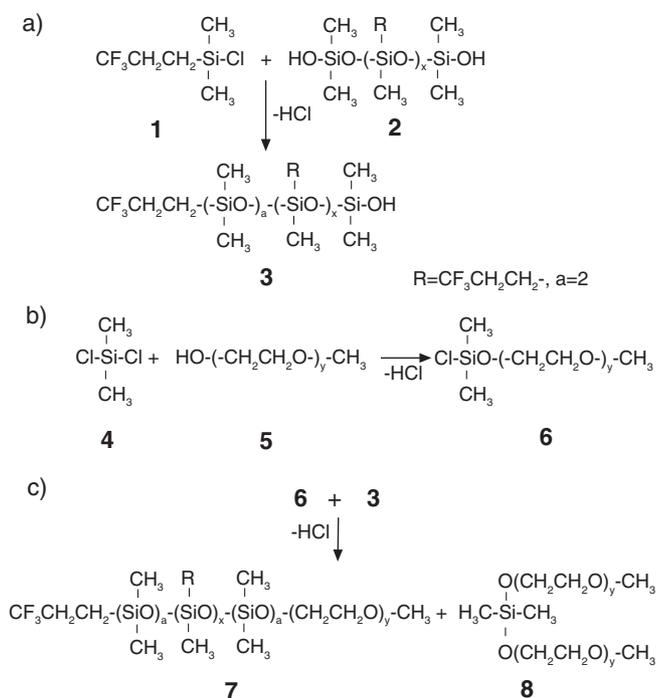


Fig. 2. Optical micrographs (Nomarski differential interference contrast method) of monodisperse water-in-mineral oil emulsions (2% w/w Span 80) that were generated under the following conditions: a) rotational speed  $u = 22 \text{ cm s}^{-1}$ , tip inner diameter  $d_{ti} = 10 \text{ }\mu\text{m}$ , gas pressure  $P = 1.5 \text{ psig}$ ; b)  $u = 55 \text{ cm s}^{-1}$ ,  $d_{ti} = 10 \text{ }\mu\text{m}$ ,  $P = 1.5 \text{ psig}$ ; c)  $u = 55 \text{ cm s}^{-1}$ ,  $d_{ti} = 5 \text{ }\mu\text{m}$ ,  $P = 2.5 \text{ psig}$  (Scale bars are 100  $\mu\text{m}$ ).

the continuous phase, and  $u$  the velocity of the continuous phase.<sup>[15]</sup> According to this simple model, for a given pair of fluids we can control the drop size by changing either the tip diameter or the velocity  $u$ , which we control by changing the angular velocity of the cup. As shown in Figures 2a and b, the diameter of the water droplets changes from 70  $\mu\text{m}$  to 28  $\mu\text{m}$  when we increase the co-flowing velocity from 22  $\text{cm s}^{-1}$  to 55  $\text{cm s}^{-1}$ , using a 10  $\mu\text{m}$  tip diameter and 1.5 psig nitrogen in both cases. On the other hand, changing the tip diameter of the micropipette to 5  $\mu\text{m}$  yields emulsions of 21  $\mu\text{m}$  diameter (Fig. 2c). In each of these emulsions, which are stabilized with the surfactant Span 80 (2.0% w/w in oil), the droplets are monodisperse; no larger droplets, as might be formed by coalescence, or smaller satellite droplets, as might be produced during the break-off, are observed. At a low ratio  $\lambda$  of droplet viscosity to continuous phase viscosity (in our experiments,  $\lambda = \eta_d/\eta_c = 0.005$ ), Stone and Zhang have shown that there is no detectable thread between the detaching drop and the remaining pendant drop, which means no satellite drops are expected.<sup>[18]</sup>

To prepare the monodisperse suspension emulsion, we injected a 1.1% w/w aqueous latex into mineral oil containing 2.0% Span 80. Although we were able to obtain monodisperse emulsions, after several hours we observed that the particles had escaped the droplets. The instability may be due to surfactant diffusing into the droplets and adsorbing onto the polymer spheres, rendering them hydrophobic. In a destabilization mechanism similar to that seen in multiple emulsions, the particles then tend to migrate into the oil phase.<sup>[19,20]</sup> Such a mechanism is consistent with the observation that at a higher surfactant concentration (5.0% Span 80), the destabilization time decreased to about one hour.

As the instability must be a result of the particle–liquid interfacial tension being lower in the oil phase than in the water, there are two approaches to remedy the problem: the first is to increase the hydrophilicity of the polymer particles by increasing the amount of hydrophilic co-monomer, while the second is to increase the polymer–oil interfacial tension. Since we are unsure about the mechanism of surfactant adsorbing onto the particles, we choose the second approach here. Instead of mineral oil, we use fluorinated silicone oil (FSO) as the continuous phase. FSO has the high viscosity that is required for generating monodisperse emulsions using the droplet break-off technique, but does not wet the particles. However, typical surfactants used to stabilize water-in-oil emulsions are not effective in FSO, so we prepared a custom surfactant as stabilizing agent for the water-in-FSO emulsion. This is a diblock copolymer of fluorinated silicone and polyethylene glycol, synthesized as described in Scheme 1. As we shall demonstrate, this suspension/surfactant/oil system does not display the type of instability observed previously.



Scheme 1. Strategy for synthesizing the block copolymer of fluorinated silicone and ethylene oxide. This copolymer is used as a stabilizer for water-in-FSO emulsions.

Figure 3a shows the monodisperse aqueous suspension emulsion containing 450 nm diameter poly(styrene/acrylamide) particles at 1.1 % w/w. It was produced using a 5 μm micropipette at a constant rotational speed of 55 cm s<sup>-1</sup> and 2.5 psig. Initially, the mean diameter was about 27 μm, and the particles inside the droplet moved around randomly due to Brownian forces (see Fig. 3b). However, as water was removed into the continuous phase (water is slightly soluble in FSO), the droplets shrank until, after 12 h, we obtained a 7 μm diameter consolidated colloidal assembly (see Fig. 3c).

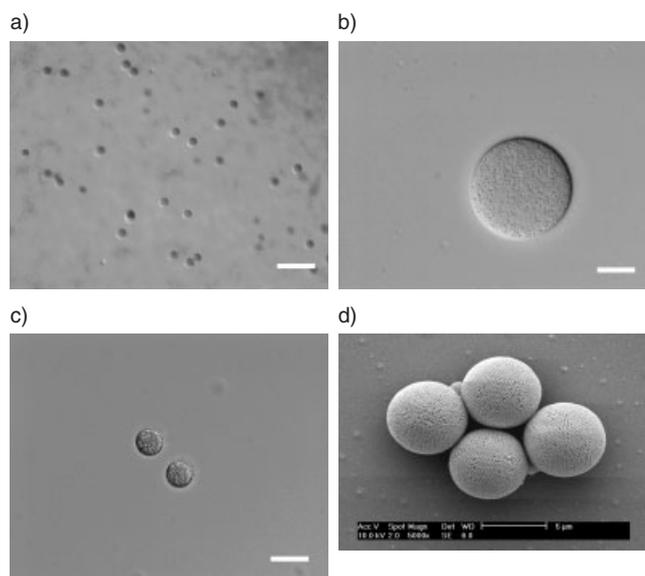


Fig. 3. Optical micrographs of monodisperse poly(styrene/acrylamide)-in-water-in-FSO emulsion a) at low and b) high magnification (generation conditions: 1.1 % w/w suspension,  $d_{ii} = 5 \mu\text{m}$ ,  $u = 55 \text{ cm s}^{-1}$ ,  $P = 2.5 \text{ psig}$ ). c) spherical colloidal assemblies after consolidation from suspension droplets in (a,b). d) Scanning electron micrograph of colloidal assemblies obtained from a 2.0 % w/w suspension of 230 nm poly(styrene/styrene sulfonate) particles ( $d_{ii} = 10 \mu\text{m}$ ,  $u = 53 \text{ cm s}^{-1}$ ,  $P = 1.0 \text{ psig}$ ), after removal of FSO by washing with hexanes. Scale bars are 100 μm (a), 10 μm (b,c), and 5 μm (d).

We can control the size of the assemblies by changing the generation conditions, the suspension concentration, or particle diameter. Figure 3d shows well-ordered 6.3 μm supraballs made from 230 nm poly(styrene/styrene sulfonate) particles.

If the number of particles within each droplet is conserved, we can predict the final volume fraction of particles inside the supraball ( $f_v$ ):

$$f_v = \left(\frac{d_i}{d_s}\right)^3 \phi_v \quad (2)$$

where  $d_s$  is the final diameter,  $d_i$  is the initial suspension diameter, and  $\phi_v$  the initial volume fraction of particles in suspension. For the consolidated assembly in Figure 3d, we estimate a volume fraction ( $f_v$ ) near the close-packing limit (0.74), although the uncertainty (15 %) in this estimate is large. We therefore expect the presence of some cubic close-packed crystallites within the droplets. The supraball in Figure 3d contains several thousand particles, as determined by:

$$N_s = f_v \left(\frac{d_s}{d_p}\right)^3 \quad (3)$$

where  $d_p$  is the diameter of a polymer particle.

In summary, we have produced uniform spherical colloidal assemblies by removing water from monodisperse suspension emulsions, which were generated by introducing an aqueous particle suspension into a co-flowing, surfactant-laden continuous phase via a tapered capillary. A new block copolymer of fluorinated silicone and polyethylene glycol was synthesized for stabilizing water-in-FSO emulsions. Our present approach may find uses in photonic crystals or, if extended to a smaller

scale, in electronic paper.<sup>[12,21]</sup> For photonic materials, it may be interesting to introduce nanoparticles or reactive sols into the interstices between latex particles.<sup>[22]</sup>

### Experimental

**Synthesis of Latex Suspension:** Polystyrene particles with hydrophilic surfaces were synthesized by emulsifier-free emulsion polymerization of styrene with hydrophilic co-monomers according to the literature [23]. Poly(styrene/acrylamide) particles have a mean diameter of 450 nm, as measured using a dynamic light scattering system (Brookhaven Instruments Inc.), while poly(styrene/styrene sulfonate) particles have a mean diameter of 235 nm. Both latexes had polydispersities of 5% or less. Co-monomers were used to make the surfaces of the particles hydrophilic, which we found necessary to avoid clogging the micropipette tips.

**Emulsion Generator:** A 7 cm diameter transparent plastic cup with surfactant-laden oil phase was rotated at constant speed. When constant angular velocity of the cup was achieved and surface fluctuations disappeared, the end of a micropipette (World Precision Instrument,  $\mu$ -Tip) was immersed in the continuous oil phase. Monodisperse emulsions were generated by pressure-driven flow through in the immersed tip. For suspension emulsions, particle aggregates or dust, which can cause clogging, were removed by filtering the suspension with a 0.8  $\mu$ m membrane. Mineral oil (heavy) and Fluorinated Silicone oil (FMS-123) were purchased from Fisher Scientific and Gelest, respectively. Their viscosities were measured with an ARES rheometer (Rheometric Scientific).

**Synthesis of Block Copolymer:** The diblock copolymer of fluorinated silicone and ethylene oxide that was used as the stabilizer for the inverse emulsion was synthesized according to the procedure in Scheme 1. Two different reaction mixtures (1a and 1b) were prepared in Schlenk flasks under nitrogen. Scheme 1a: (3,3,3-trifluoropropyl) dimethylchlorosilane (**1**) (1.9 g, 10 mmol) was added to a solution of silanol terminated polymethyl-3,3,3-trifluoropropylsiloxane (**2**) ( $M_n = 2300$ , 22.8 g, 10 mmol) in 50 mL of dry THF. Scheme 1b: dichlorodimethylsilane (**4**) (1.29 g, 10 mmol) was added to a solution of poly(ethylene glycol) methyl ether (**5**) ( $M_n = 350$ , 3.5 g, 10 mmol) in 10 mL of dry THF. These reactions were stirred at 25 °C under reduced pressure (100 mm Hg), during which HCl gas was evolved. After 24 h the reaction mixture (Scheme 1b) was transferred under nitrogen to the reaction mixture (Scheme 1a) giving product (**7**) (see Scheme 1c). Stirring was continued for 24 h at 25 °C. The solvent was removed under reduced pressure. We obtained a mixture of block copolymer (**7**) and byproduct (**8**). This byproduct (**8**) was easily removed by phase separation giving (**7**) (23 g, 80%). The following spectral properties were observed: <sup>1</sup>H NMR:  $\delta$  [ppm] 3.66 ( $CH_2CH_2-O$ , 4H), 3.49 ( $OCH_3$ , 3H), 2.04 ( $Si-CH_2CH_2CF_3$ ), 0.78 ( $SiCH_2CH_2CF_3$ , 2H), 0.11 ( $CF_3CH_2CH_2-Si-CH_3$ , 3H), 0.07 ( $Si(CH_3)_2$ , 6H).

**Materials:** (3,3,3-Tripropyl)dimethylchlorosilane (Gelest Co.) (**1**), silanol terminated polymethyl-3,3,3-trifluoropropylsiloxane (**2**) (United Chemical Co.,  $M_n = 2300$ ), dimethyldichlorosilane (**4**) (Gelest Co.), and poly(ethylene glycol) methyl ether (**5**) (Aldrich,  $M_n = 350$ ) were used under nitrogen without purification. THF was purified by first purging with dry nitrogen, followed by passage through columns of activated alumina [24].

**Instrumentation:** NMR spectra were measured on Bruker AVANCE 200 MHz spectrometer using chloroform-*d* as solvent.

Received: April 9, 2002  
Final version: May 19, 2002

- [1] A. D. Dinsmore, J. C. Crocker, A. G. Yodh, *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 5.
- [2] O. D. Velev, E. W. Kaler, *Adv. Mater.* **2000**, *12*, 531.
- [3] E. Snoeks, A. van Blaaderen, T. van Dillen, C. M. van Kata, M. L. Bronersma, A. Polman, *Adv. Mater.* **2000**, *12*, 1511.
- [4] Y. Lu, Y. Yin, Y. Xia, *Adv. Mater.* **2000**, *12*, 415.
- [5] P. Jiang, J. F. Bertone, V. L. Colvin, *Science* **2001**, *291*, 453.
- [6] Z. Zhong, Y. Yin, B. Gates, Y. Xia, *Adv. Mater.* **2000**, *12*, 206.
- [7] Y. Yin, Y. Lu, Y. Xia, *J. Am. Chem. Soc.* **2001**, *123*, 771.
- [8] Y. Yin, Y. Xia, *Adv. Mater.* **2001**, *13*, 267.
- [9] M. S. Fleming, T. K. Mandal, D. R. Walt, *Chem. Mater.* **2001**, *13*, 2210.
- [10] A. L. Hiddessen, S. D. Rodgers, D. A. Weitz, D. A. Hammer, *Langmuir* **2000**, *16*, 9744.
- [11] K. Furusawa, O. D. Velev, *Colloids Surf. A* **1999**, *159*, 359.
- [12] O. D. Velev, A. M. Lenhoff, E. W. Kaler, *Science* **2000**, *287*, 2240.
- [13] G.-R. Yi, J. H. Moon, S.-M. Yang, *Adv. Mater.* **2001**, *13*, 1185.
- [14] O. D. Velev, K. Nagayama, *Langmuir* **1997**, *13*, 1856.
- [15] P. B. Umbanhowar, V. Prasad, D. A. Weitz, *Langmuir* **2000**, *16*, 347.
- [16] M. P. Aronson, M. F. Petko, *J. Colloids Interface Sci.* **1993**, *159*, 134.

- [17] R. Clift, J. R. Grace, M. E. Weber, *Bubbles, Drops, and Particles*, Academic Press, New York **1978**.
- [18] D. F. Zhang, H. A. Stone, *Phys. Fluids* **1997**, *9*, 2234.
- [19] C. Laugel, P. Rafidison, G. Potard, L. Agudisch, A. Baillet, *J. Controlled Release* **2000**, *63*, 7.
- [20] M. F. Ficheux, L. Bonakdar, F. Leal-Calderon, J. Bibette, *Langmuir* **1998**, *14*, 2702.
- [21] T. Thorsen, R. W. Roberts, F. H. Arnold, S. R. Quake, *Phys. Rev. Lett.* **2001**, *86*, 4163.
- [22] F. Iskandar, Mikrajuddin, K. Okuyama, *Nano Lett.* **2001**, *1*, 231.
- [23] H. Tamai, A. Fujii, T. Suzawa, *J. Colloids Interface Sci.* **1987**, *116*, 37.
- [24] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. Timmers, *J. Organomet.* **1996**, *15*, 1518.

## Controlled Fabrication of Large-Scale Aligned Carbon Nanofiber/Nanotube Patterns by Photolithography

By Shaoming Huang,\* Liming Dai, and Albert W. H. Mau

Synthesizing aligned carbon nanotubes and patterning aligned/non-aligned carbon nanotubes has attracted much attention in recent years because of their paramount importance in many of the applications of these materials, e.g., flat panel displays, nanoelectronics, and sensors.<sup>[1]</sup> Aligned carbon nanotubes can be generated by postsynthesis fabrication,<sup>[2]</sup> by pyrolysis of hydrocarbons or other compounds over pre-deposited catalysts on substrates, e.g., the pyrolysis of 2-amino-4,6-dichloro-*s*-triazine over prepatterned Co catalyst on silica<sup>[3]</sup> and acetylene on iron nanoparticles embedded in a mesoporous silica temperate<sup>[4]</sup> or porous silicon,<sup>[5]</sup> or by pyrolysis of some organometallic compounds such as ferrocene, which contain both the metal catalyst and carbon source required for carbon nanotube growth.<sup>[6,7]</sup> Patterning aligned/non-aligned carbon nanotubes on substrates has been also demonstrated using different techniques, including offset printing,<sup>[8]</sup> standard lithography,<sup>[5,9–11]</sup> soft lithography,<sup>[12–14]</sup> and self-assembly<sup>[15]</sup> to prepattern catalysts. This is followed by carbon nanotube growth, or pre patterning of substrates for site-selective growth of carbon nanotubes.<sup>[10,16,17]</sup> Although carbon nanotubes have many potential applications and are of fundamental scientific importance, the preparation of structurally near-perfect carbon nanotubes by a variety of techniques, including laser ablation, arc discharge, and chemical vapor deposition, has always involved high temperatures. Many efforts have been made to synthesize carbon nanotubes at low temperatures.<sup>[18–20]</sup> Recently, Ren et al.<sup>[9,21]</sup> developed a technique to grow vertically aligned carbon nanofibers (CNFs) at a relatively low temperature (660 °C) and patterned growth of individually aligned vertical carbon fibers was also demonstrated.<sup>[9]</sup> Experimental results showed that CNFs also possess excellent field emission properties<sup>[22]</sup> and are of particular in-

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