Monatsh Chem (2010) 141:1267–1272
DOI 10.1007/s00706-010-0364-7

REVIEW

The scale-up of material microstructuring: from scanning probes to self-assembly

Tobias Kraus

Received: 25 June 2010 / Accepted: 29 June 2010 / Published online: 25 September 2010

Abstract The behaviour of materials is governed by their microstructures, whether they are naturally occurring or artificially designed. Engineered microstructures lead to materials with new and useful functions, but their real-world application requires scalable microstructuring methods for production. This review discusses several principles of fabrication and their scalability. Replication by imprint and multiplexed probes are obvious candidates for scale-up, but they limit the choice of materials. The assembly of interacting particles is a promising, scalable fabrication method. A wide range of materials can be obtained as particles which assemble into regular superstructures, but large-scale structuring at high precision and yield as yet remains a challenge.

Keywords Microstructure · Microfabrication · Nanotechnology · Particles

Introduction

The microstructure of materials governs their behaviour. High-resolution microscopy, advanced spectroscopy and improved modelling have enabled researchers to analyse the microstructure's influence in detail. In addition, methods derived from semiconductor technology now allow researchers to prepare rationally structured materials. Microstructures were thus adapted from living organisms or de novo from physical insight in order to evoke specific behaviour in synthetic materials. Biomimetic materials exhibit the properties of their natural counterpart, for example, the adhesion of gecko feet [1]. Designed materials show previously unknown behaviour, e.g. a negative refractive index, as in artificial electromagnetic metamaterials [2]. Other materials refine properties of their naturally occurring counterparts, for example, the photonic band gap of natural opals [3]. Self-healing and, in general, responsive materials have mobile or reactive components that are strategically placed to cause meaningful reactions to external stimuli according to an engineered sequence [4] (Fig. 1).

Implicitly and explicitly defined microstructures

To synthesize such "engineered materials", structural information must be derived from nature or modelling and then physically realized in the microstructure of the material. This requires a synthesis process very unlike traditional approaches from metallurgy or polymer technology, which only enable the engineer to bias the microstructure. Information input is limited, and the resulting structure is a complex function of the process parameters. The free parameters only implicitly define average structural features. Individual elements, for example, the grains in a piece of steel, have unpredictable positions and a broad size distribution. This is often sufficient for the economical production of a material with a defined property, but insufficient for rational microstructure design.

In contrast, microfabrication technology provides full control of structure. The technology was originally developed for the production of microelectronic circuitry, where each functional element is unique. Comprehensive information enters the fabrication process and is explicitly

T. Kraus (✉)
Structure Formation Group, Leibniz Institute for New Materials (INM), Campus D2 2, 66123 Saarbrücken, Germany
e-mail: tobias.kraus@inm-gmbh.de

translated into structure. A probe, usually an electron beam or the tip of a scanning probe microscope, is moved such that the desired geometry is formed on a mask. The mask is then transferred into a material structure via a lithography step. In the ideal case, the fabrication process is a conformal mapping of the design data on the target substrate. This is sufficient for rational microstructure design even with extreme complexity, but is usually an extreme waste for the synthesis of designed materials.

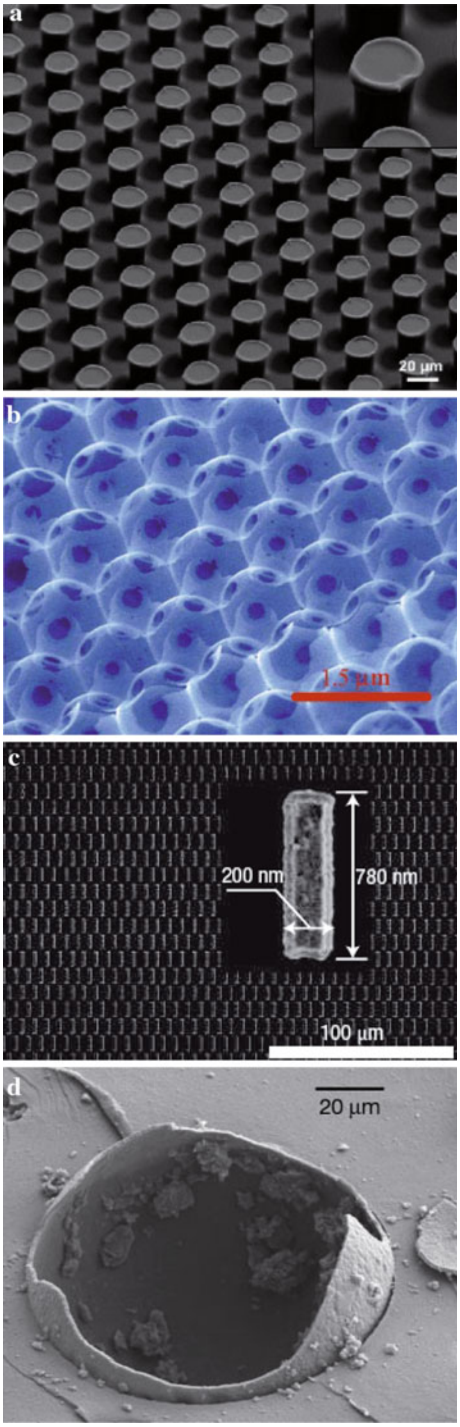

Fig. 1 Engineered materials with artificially fabricated microstructures: **a** shows a biomimetic, gecko-inspired dry adhesive from del Campo et al. [5], **b** is a reverse opal that exhibits a photonic bandgap around 1.5 µm from Blanco et al. [6], **c** shows an overview and a building block of a metamaterial with a negative refractive index at a wavelength close to 1.5 µm from Shalaev et al. [2], **d** is a microsphere that contained a monomer to close polymer cracks in a self-healing material from White et al. [4] (reproduced with permissions)

Replication and probes

Typically, the structures in engineered materials are arranged in small unit cells that repeat to form a macroscopic material (Fig. 2). The actual patterning information is limited to the unit cell. Thus, replication is a first step towards the scale-up of designed materials. The expensive primary patterning is performed only once and on a limited area; large areas are structured by transferring this master to the substrate multiple times. Common transfer methods include photolithography, where light intensity is modulated by the master [7], and imprint or printing [8–10], where mechanical contact leads to deformation of the substrate by the master (Fig. 3). Many functional microstructures are now routinely fabricated by replication, including mass products such as holograms [11]. Replication is expected to become one of the key technologies in emerging fields such as flexible electronics. The method will then also be available for the production of bulk materials.

Replication limits fabrication to materials that can be photopatterned or imprinted. It also does not solve the problem of three-dimensional structures: while two-dimensional replicas can be stacked on top of each other, this

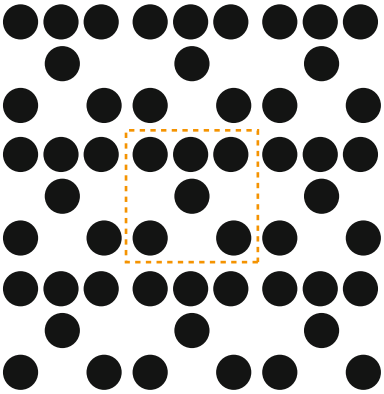

Fig. 2 Many structured materials are composed of relatively small unit cells (*orange, dotted box*) that are repeated to form the bulk material

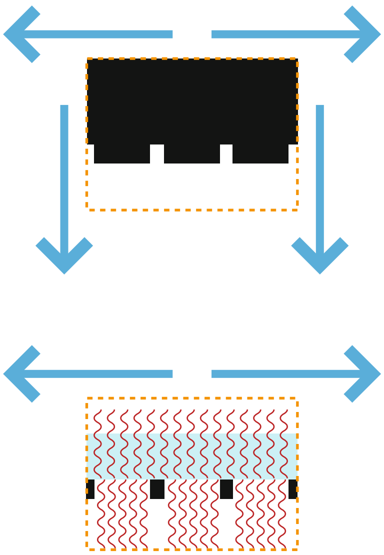

Fig. 3 Replication methods, such as printing or imprinting (*top*) or photolithography (*bottom*) can be used to create large numbers or repeating unit cells

is far too slow to make macroscopic bodies and not suitable for all but the simplest three-dimensional (3D) structures. An alternative is to multiplex the patterning probe.

In a multiplexed approach, multiple parts of a material are addressed concurrently. The multiplexed probes can be the maxima of an interference pattern as in interference lithography (Fig. 4) [12], or the synchronously moving tips of an atomic force microscope (AFM) array (Fig. 5) [13, 14]. Interference patterns extend in three dimensions, thus enabling 3D fabrication. However, their geometry can only be modulated in a limited range. AFM tips can be heated to engrave 3D structure by evaporating defined parts of a material [15]. Single tips are slow, however, and AFM arrays, which depend on many small tips that all must function correctly, are complex and still rather slow. Such problems often plague multiplexed patterning. It is tempting to get rid of the probe altogether.

Interacting particles

When parting with a central source of order, information has to enter the system via a different route. As interaction lengths are limited, information has to be distributed throughout the ordering system. An elegant solution is to encode small building blocks so that they arrange through anisotropic interactions [16]. This is similar to how viruses assemble in an infected cell: individual components are synthesized by the hijacked cell machinery and assemble into the functional virus [17]. In the inanimate world, supramolecular chemists synthesize molecules that interact to form complex superstructures. Similarly, colloidal particles have been found to interact with each other depending on their geometry and chemical nature, thus forming complex nanostructures (Fig. 6). This does not require specific interactions: even isotropic interactions of different monodispersed particles are sufficient to produce a plethora of assembly geometries. In one of the first publications on the topic, Murray's group already reported superstructures with 15 different unit cells that formed from binary mixtures of nanoparticles they had synthesized earlier [18].

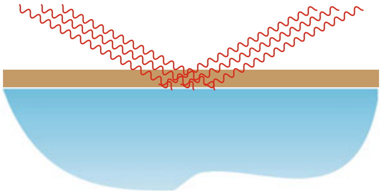

Fig. 4 Interference lithography is based on overlapping beams of electromagnetic radiation that pattern a material due to the intensity modulations in the interference pattern

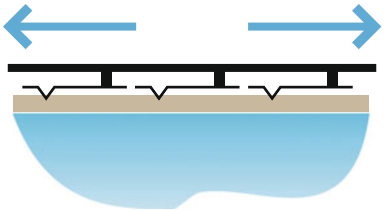

Fig. 5 A multiprobe array (here composed of multiple AFM tips) writes structures at multiple positions in parallel

It is intriguing that this principle works on many different length scales [20]. A common problem in modern materials synthesis is hierarchical patterning. In many cases, macroscopic structures have to be combined with micron-scale and nanoscale features to obtain a certain effect [21] (Fig. 7). Biological systems master such multiscale synthesis easily because they synthesize materials from the smallest building units under molecular control. This is hard to mimic by using conventional microfabrication. Components from different length scales that contain the structural information to form hierarchical structures are an interesting alternative. They can be optimized independently and combined in a modular fashion, an approach much more compatible with engineering principles [22–26].

Structure formation due to distributed information is often called "self-assembly" or "self-organization" [20]. As a synthetic tool, self-assembly is not as versatile as conventional microfabrication, and self-assembled structures often exhibit defects and poor long-range order. It is, however, suitable for the synthesis of designed materials. Functional features of materials originate in microstructural regularity, which can be efficiently encoded and formed in self-assembling systems. Regularity can relate to connectivity, symmetry or termination, but also more complex

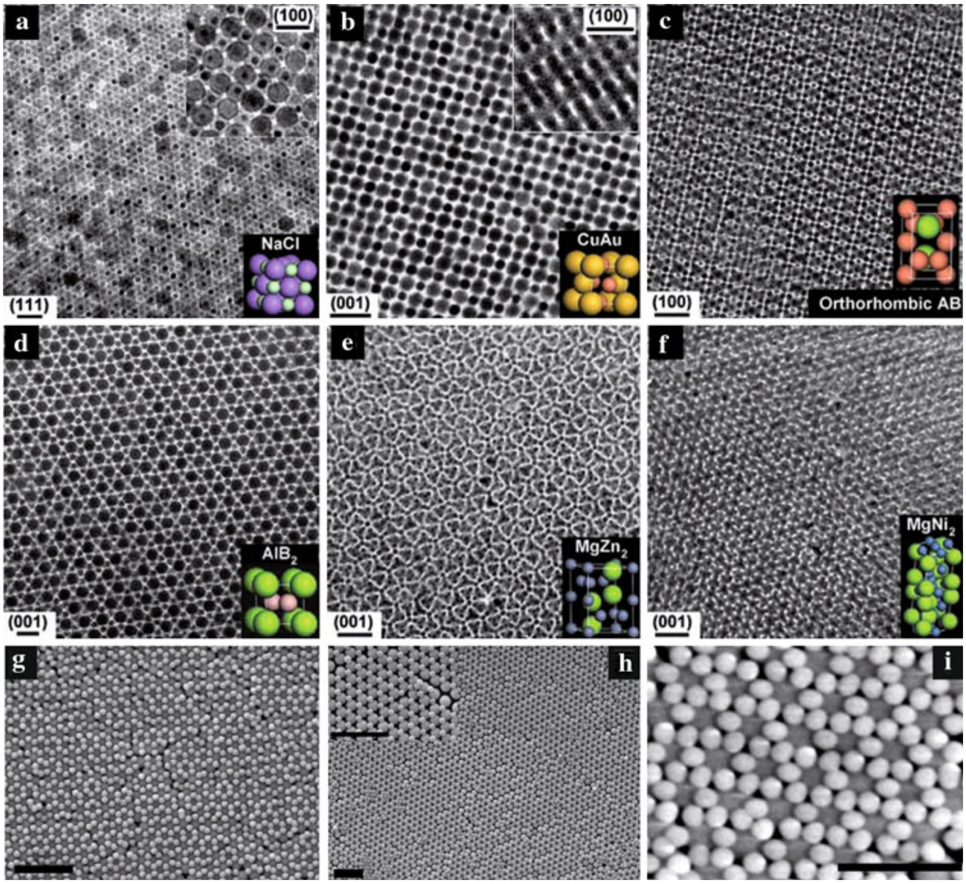

Fig. 6 Superstructures from binary mixtures of particles. Structures from Shevchenko et al. [18] in **a**–**f** are based on nanoparticle mixtures, their assembly is probably due to direct particle–particle interactions (*scale bars* 20 nm, but 10 nm in **e**). Structures in **g**, **h** (from Velikov et al. [19]) are formed by capillary interactions in multiple steps, where the bottom layer templates the arrangement of the top particle layer (*scale bars* **g**, **h** 2 µm, **i** 1 µm) (reproduced with permissions)

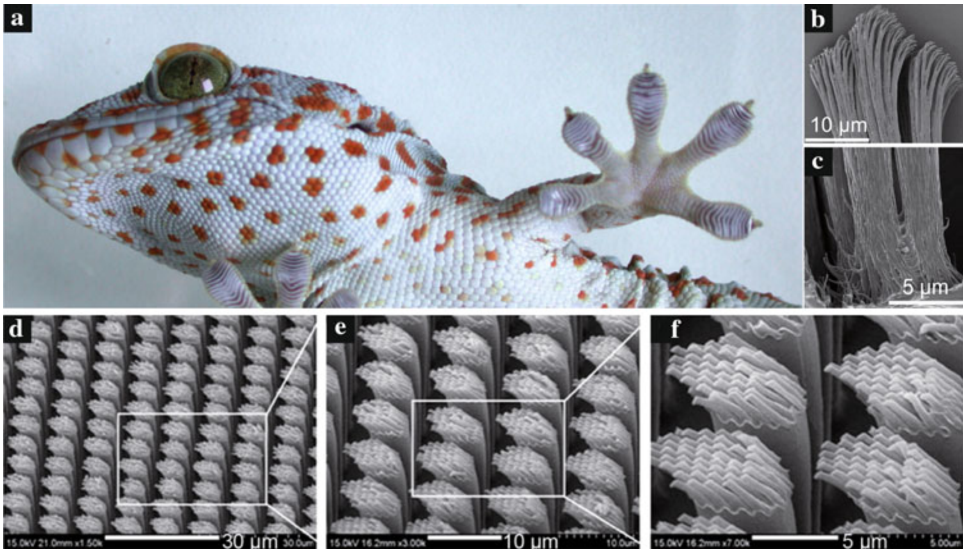

Fig. 7 Hierarchical microstructures let geckos (**a**) walk on the ceiling (Gecko image from S.N.Gorb, University of Kiel, Germany). Their feet are covered with rows of setae (**c**) that end in fine spatula (**b**), which can make strong, reversible contacts even with rough surfaces (from Autumn et al. [22]). Some artificial, gecko-inspired structures (by Jeong et al. [23]) mimic this hierarchy **d**–**f** to achieve similarly high adaptability and strong adhesion (reproduced with permissions)

features such as fractal dimension or percolation. Instead of simple geometrical order, the distributed information may just define a specific sequence of different particles that is to be repeated. For example, binary mixtures of nanoparticles form supercrystals with good short-range order and broad structural diversity. The resulting materials exhibit interesting electronic properties notwithstanding the fact that the particle assembly does not produce long-range order [27]. For electronic properties in these materials, short-range periodicity and defined interfaces are decisive, while long-range deviations from periodicity appear to be tolerated.

Information enters the particle aggregation process mainly through the (geometry-dependent) interaction potential of the involved particles and the conditions during aggregation. With narrowing size distribution of the involved particles and more controlled processing, increasingly predictable structures are formed. The particle-based approach is convenient because particle geometry and interaction can be analysed and modified in great detail a priori, particles retain their identity and can be observed during the agglomeration process, and many different base materials can be shaped into particles. On the other hand, it is challenging because the quality of the constituent particles has to be very high, many interactions influence aggregation and the resulting structures have large internal interfaces that often govern their behaviour.

Producing bulk materials from suspended particles is an old principle: in food technology and cosmetics for example, particle aggregation has long been exploited to adjust texture. Cheese production, an ancient technology, relies on the control of agglomerate structures in curd to tune the density and overall texture of the resulting cheese. Casein micelles from milk arrange first into unidirectional chains without branching which then form networks of increasing density, long before they lose their individual spherical structure in ripened cheese [28] (Fig. 8). For particles with a narrow size distribution, the range of attainable bulk materials is extended to include crystalline phases. When these particles interact in a complex manner or multiple populations of different particles are involved, many different phases become attainable.

It is as yet unclear which processes govern the assembly of monodispersed nanoparticles into ordered structures, or why certain structures form. In some cases, the reason will simply be energy minimization. The interacting particle system is ergodic and finds a minimum energy configuration in which it then settles. In many cases, however, this principle alone cannot explain the experimental results [18]. In addition, entropic effects are relevant. It is well known that the total entropy of certain, apparently ordered systems is greater than that of many apparently disordered systems. Although the overall configurational entropy in the ordered arrangements is smaller, the entropy contribution of the individual particles can more than balance this reduction. Some researchers have tried to explain the arrangements using purely geometrical space-filling arguments [29]. If this analogy to atomic systems [30] should hold, many different particle arrangements would be predictable and accessible simply by tuning particle size.

Not all particle-ordering processes take place close to equilibrium or result in an equilibrium situation. On the contrary, the frequently used convective particle assembly process is a kinetically driven, non-equilibrium process. Hydrodynamic effects guide particles into their respective positions [31]. Binary mixtures of particles form regular supercrystals under capillary action that resemble those originating from direct particle interactions [19] (Fig. 6). Kinetic agglomeration is known to be dependent on the short-range interaction potential of the particles [32]; the fractal dimensions of the disordered aggregates formed depend on the magnitude of the potential. Such processes are sensitive to process parameters like temperature and viscosity.

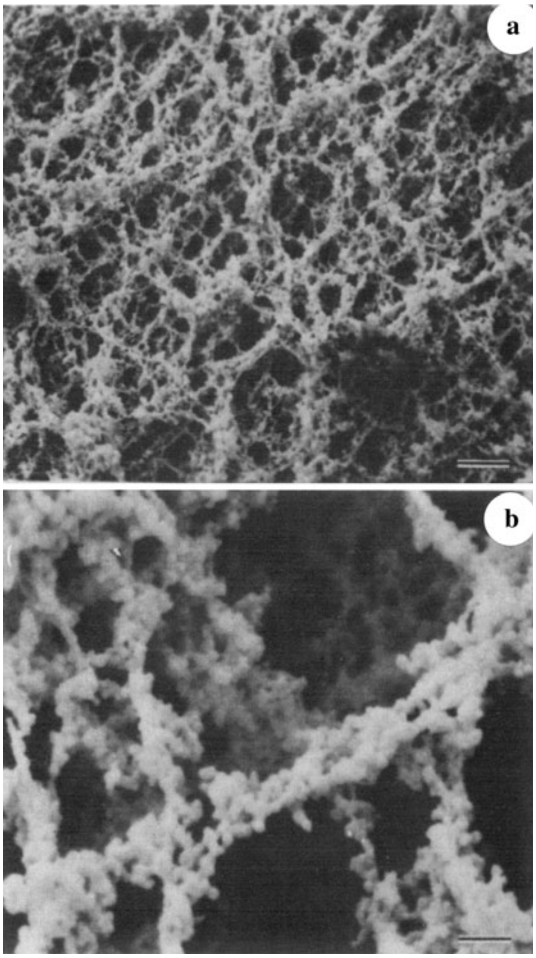

Fig. 8 Micrographs of curd at an early stage of cheese-making (two magnifications, *scale bars* are 10 and 1 μm, respectively). Curd is formed from milk when the casein micelles assemble into networks after acid has been added (micrographs were taken 5 min after setting). Depending on the process conditions, networks with different density and structure form and define the texture of the final cheese. Electron micrographs are by Glaser et al. [28] (reproduced with permissions)

Assembly processes and defects

Process design is critical even for those structure formation processes in which an equilibrium state is reached. The motion of colloidal particles is slow compared to that of molecules and is affected by many more processes than that of molecules. Hydrodynamic instabilities, for example, can severely distort the particle order. In addition, structural information in ordering particle systems is less explicit than in conventional patterning processes, so that secondary minima or bifurcations frequently occur and give rise to unwanted structures. Thus, in contrast to classical microfabrication processes, large-scale inhomogeneities are not the main limitation of self-assembly. Instead, typical defects involve severe local deviations from the desired structure, from point defects to whole domains that exhibit different (or random) arrangement. Suppressing such instabilities is the main challenge in nanoparticle assembly on large scales. It is indeed possible even in relatively simple and cost-effective setups [33], but it requires diligent process optimization and rigorous control of the conditions.

Even a perfectly controlled process for particle assembly will incur a small percentage of faults that amount to large numbers in macroscopic pieces of assembled material. In many traditional engineering disciplines, the process would thus be regarded as useless. In modern engineering, however, concepts such as defect-tolerant computing and fault-tolerant support structures are routinely applied [34]. In materials science, a slight bias in otherwise random microstructures can lend important properties to materials. Convergence will likely occur as more and more engineers employ microstructuring: only structural features which entail function will be defined, at a level that is just sufficient for functionality; the rest is left to stochastics. Likewise, hitherto random structures will be increasingly biased to improve their performance. Such efficient structuring is common to biological systems, where variations are abundant, but critical structural features are reliably conserved. It demands a high level of understanding from the engineer, who needs to know which aspects are truly functional at all scales.

Conclusions

The development of scalable microstructuring technologies, from electron beam patterning to particle self-assembly, has the potential to make engineered materials available for mass applications. Particle assembly is similar to the development of chemical nanoparticle synthesis: a simple principle yields macroscopic amounts of nanostructures. As in nanoparticle synthesis, the actual assembly process is rather complex and requires considerable know-how in scale-up. When it is understood, however, particle-based structuring will have the potential for relevant technological innovation.

Acknowledgments The author thanks Marleen Kamperman and Eoin Murray for helpful discussions and Eduard Arzt for his continuous support.

References

1. Arzt E, Gorb S, Spolenak R (2003) Proc Natl Acad Sci U S A 100:10603
2. Shalaev VM, Cai WS, Chettiar UK, Yuan HK, Sarychev AK, Drachev VP, Kildishev AV (2005) Opt Lett 30:3356
3. Dimitrov AS, Nagayama K (1996) Langmuir 12:1303
4. White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriram SR, Brown EN, Viswanathan S (2001) Nature 409:794
5. del Campo A, Greiner C, Arzt E (2007) Langmuir 23:10235
6. Blanco A, Chomski E, Grabtchak S, Ibisate M, John S, Leonard SW, Lopez C, Meseguer F, Miguez H, Mondia JP, Ozin GA, Toader O, van Driel HM (2000) Nature 405:437
7. Madou MC (2010) Manufacturing techniques for microfabrication and nanotechnology. CRC, Boca Raton
8. Michel B, Bernard A, Bietsch A, Delamarche E, Geissler M, Juncker D, Kind H, Renault JP, Rothuizen H, Schmid H, Schmidt-Winkel P, Stutz R, Wolf H (2001) IBM J Res Dev 45:697
9. Rolland JP, Maynor BW, Euliss LE, Exner AE, Denison GM, DeSimone JM (2005) J Am Chem Soc 127:10096
10. Gates BD, Xu QB, Stewart M, Ryan D, Willson CG, Whitesides GM (2005) Chem Rev 105:1171
11. Renesse RL (2005) Optical document security, 3rd edn. Artech, Boston
12. Moon JH, Ford J, Yang S (2006) Polym Adv Technol 17:83
13. Sekula S, Fuchs J, Weg-Remers S, Nagel P, Schuppler S, Fragala J, Theilacker N, Franueb M, Wingren C, Ellmark P, Borrebaeck CAK, Mirkin CA, Fuchs H, Lenhert S (2008) Small 4:1785
14. Salaita K, Wang YH, Fragala J, Vega RA, Liu C, Mirkin CA (2006) Angew Chem Int Ed 45:7220
15. Pires D, Hedrick JL, De Silva A, Frommer J, Gotsmann B, Wolf H, Despont M, Duerig U, Knoll AW (2010) Science 328:732
16. Glotzer SC, Solomon MJ (2007) Nat Mater 6:557
17. Lindsey JS (1991) New J Chem 15:153
18. Shevchenko EV, Talapin DV, Kotov NA, O'Brien S, Murray CB (2006) Nature 439:55
19. Velikov KP, Christova CG, Dullens RPA, van Blaaderen A (2002) Science 296:106
20. Whitesides GM, Grzybowski B (2002) Science 295:2418
21. Murphy MP, Kim S, Sitti M (2009) ACS Appl Mater Interfaces 1:849
22. Autumn K, Liang YA, Hsieh ST, Zesch W, Chan WP, Kenny TW, Fearing R, Full RJ (2000) Nature 405:681
23. Jeong HE, Lee JK, Kim HN, Moon SH, Suh KY (2009) Proc Natl Acad Sci U S A 106:5639
24. Kraus T, Malaquin L, Delamarche E, Schmid H, Spencer ND, Wolf H (2005) Adv Mater 17:2438
25. Pinto YY, Le JD, Seeman NC, Musier-Forsyth K, Taton TA, Kiehl RA (2005) Nano Lett 5:2399
26. Sharma J, Chhabra R, Liu Y, Ke YG, Yan H (2006) Angew Chem Int Ed 45:730
27. Murray CB, Kagan CR, Bawendi MG (2000) Ann Rev Mat Sci 30:545
28. Glaser J, Carroad PA, Dunkley WL (1980) J Dairy Sci 63:37
29. Chen Z, O'Brien S (2008) ACS Nano 2:1219
30. Laves F (1956) In: Proceedings of theory of alloy phases: a seminar on theory of alloy phases held during the thirty-seventh national metal congress and exposition, Philadelphia, USA, October 15 to 21, 1955, American Society for Metals, p 125
31. Solomon T, Solomon MJ (2006) J Chem Phys 124:134905
32. Weitz DA, Huang JS, Lin MY, Sung J (1985) Phys Rev Lett 54:1416
33. Malaquin L, Kraus T, Schmid H, Delamarche E, Wolf H (2007) Langmuir 23:11513
34. Heath JR, Kuekes PJ, Snider GS, Williams RS (1998) Science 280:1716