Supramolecular Assembly of Nanoparticles at Liquid–Liquid Interfaces

1 AUTHOR:

Wolfgang H. Binder
Martin Luther University Halle-Wittenberg
182 PUBLICATIONS **4,757** CITATIONS

Highlights

Supramolecular Assembly of Nanoparticles at Liquid–Liquid Interfaces**

Wolfgang H. Binder*

The supramolecular organization of nanoparticles, nanocrystals and other nanometer-sized objects (NPs) is an important prerequisite for permanent applications in the field of nano-(bio)technology.[1] There is an intense search for a simple and general strategy to organize NPs on interfaces through self-assembly processes, as NPs exhibit a wide range of size-dependent physical effects (optical, electrical, magnetic, etc.).[2] Such processes require adequate stabilization of the NP at interfaces with a high degree of organizational selectivity. Sufficient dynamic freedom is necessary in the course of the ordering process and once completed, the assembly must be stabilized. Three different approaches are currently explored to effect ordering of NPs by the self-assembly processes (Figure 1):

a) Crystallization of nanoparticles[1a,2a,2b,3] leads to a 3D ordering to produce so-called "colloidal crystals", in which high levels of order are possible through sedimentation and precipitation processes. An advantage of this process is the high level of order within the materials obtained. A main disadvantage lies in the low rate of sedimentation, which may require weeks to generate the ordered materials.
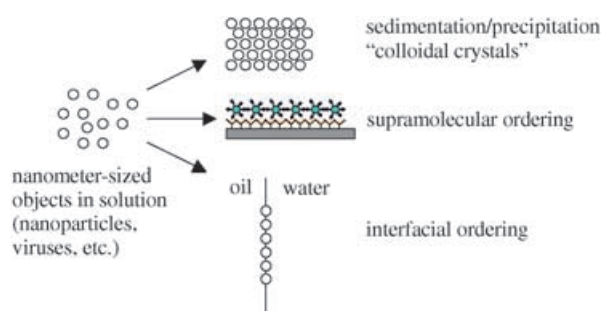

Figure 1. Strategies for the self-assembly of nanoparticles.

b) Another type of self-assembly process uses directed supramolecular interactions between a surface and the NP (for example: electrostatic interactions,[4] oligonucleotides,[5] metal complexes,[6] directed hydrogen bonds,[7] and hydrophobic forces[8]). This technique is usually carried out by a wet-deposition processes. A general disadvantage of using direct supramolecular interactions for assembly lies in the formation of irregular arrays that result from initially strong attachments, which usually do not allow the correction of errors or mismatches during the assembly process.

c) Liquid–liquid interfaces offer an important alternative scaffold for the organization of nanometer-sized objects. For example, interfacial ordering effects[9] can be used for the self-assembly of NPs and viruses. Of key importance is the assembly of NPs at an oil–water interface where the interfacial tension is high. In this process, the assembly is highly dynamic, which enables errors to be corrected rapidly. At the macroscopic level, such processes have

been known for over 100 years as "Pickering emulsions",[10] in which large particles ($d > 1\ \mu m$) stabilize emulsions efficiently by adsorption to the liquid–liquid interface.

The theory of the self-assembly of NPs and other nanometer-sized objects at liquid–liquid interfaces was developed initially by Binks et al.[11] (Figure 2). The high interfacial energy between oil and water can be
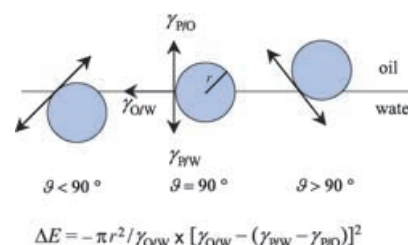

$$\Delta E = -\pi r^2 / \gamma_{O/W} \times [\gamma_{O/W} - (\gamma_{P/W} - \gamma_{P/O})]^2$$

Figure 2. Energy balance (ΔE) of particle assembly at interfaces; adapted from ref. [9a]; γ: interfacial energy, P: particle, W: water, O: oil, r: effective NP radius.

decreased by the assembly of the NPs at the interface. This decrease in surface energy favors the formation of a monolayer of NPs located at the interface. Clearly this process is counterbalanced by the kinetic energy of the NPs in solution. The energetics of the assembly process can be calculated from several parameters according to the equation outlined in Figure 2. The placement of one NP at the interface leads to a decrease in the interfacial energy, which

[*] Prof. Dr. W. H. Binder
Institute of Applied Synthetic Chemistry
Division of Macromolecular Chemistry
Getreidemarkt 9/163/MC
1060 Vienna (Austria)
Fax: (+43) 1-58801-16299
E-mail: wbinder@mail.zserv.tuwien.ac.at

is expressed as the difference between the energies of the oil–water ($\gamma_{O/W}$), the particle–water ($\gamma_{P/W}$), and the particle–oil ($\gamma_{P/O}$) interfaces, in which R is the effective radius of the nanoparticle. Three parameters influence the energy of the assembly process:

a) Simple surface modification of the NPs can be used to modulate the interfacial energies $\gamma_{P/O}$ and $\gamma_{P/W}$; either covalently bound or adsorbed ligands may be used for this. An important aspect of NP surface modification is the influence of the ligand on the properties of the NP core which may limit the range of feasible surface modifications.

b) The nature of the oil–water interface (modification of $\gamma_{O/W}$).

c) The effective radius (R) of the nanoparticles. According to this theory, smaller NPs should adsorb more weakly to the interface than larger NPs.

All three parameters can be used to control the exact location of the NPs; only if the contact angle is exactly 90° will the particle be located exactly at the middle of the oil–water interface (that is, positioned equally between the oil and water phases). In all other cases, the oil or the water will be favored as an adsorption site. The energy of the adsorption process can be determined in the following way: based on known values[12b] ($\gamma_{O/W} = 35.7\ \mathrm{mN\,m^{-1}}$; $\gamma_{P/O} = 15\ \mathrm{mN\,m^{-1}}$; $\gamma_{P/W} = 40\ \mathrm{mN\,m^{-1}}$) the energy is strongly dependent on NP size. A particle with $d \approx 1\ \mu m$ yields a stabilizing interfacial energy of $\Delta E \approx 10^7\ k_BT$, which leads to an almost irreversible adsorption at this interface. Particles with smaller radii adsorb with smaller energy values, as ΔE is proportional to r^2 (for $d = 100\ \mathrm{nm}$, $\Delta E \approx 10^5\ k_BT$; $d = 10\ \mathrm{nm}$, $\Delta E \approx 10^3\ k_BT$, $d = 1\ \mathrm{nm}$, $\Delta E \approx 10^1\ k_BT$).

So much for theory—but what is theory without proof? Russell and co-workers[12] (Figure 3a) recently investigated the assembly of CdSe nanoparticles of two different radii (2.7 nm and 4.6 nm) by competitive adsorption, stabilized with phosphinoxide ligands. Discrimination in adsorption can be followed by taking advantage of the size-dependent fluorescence (F) of the CdSe NPs: the initial fluorescence of adsorp-
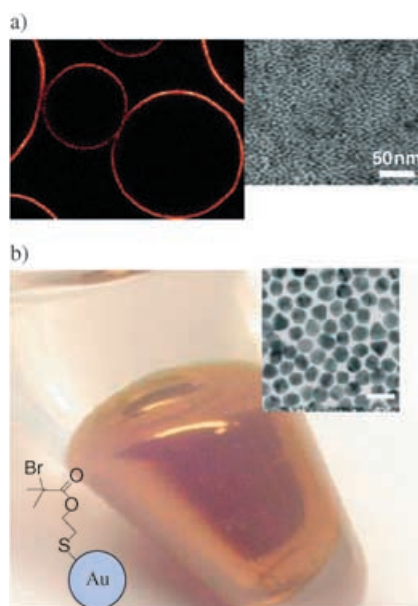

Figure 3. a) Left: fluorescence confocal microscope image of CdSe-particle-coated water droplets dispersed in toluene; right: TEM image of a dried film; from ref. [12a]. b) Photograph of self-assembled Au nanoparticles ($d = 12$ nm) covered with 2,2′-dithiobis(1-(2-bromo-2-methylpropionyloxy)ethane) at a toluene–water interface. Inset: HRTEM image of the film (scale bar = 25 nm); from ref. [9a].

tion of the smaller particles ($r = 2.7$ nm, $\lambda_F = 525$ nm) at a toluene–water interface was followed by a change at $\lambda = 610$ nm, which indicates the interfacial adsorption of the larger particles added subsequently. This not only gives proof to the theory that larger particles may win the adsorption process in competition with smaller NPs, but also allows determination of the time constant of the selective adsorption process. The particles are mobile (in a fluid phase) at the interface without the formation of ordered arrays. Extending this concept yields isolable films after evaporation of the solvent. Furthermore, charged gold NPs[9c] and voltage-induced processes[13] effect the same type of assembly at interfaces. A related concept developed by Möhwald and co-workers[9a] (Figure 3b) uses Au, Ag or γ-Fe$_2$O$_3$ NPs that have been surface-modified with a 2-bromo-2-methylpropionate ligand. The contact angle of these particles has a value close to 90°, resulting in the assembly of the particles exactly in the middle of a toluene–water interface. The formation of a thin film (transferable by Langmuir–Blodgett techniques) with metallic gold reflectance and blue trans-

mittance demonstrates the formation of closely packed NP layers. "Nanoalloys", controlled mixtures of different nanoparticles (assemblies of Ag and Au NPs, for example), can also be formed at the interface given that the NP size and packing permits the formation of matching lattices.

The method is not restricted to metallic, siliceous or semiconductive NPs.[14] Regular biological objects are as important for the formation of thin films and nanometer-sized membranes as are NPs. A recent example of viral assembly (with $r = 33$ nm) was demonstrated by Russell and co-workers[15] with Cowpea Mosaic Virus (CPMV) at a perfluorodecaline–water interface. The virus offers an excellent system, as it is stable in organic solvents and is easily isolated in large quantities from infected black-eyed pea plants. Detection was assisted by chemical labeling with a fluorescent dye (rhodamine). Cross-linking of the CPMV particles at the interface was carried out with glutaraldehyde or biotin groups (Figure 4). Noncovalent cross-linking with the biotin–avidin interaction was superior to chemical cross-linking with glutaraldehyde, as stable and ultrathin membranes consisting of the assembled viruses were obtained. This proves the assembly concept proposed by Whitesides and Boncheva,[16] that a self-assembling system needs a sufficient degree of reversibility to form highly ordered arrays. Otherwise, disordered (glassy) arrays are produced. Thus interfaces not only provide a scaffold for the facile assembly of NPs, but also retain sufficient flexibility to rapidly correct errors during the assembly process, leading to a high degree of order with a rapid process.

The assembly of NPs at polymeric surfaces[17] demonstrates the broad applicability of the interfacial assembly concept. The interface of immiscible block-copolymer micelles provide an environment in which the surface energy in a nonaqueous system (block-copolymer micelles formed in a selective solvent for one block) is comparable to the interfacial energy of oil–water interfaces. Thus Au NPs (with $r = 5.4$ nm) can be assembled within micelles composed of polystyrene-*block*-poly(4-vinylpyridine) (PS-PVP) in toluene—a selective
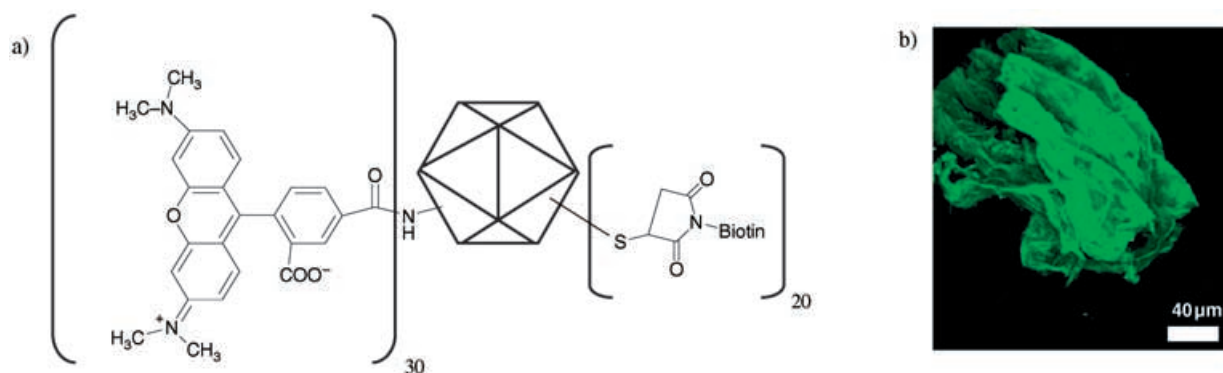
Figure 4. a) CPMV particles modified with rhodamine and biotin. b) Optical micrograph of a CPMV membrane after self-assembly and cross-linking; from ref. [15a].

Figure 6. Formation of heterodimeric nanoparticles through the assembly of Fe_3O_4 nanoparticles on a liquid–liquid interface and subsequent seeding of Ag nanoparticles on the outside of the Fe_3O_4 nanoparticles; adapted from ref. [21].

solvent for the PS block (Figure 5a). Subsequent spin coating leads to an ultrathin film that concentrates the nanoparticles at the interface between the micellar core and corona in a hexagonal pattern ($d \approx 40$ nm per hexagon).[18] An extension of this concept relies on the formation of "honeycomb-patterns"[19] from a homopolymer (polystyrene) under humid conditions from a solution containing CdSe nanoparticles (Figure 5 b, c).[20] During evaporation, the CdSe NPs assemble at the interface between $CHCl_3$ and water, leaving behind the micrometer-sized honeycomb pattern of the polymer with the CdSe NPs concentrated at the former location of the evaporated water droplet.

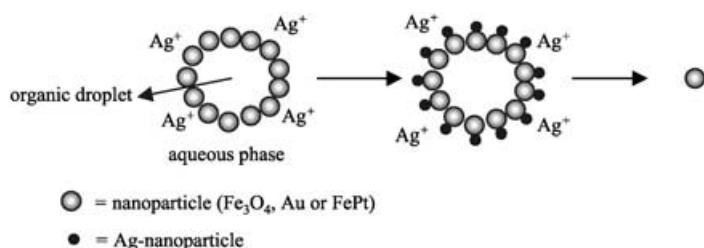The interfaces can also be used as a medium for chemical reactions in the

synthesis of heterodimeric nanoparticles.[21] For example, preassembled Fe_3O_4 nanoparticles ($d = 8$ nm) can be assembled at the interface of a dichloromethane droplet and water (Figure 6). Owing to the high density and stability of the assembly, these particles can act as seeds for the subsequent nucleation of Ag NPs ($d = 5.5$ nm) only on the outside of the Fe_3O_4 assemblies. This is an elegant approach to heterodimeric nanoparticles, consisting of two different materials.

In summary, interfaces are ubiquitous in nature and can be used broadly as ideal means for the self-assembly of nanoparticles. The ease and speed of this approach make it an excellent method for large-scale use and potentially valuable for industrial application. Especially in the area of thin-membrane generation, the functionalization and modification of nanometer-scale objects at specific positions, the size selection of

nanometer-sized objects, and the controlled mixing of nanoparticles all give this method great potential for future applications in the field of nanotechnology.
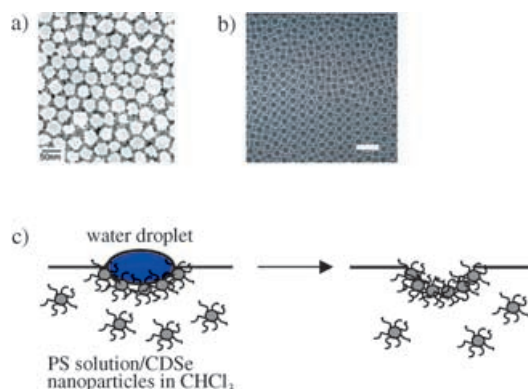
Figure 5. a) Assembly of Au nanoparticles at a polymer interface (*block*-copolymer micelles); from ref. [18a]. b) Optical fluorescence image of CdSe nanoparticles ($d = 4$ nm) of a sample obtained from solvent casting a polystyrene film from chloroform with CdSe nanoparticles under humid conditions (scale bar = 16 µm); from ref. [20]. c) Mechanism of pattern formation and concomitant particle assembly at the water–chloroform interface; from ref. [20].

[1] a) E. Katz, I. Willner, *Angew. Chem.* **2004**, *116*, 6166–6235; *Angew. Chem. Int. Ed.* **2004**, *43*, 6048–6108; b) *Nanobiotechnology* (Eds.: C. M. Niemeyer, C. A. Mirkin), Wiley-VCH, **2004**; c) *Nanoparticles* (Ed.: G. Schmid), Wiley-VCH, **2004**; d) E. Katz, A. N. Shipway, I. Willner in *Nanoscale Materials* (Eds.: L. M. Liz-Marzan, V. P. Kamat), Kluwer, Norwell, **2003**, pp. 317–343; e) C. Niemeyer, *Angew. Chem.* **2001**, *113*, 4254–4287; *Angew. Chem. Int. Ed.* **2001**, *40*, 4128–4158.

[2] a) C. P. Collier, T. Vossmeyer, J. R. Heath, *Annu. Rev. Phys. Chem.* **1998**, *49*, 371–404; b) C. B. Murray, C. R. Kagan, M. G. Bawendi, *Annu. Rev. Mater. Sci.* **2000**, *30*, 545–610; c) P. Alivisatos, *Science* **1996**, *271*, 933–937; d) E. Granot, P. Fernando, I. Willner, *J. Phys. Chem. B* **2004**, *108*, 5875–5881; e) B. B. Yellen, G. Friedman, *Adv. Mater.* **2004**, *16*, 111–115; f) H. Weller, *Angew. Chem.* **1998**, *110*, 1748–1750;

Angew. Chem. Int. Ed. **1998**, *37*, 1658–1659.

[3] Representative reviews: a) A. L. Rogach, D. V. Talapin, E. V. Shevchenko, A. Kornowski, M. Haase, H. Weller, *Adv. Funct. Mater.* **2002**, *12*, 653–664; b) E. V. Shevchenko, D. V. Talapin, A. L. Rogach, A. Kronowski, M. Haase, H. Weller, *J. Am. Chem. Soc.* **2002**, *124*, 11480–11485; c) E. Shevchenko, D. Talapin, A. Kronowski, F. Wiekhorst, J. Kötzler, M. Haase, A. Rogach, H. Weller, *Adv. Mater.* **2002**, *14*, 287–290; an example of convective self-assembly: d) S. Vengallatore, Y. Peles, L. R. Arana, S. M. Spearing, *Sens. Actuators A* **2004**, *113*, 124–131.

[4] Two representative reviews: a) M.-C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293–346; b) S. Maenosono, T. Okubo, Y. Yamaguchi, *J. Nanopart. Res.* **2003**, *5*, 5–15; see also: c) M. Mizuno, Y. Sasaki, A. C. C. Yu, M. Inoue, *Langmuir* **2004**, *20*, 11305–11307; d) A. Gole, C. J. Orendorff, C. J. Murphy, *Langmuir* **2004**, *20*, 7117–7122; e) Z. Zhong, S. Patskovsky, P. Bouvrette, J. H. T. Luong, A. Gedanken, *J. Phys. Chem. B* **2004**, *108*, 4046–4052; f) X.-M. Li, V. Paraschiv, J. Huskens, D. N. Reinhoudt, *J. Am. Chem. Soc.* **2003**, *125*, 4279–4284; g) K. Lee, F. Pang, G. T. Carroll, N. J. Turro, J. T. Koberstein, *Langmuir* **2004**, *20*, 1812–1818; h) H. Tanaka, M. Mituishi, T. Miyashita, *Langmuir* **2003**, *19*, 3103–3105; i) S. Maenosono, T. Okubo, Y. Yamaguchi, *J. Nanopart. Res.* **2003**, *5*, 5–15; j) L. Sheeney-Hai-Ichida, B. Basnar, I. Willner, *Angew. Chem.* **2004**, *116*, 80–85; *Angew. Chem. Int. Ed.* **2004**, *43*, 78–83; k) A. N. Shipway, M. Lahav, R. Gabai, I. Willner, *Langmuir* **2000**, *16*, 8789–8795; l) J. B. Carroll, B. L. Frankamp, S. Srivastava, V. M. Rotello, *J. Mater. Chem.* **2004**, *14*, 690–694; an example of nanoparticle binding onto polymeric surfaces: m) I. Tokareva, S. Minko, J. H. Fendler, E. Hutter, *J. Am. Chem. Soc.* **2004**, *126*, 15950–15951; n) M. Carrara, J. J. Kakkassery, J.-P. Abid, D. J. Fermin, *ChemPhysChem* **2004**, *5*, 571–575; o) R. Bhat, J. Genzer, B. N. Chaney, H. W. Sugg, A. Liebmann-Vinson, *Nanotechnology* **2003**, *14*, 1145–1152.

[5] a) M. Andersson, K. Elihn, K. Fromel, K. D. Caldwell, *Coll. Surf. B: Biointerfaces* **2004**, *34*, 165–171; b) L. M. Demer, D. S. Ginger, S.-J. Park, Z. Li, S.-W. Chung, C. A. Mirkin, *Science* **2002**, *296*,

1836–1838; c) Y. Cao, R. Jin, C. A. Mirkin, *J. Am. Chem. Soc.* **2001**, *123*, 7961–7962; d) S. Park, A. A. Lazarides, C. A. Mirkin, P. W. Brazis, C. R. Kannewurf, R. L. Letsinger, *Angew. Chem.* **2000**, *112*, 4003–4006; *Angew. Chem. Int. Ed.* **2000**, *39*, 3845–3848; e) N. L. Rosi, C. S. Thaxton, C. A. Mirkin, *Angew. Chem.* **2004**, *116*, 5616–5619; *Angew. Chem. Int. Ed.* **2004**, *43*, 5500–5503; f) J. J. Storhoff, C. A. Mirkin, *Chem. Rev.* **1999**, *99*, 1849–1862, and references therein; g) L. M. Demers, C. A. Mirkin, *Angew. Chem.* **2001**, *113*, 3159–3161; *Angew. Chem. Int. Ed.* **2001**, *40*, 3069–3071.

[6] A. Mulder, J. Huskens, D. N. Reinhoudt, *Org. Biomol. Chem.* **2004**, *2*, 3409–3424, and references therein.

[7] a) A. K. Boal, F. Ilhan, J. E. DeRouchey, T. Thurn-Albrecht, V. M. Rotello, *Nature* **2000**, *404*, 476–478; b) A. K. Boal, V. M. Rotello, *Langmuir* **2000**, *16*, 9527–9532; c) R. Zirbs, F. Kienberger, P. Hinterdorfer, W. H. Binder, *Langmuir* **2005**, in press.

[8] a) V. Mahalingam, S. Onclin, M. Peter, B. J. Ravoo, J. Huskens, D. B. Reinhoudt, *Langmuir* **2004**, *20*, 11756–11762; b) A. Mulder, S. Onclin, M. Peter, J. P. Hoogenboom, H. Beijleveld, J. ter Maar, M. F. Garcia-Parajo, B. Ravoo, J. Huskens, N. F. van Hulst, D. N. Reinhoudt, *Small* **2005**, *1*, 242–253; c) A. Sanyal, T. B. Norsten, O. Uzun, V. M. Rotello, *Langmuir* **2004**, *20*, 5958–5964.

[9] a) H. Duan, D. Wang, D. G. Kurth, H. Möhwald, *Angew. Chem.* **2004**, *116*, 5757–5760; *Angew. Chem. Int. Ed.* **2004**, *43*, 5639–5642; b) Y. Lin, H. Skaff, T. Emrick, A. D. Dinsmore, T. P. Russell, *Science* **2003**, *299*, 226–229; c) F. Reincke, S. G. Hickey, W. K. Kegel, D. Vanmaekelbergh, *Angew. Chem.* **2004**, *116*, 464–468; *Angew. Chem. Int. Ed.* **2004**, *43*, 458–462.

[10] a) R. Aveyard, B. P. Binks, J. H. Clint, *Adv. Coll. Interfac. Sci.* **2003**, *100–102*, 503–546; a theoretical description: b) P. P. Kralchevski, I. B. Ivanov, K. P. Ananthapadmanabhan, A. Lips, *Langmuir* **2005**, *21*, 50–63.

[11] a) B. Binks, J. H. Clint, *Langmuir* **2002**, *18*, 1270–1273, and references therein; b) B. P. Binks, S. O. Lumsdon, *Langmuir* **2000**, *16*, 8622–8631.

[12] a) Y. Lin, A. Böker, H. Skaff, D. Cookson, A. D. Dinsmore, T. Emrick, T. P. Russell, *Langmuir* **2005**, *21*, 191–194;

b) Y. Lin, H. Skaff, T. Ermick, A. D. Dinsmore, T. P. Russell, *Science* **2003**, *299*, 226–229.

[13] B. Su, J.-P. Abid, D. J. Fermin, H. H. Girault, H. Hoffmannova, P. Krtil, Z. Samec, *J. Am. Chem. Soc.* **2004**, *126*, 915–919.

[14] a) J.-W. Hu, G.-B. Han, S.-G. Sun, Z.-Q. Tian, *Langmuir* **2004**, *20*, 8831–8838; b) S. Chen, H. Yao, K. Kimura, *Langmuir* **2001**, *17*, 733–739; J. K. Sakata, A. Dwoskin, J. L. Vigorita, E. M. Spain, *J. Phys. Chem. B* **2005**, *109*, 138–141; U. K. Gautam, M. Gosh, C. N. R. Rao, *Langmuir* **2004**, *20*, 10775–10778; c) H. Schwartz, Y. Harel, S. Efrima, *Langmuir* **2001**, *17*, 3884–3892; d) D. Rautaray, R. Kavathekar, M. Sastry, *Faraday Discuss.* **2005**, *129*, 205–217; e) M. Platt, R. A. W. Dryfe, E. P. L. Roberts, *Electrochim. Acta* **2004**, *49*, 3937–3945.

[15] a) J. T. Russell, Y. Lin, A. Böker, L. Su, P. Carl, H. Zettl, J. He, K. Still, R. Tangirala, T. Emrick, K. Littrell, P. Thiyagarajan, D. Cookson, A. Frey, Q. Wang, T. P. Russell, *Angew. Chem.* **2005**, *117*, 2472–2478; *Angew. Chem. Int. Ed.* **2005**, *44*, 2420–2426; b) Y. Lin, H. Skaff, A. Böker, A. D. Dinsmore, T. Emrick, T. P. Russell, *J. Am. Chem. Soc.* **2003**, *125*, 12690–12691.

[16] G. M. Whitesides, M. Boncheva, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4769–4774.

[17] For a review, see: a) I. W. Hamley, *Nanotechnology* **2003**, *14*, R39–R54; b) R. Glass, M. Möller, J. Spatz, *Nanotechnology* **2003**, *14*, 1153–1160; c) S.-W. Yeh, Y.-T. Chang, C.-H. Chou, K.-H. Wie, *Macromol. Rapid Commun.* **2004**, *25*, 1679–1686, and references therein.

[18] a) B.-H. Sohn, J.-M. Choi, S. I. Yoo, S.-H. Yun, W.-C. Zin, J. C. Jung, M. Kanehara, T. Hirata, T. Teranishi, *J. Am. Chem. Soc.* **2003**, *125*, 6368–6369; b) J. J. Chiu, B. J. Kim, E. J. Kramer, D. J. Pine, *J. Am. Chem. Soc.* **2005**, *127*, 5036–5037.

[19] G. Widawski, M. Rawiso, B. Francois, *Nature* **1994**, *369*, 387–389.

[20] A. Böker, Y. Lin, K. Chiapperin, R. Horowitz, M. Thompson, V. Careon, T. Xu, C. Abetz, H. Skaff, A. D. Dinsmore, T. Emrick, T. P. Russell, *Nat. Mater.* **2004**, *3*, 302–306.

[21] H. Gu, Z. Yang, J. Gao, C. K. Chang, B. Xu, *J. Am. Chem. Soc.* **2005**, *127*, 34–35.