

MATERIALS SCIENCE

Colloids get complex

Alfons van Blaaderen

Self-organization of soft-matter components can create complex and beautiful structures. But the intricate structures created by adding a second stage of organization could reveal more than just a pretty face.

The term 'soft matter' denotes materials that are easily deformed by external stresses, and encompasses liquid crystals, polymers, surfactants and colloids (particles dispersed within another medium). Their basic constituents have characteristic sizes of between several nanometres and several micrometres, and, crucially, have the potential to self-organize, forming beautiful, regular three-dimensional structures. A triplet of recent papers¹⁻³ presents the latest such structures: complex colloids formed through self-organization on scales up to a micrometre.

Alternative terms that have been used to describe these colloid structures — 'colloidal molecules', or 'patchy particles' — hardly do justice to their intricacy. What is considered a complex colloid is, admittedly, somewhat arbitrary: the colloidal 'ice-cream cones' (Fig. 1a) produced some years ago⁴, which resulted from repeated polymerization and the subsequent phase separation of the polymers formed, would certainly have merited the term complex colloid. The innovation of recent efforts, however, is that structures are being designed with a second stage of self-organization in mind. Such an approach, in which colloidal

particles are first formed at soft-matter scales, and then built up to far more intricate structures, should allow unprecedented control over the three-dimensional organization of materials, as well as the combination of different materials over several length scales.

The results of Cho *et al.*¹, published in the *Journal of the American Chemical Society*, exemplify the fruits of this technique. The authors created complex colloidal structures (Fig. 1b, c) by drying emulsion droplets containing 'bidisperse' charged colloids, consisting of components of two quite different sizes — one on the nanometre and one on the micrometre scale. Using the same or opposite charges on the two components, an amazing richness of structural motifs could be obtained. Equally impressive results have been published by Lin *et al.*² (Fig. 1d) in *Chemistry of Materials* and by Zoldesi and Imhof³ (Fig. 1e) in *Advanced Materials*. Their structures were fabricated by depositing silica on liquid crystals formed by surfactants², and through the regular deformation by osmotic stresses of thin siloxane shells grown around emulsion droplets that are monodisperse (all the same shape and size).

It is important to mention at this point that

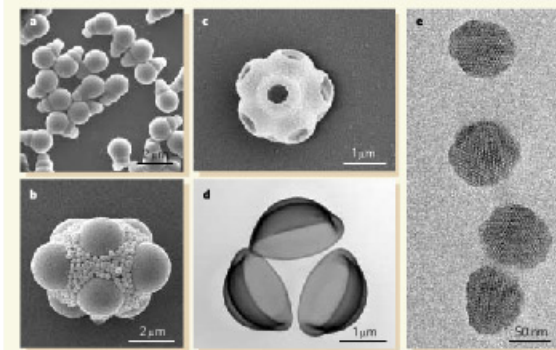


Figure 1 A selection of complex colloids achieved by various means of self-organization. **a**, 'Ice-cream cones' resulting from repeated polymerization and phase separation between polymers of different composition⁴. **b**, **c**, Through controlled drying of a binary dispersion in water-in-oil emulsion droplets¹; **b**, **c**, both colloids same charge; **c**, colloids with opposite charge. **d**, Through silica deposition on liquid crystal phases formed by surfactants². **e**, Through osmotic stress deformation of thin siloxane shells after growing them on monodisperse oil droplets³. (Courtesy of: **a**, John Wiley, Inc.; **b**, **c**, American Chemical Society; **d**, C. M. van Kats, D. C. 't Hart and I. D. Meeldijk; **e**, C. I. Zoldesi and A. Imhof. All scale bars are approximate.)

NEWS & VIEWS



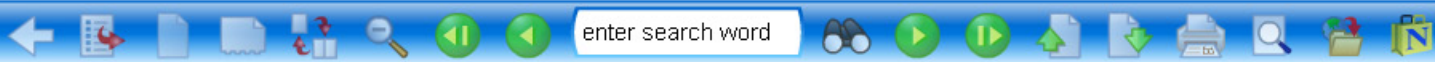
50 YEARS AGO

"The training of university teachers" — The question of the advisability and possibility of providing new recruits to university teaching with some initial guidance in the technique of their calling has been examined by S. Radcliffe, lecturer in German at the University of Bristol... In general, lecturers are conscientious about the matter of their lectures, but give little thought to their form or their delivery... [Radcliffe] suggests that an artist requires some basic instruction, at least in the rudiments of his craft. The following are a few of the purely mechanical skills which might be considered desirable in a good teacher or lecturer. First, the adoption of a fitting speed and clarity of diction. Secondly, the clear formulation and appropriate stressing of the main points of the subject under review. Thirdly, the ability to use a blackboard successfully. Fourthly, the 'staging' of material to make it come 'alive'... Learning the students' names is an essential requirement in establishing closer contact with them... The prompt return of written work not only helps to keep up students' interest in their subject, but also gives the right to demand written work from the students within the time-limit specified.
From *Nature* 4 February 1956.

100 YEARS AGO

"The Revolution of the Corpuscle" A corpuscle once did oscillate so quickly to and fro, He always raised disturbances wherever he did go. He struggled hard for freedom against a powerful foe — An atom — who would not let him go. The aether trembled at his agitations In a manner so familiar that I only need to say, In accordance with Clerk Maxwell's six equations It tickled people's optics far away. You can feel the way it's done. You may trace them as they run — dy by dy less dz by dz is equal $K dx/dt$
From *Nature* 1 February 1906.

50 & 100 YEARS AGO



NEWS & VIEWS

NATURE | Vol 439 | 2 February 2006

complex shape is no prerequisite for complex interaction. The adsorption of charged molecules on colloids with sizes of the order of micrometres⁸ and several nanometres⁹ has been shown, for example, to result in charges small enough that ionic colloidal crystals — crystals comprising particles of opposite charge — can form. The added complexity of the interactions between oppositely charged spheres, compared with components with the same charge, has already resulted in the number of different types of binary colloidal crystal that have been fabricated doubling within a few months¹⁰.

Starting self-assembly with complex colloids, however, offers increased possibilities. This is nicely demonstrated by a modest goal that many groups are aiming for: the creation of colloidal crystals with diamond symmetry. Such structures could be used to create a photonic crystal with a robust 'band gap' that can inhibit the propagation of light and modify the spontaneous emission of photons at visible wavelengths. These crystals are potentially as useful for manipulating the flow of light waves as semiconductor crystals have become for manipulating the flow of electrons. The interest in these three-dimensional structures is so great that they have even been assembled do-it-yourself style by placing thousands of colloids into a diamond lattice one by one¹¹. But, whereas just a few years ago most considered the creation of diamond lattices by self-assembly to be wishful thinking, several approaches now seem to make it an immediate prospect. Some proposed schemes, based on theory and computer simulations, make use of complex spherical colloids with either tetrahedrally arranged attractive patches¹² or, remarkably, non-additive spherically symmetric potentials that might be produced using particles coated with complementary strands of DNA (that is, that can bind together to form double-stranded DNA)¹³.

For a second self-organization step to succeed in any system, all particles must be monodisperse and the yield of the first step must be high. The polydisperse emulsion droplets created by Cho *et al.*¹ are therefore at present unsuited for self-organization into more complex three-dimensional structures, because no two colloid particles that they produce are exactly the same. But the path to monodispersity, clearly outlined by the authors, should not be too arduous.

Going even further than this, a crystalline arrangement of smaller monodisperse nanoparticles between larger spheres, or a mixture of oppositely charged and monodisperse nanocrystals of different composition, could be created. Transistors with a conventional two-dimensional layout can be made from self-organized colloidal crystals of nanoparticles¹⁴; by self-organizing such semiconducting colloidal crystals between larger colloids, such as those devised by Cho *et al.*, individual transistors could be arranged into regular, three-dimensional structures. A three-dimensional

wiring system could also conceivably be established by using spheres that comprise a conducting and an insulating part as the larger building blocks, allowing each transistor to be addressed individually as it sits in the lattice.

Even though the complex colloidal structures now being created are beginning to show a faint resemblance to the beautiful silica structures produced by diatoms, natural examples of self-organization on multiple length scales and from different materials are generally still far ahead of any human design. Such structures are always available in case we run out of inspiration¹⁵.

Alfons van Blaaderen is at the Debye Institute,

Utrecht University, Utrecht, The Netherlands. e-mail: A.vanBlaaderen@phys.uu.nl

1. Cho, Y.S. *et al.* *J. Am. Chem. Soc.* **127**, 15948–15975 (2005).
2. Lin, Y.S. *et al.* *Chem. Mater.* **17**, 4570–4573 (2005).
3. Zoldesi, C.I. & Imhof, A. *Adv. Mater.* **17**, 924–928 (2005).
4. Sheu, H.R., El-Aasser, M.S. & Vanderhoff, J.W. *J. Polym. Sci. A* **28**, 629–651 (1990).
5. Louisson, M.E. *et al.* *Nature* **436**, 235–239 (2005).
6. Shvachenko, E.V., Talapin, D.V., Katou, N.A., O'Brien, S. & Murray, C.B. *Nature* **439**, 55–59 (2006).
7. Garcia-Santamaria, F. *et al.* *Adv. Mater.* **14**, 1144–1147 (2002).
8. Zhang, Z., Keys, A.S., Chen, T. & Glatzer, S.C. *Langmuir* **21**, 11547–11551 (2005).
9. Tkachenko, A.V. *Phys. Rev. Lett.* **89**, 148303 (2002).
10. Talapin, D.V. & Murray, C.B. *Science* **310**, 86–89 (2005).
11. Mann, S. *Biomimicry: Principles and Concepts in Biomimetic Materials Chemistry* (Oxford Univ. Press, 2001).

NEUROBIOLOGY

Memories of a fruitfly

William G. Quinn

Despite its tiny size, the fruitfly brain is staggeringly intricate. So teasing apart how it remembers things — even a simple line pattern — is a daunting task. Progress is being made, thanks to genetic innovations.

Neuroscientists these days have a satisfactory understanding of how individual neurons work and of how they communicate with their immediate neighbours. By contrast, understanding at the next level of organization is hazier; for example, how neurons form functional circuits, how these circuits encode behaviour and particularly how experience changes the activity and connectivity in circuits to alter behaviour.

In this fog, a natural question is: how simple a system can one study profitably? Molluscs such as the marine snail *Aplysia* have yielded much insight because they have large, simple neuronal circuits. However, these animals perform only very basic behaviours. Insects, on the other hand, often have intricate neural circuits and complex stereotyped behaviours, such as the dance language of the honeybee. But their neurons have seemed too small and tangled for conventional analyses. Advances in genetic techniques have overcome this problem of scale, and in this issue Liu *et al.* (page 551)¹ use these ingenious methods to begin to dissect finely how the fruitfly *Drosophila* learns visual patterns.

The authors take advantage of 'jumping genes', which can hop about the fly genome and splice themselves into chromosomes at random points. A jumping gene can be tailored to carry along another gene of interest — a transgene. If the transgene (called 'TG-1', say) is jumped into the DNA near a naturally occurring gene, it is usually expressed in the same tissues as the natural gene². This jumping-gene method is now highly developed in *Drosophila*, so that large numbers of fly

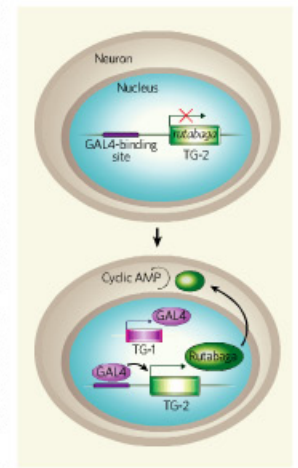
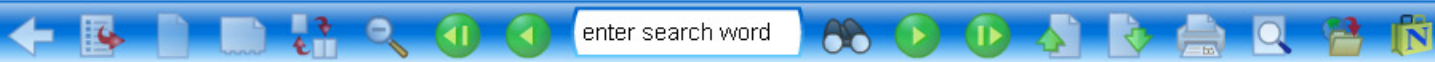


Figure 1 | Expressing a learning enzyme in selected cells. Liu *et al.*¹ used a strain of fruitfly that lacks a functional *rutabaga* gene, and added a substitute *rutabaga* gene (TG-2) that could be controlled by the transcriptional activator GAL4. By breeding these flies with various strains that express GAL4 only in certain subsets of neurons (from TG-1), they could ensure that the Rutabaga protein was produced only in those neurons. They then tested the flies' memories of various visual patterns.



NEWS & VIEWS

NATURE | Vol 439 | 2 February 2006

- 4. Suh, G. S. et al. *Nature* **438**, 854-859 (2004).
- 5. Yu, D. et al. *Colloid* **123**, 545-557 (2005).
- 6. Heisenberg, M. & Wolf, R. J. *Comp. Phys. A* **130**, 113-130 (1979).
- 7. Dill, M. et al. *Nature* **365**, 751-753 (1993).
- 8. Salber, P. P. et al. *Colloid* **37**, 205-215 (1984).
- 9. Zana, T. et al. *Science* **288**, 672-675 (2000).
- 10. Honesch, U., Fischbach, K. F. & Heisenberg, M. *Colloid Tissue Res.* **257**, 343-366 (1989).
- 11. Lee, T. & Luo, L. *Trends Neurosci.* **24**, 251-254 (2000).

CHEMISTRY

Catalysts live and up close

Bert M. Weckhuysen

Designing efficient solid-state catalysts would be easier if we knew which parts of them do what. Fluorescence microscopy could help: the technique allows single catalytic events to be observed in real time.

Catalysts are the workhorses of the chemical industry: more than 80% of all modern chemicals come into contact with at least one catalyst during their manufacture. They can also be extremely complex: solids with large surface areas, for example, possess many potential active sites in their crystal structure. In this issue, Roelfaers *et al.*¹ (page 572) premiere a method of 'filming' single catalytic events in real time on a solid crystal, allowing catalytic activity to be mapped over its whole surface. The innovation is a step further on the road to the 'rational design' of catalysts, which offers the prospect of improved formulations for existing catalysts, and more effective and selective catalysts created from scratch.

Rational design remains in most cases a pipe-dream: the experimental tools available for monitoring catalysts in action are still, in the main, too rudimentary. Nevertheless, this area of research — often referred to as *in situ* spectroscopy — has seen tremendous progress over the past decade, partially as a result of improvements in analytical instrumentation²⁻⁴. The latest contribution¹ exploits a method known as fluorescence microscopy. This technique has been used, for instance, in combinatorial catalysis, to screen whole series of catalyst libraries for the formation of fluorescence, and for monitoring the disappearance of specific organic molecules during catalytic transformations⁵⁻⁷. It has also been used to track the diffusion patterns of fluorescent molecules, and to determine their diffusion coefficients in different porous oxides^{8,11}. Furthermore, fluorescence microscopy can monitor the adsorption and desorption of a dye molecule by individual crystals of a catalyst material¹².

The distinctive aspect of Roelfaers and colleagues' work¹, however, is the use of high-resolution fluorescence microscopy to observe a catalytic crystal at work in liquid-phase reactions. The high sensitivity of their approach enabled the authors to monitor single catalytic events in real time by observing a 'reporter' molecule that becomes fluorescent only after catalytic action. They could thus beautifully map the spatial distribution of active sites over a single catalytic crystal.

The authors tested the method on a layered double hydroxide (LDH) catalyst consisting of prismatic crystals with large basal planes and lateral faces (see Fig. 1 on page 573). Intriguingly, the tracks of the fluorescing molecules revealed that one reaction, ester hydrolysis, is catalysed only by active sites on the lateral faces of the LDH particle, whereas another reaction, transesterification, occurs on the entire outer crystal surface. In the terminology of surface scientists, ester hydrolysis is a structure-sensitive reaction, whereas transesterification is not.

Such 'crystal-face-dependent' catalysis has already been observed on metal single-crystal surfaces, for example in the synthesis of ammonia, where the rate of product formation is found to depend critically on the orientation of the crystalline iron catalyst¹³. But the current work is, I believe, the first of its kind to use catalytic solids in liquid-phase applications.

Whether fluorescence microscopy can be introduced as a more general method for *in situ* spectroscopy in catalysis research clearly depends on the availability of a sufficient range of fluorescent molecules that respond to different reactions. Attention should also be paid to the question of whether fluorescent reporter molecules behave like non-fluorescent molecules, and so indeed reproduce the distribution of catalytic sites reliably. Finally, fluorescence quenching — which may significantly affect the intensity of fluorescent emission — could become a problem, especially when the approach is extended to more severe reaction conditions.

Currently, work on the *in situ* spectroscopy of catalytic solids is divided, roughly speaking, into two groups, probably reflecting the differing expertise of the chemists involved. The first group focuses on the inorganic part of the catalyst material, and aims to capture its oxidation state and the geometrical structure of its bonds (its 'coordination environment'). This group uses techniques such as absorption spectroscopy and electron paramagnetic resonance. The second group, which focuses on the organic parts of the catalyst, uses nuclear magnetic resonance and vibrational

spectroscopic techniques, such as infrared and Raman spectroscopy, to illuminate reaction mechanisms and potential reaction intermediates.

With Roelfaers and colleagues' work¹, the organic chemists gain a new tool for their *in situ* spectroscopic work. Further efforts should be directed towards combining both schools of thought, focusing, with nanometre resolution, on both the inorganic and organic parts of a catalyst. That could allow crucial insights into changes in the coordination environment of an active site, as well the reaction intermediates formed. The results could then be interpreted in terms of catalytic reactivity and selectivity in a 'joined-up' fashion. Although combining two or more spectroscopic techniques might seem simple, many hurdles must be cleared before it becomes a reality^{14,15}.

But the main challenge is to push the resolution of *in situ* spectroscopic tools into the nanometre range. Transmission electron microscopy offers resolution at the atomic scale (around a tenth of a nanometre). Coupling this with electron energy-loss spectroscopy, in which the sample is bombarded with a monoenergetic beam of electrons, allows chemical mapping of a catalytic surface. However, the energy resolution of this technique is still too low to identify the different oxidation states of the bombarded material. Moreover, electron-based techniques also need low pressures (in the millibar range), and thus the results obtained may deviate from those of experiments performed under true reaction pressures.

So there is room for other spectroscopic tools that, in combination with Roelfaers and colleagues' fluorescence microscopy¹, could deliver both inorganic and organic information about a catalytic process, creating a powerful *in situ* nanospectroscopy technique for taking snapshots of a wide variety of catalytic solids at work. If this endeavour succeeds, rational catalyst design will be a step closer to realization.

Bert M. Weckhuysen is in the Department of Chemistry, Debye Institute, Utrecht University, Sorbonnelaan 16, PO Box 80083, 3508 TB Utrecht, the Netherlands.
e-mail: b.m.weckhuysen@chem.uu.nl

1. Roelfaers, M. B. J. et al. *Nature* **439**, 572-575 (2006).
2. Haw, J. F. (ed.) *In-Situ Spectroscopy in Heterogeneous Catalysis* (Wiley-VCH, Weinheim, 2002).
3. Weckhuysen, B. M. (ed.) *In-Situ Spectroscopy of Catalysts* (Am. Soc. Stevenson Ranch, CA, 2004).
4. Weckhuysen, B. M. *Chem Commun* 97410 (2002).
5. Hunger, M. & Weckhuysen, J. *Angew. Chem. Int. Edn* **40**, 2954-2971 (2001).
6. Thomas, J. M. *Angew. Chem. Int. Edn* **38**, 3589-3628 (1999).
7. Shogreness, K. H., Kim, P. & Harwig, J. F. *J. Am. Chem. Soc.* **121**, 7123-7127 (1999).
8. Copeland, G. T. & Miller, S. J. *J. Am. Chem. Soc.* **121**, 4306-4307 (1999).
9. Su, H. et al. *Anal. Chem.* **73**, 4434-4440 (2001).
10. Hellmegg, C. et al. *N. J. Phys.* **7**, 23 (2005).
11. Seebacher, C. et al. *J. Phys. Chem.* **104**, 5391-5395 (2001).
12. Roelfaers, M. B. J. et al. *ChemPhysChem* **6**, 2295-2299 (2005).
13. Spencer, N. D. et al. *J. Catal.* **74**, 129-135 (1982).
14. Bruckner, A. *Chem. Commun.* 1761-1763 (2005).
15. Beale, A. M. et al. *Chem. Commun.* 3015-3017 (2005).