

## NANOTECHNOLOGY

## The third way

The emergence of nanoscale features — such as magnetic and electronic patterns — in materials that are otherwise homogeneous provides a potential alternative to conventional top-down and bottom-up fabrication techniques. The way these features arise in manganite crystals is contentious, but could be explained using elasticity theory.

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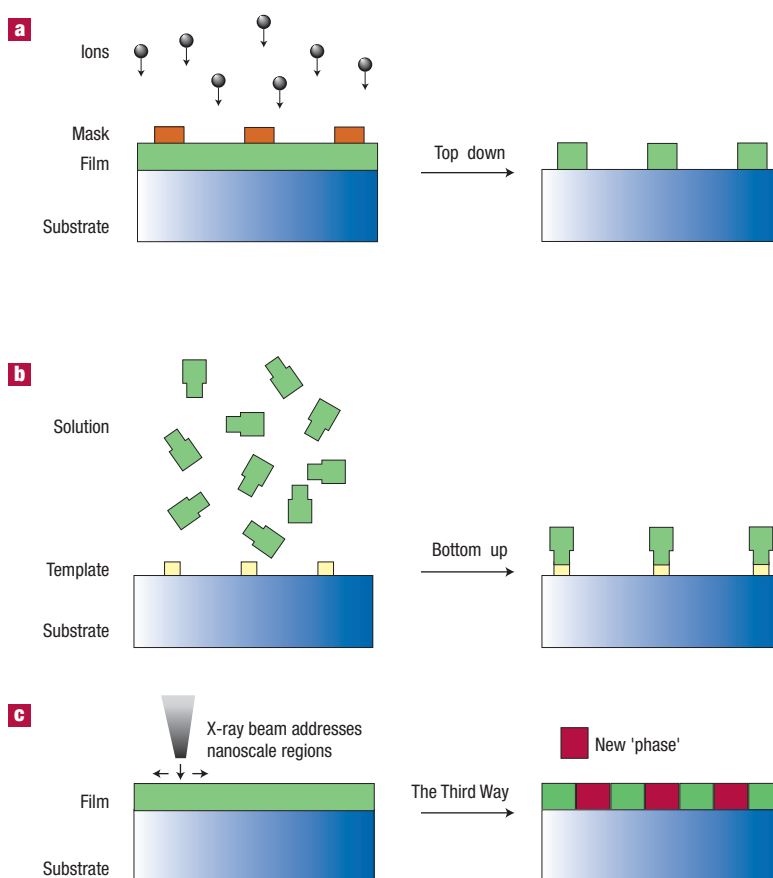
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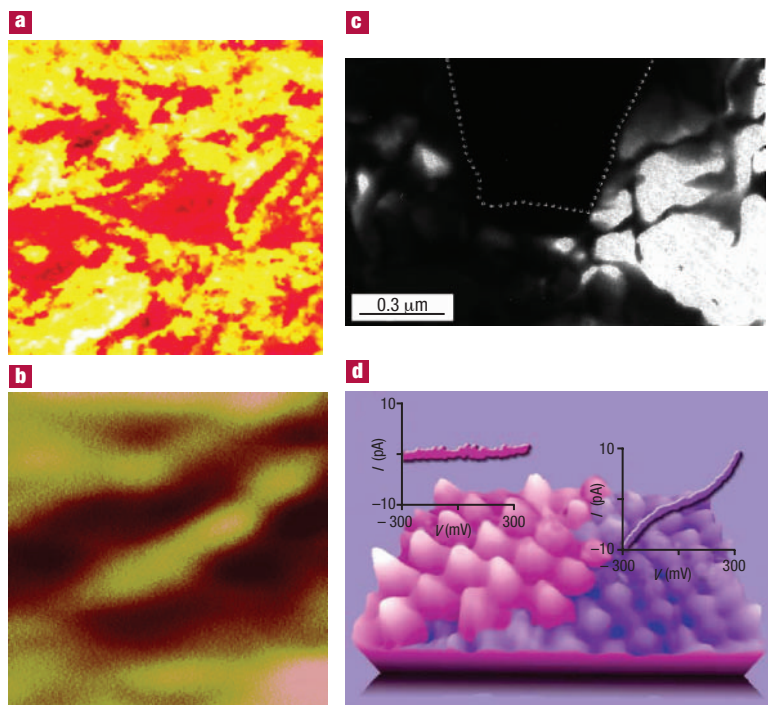
During the past few years, the manganites have undergone a second renaissance. These perovskite oxides of manganese first rose to prominence when it was discovered<sup>1</sup> in 1994 that large changes in electrical resistivity could be brought about by an applied magnetic field, a phenomenon known as colossal magnetoresistance. Unfortunately, magnetoresistance effects in the manganites are strongly temperature dependent. This, together with several other factors, has prevented the commercial exploitation of manganites in devices such as disc-drive read-heads. But fundamental and practical interest in the manganites is resurgent once more, because modern imaging techniques have revealed that the electronic and magnetic properties possess spatial variations over a wide range of length scales. These magnetic and electronic textures are poorly understood at present, but by considering the accompanying strain textures, Ken Ahn and colleagues report in *Nature* the basis of a convincing theoretical model for the observed complexities<sup>2</sup>.

The occurrence of magnetic and electronic texture in the manganites is exciting because it is unusual for such variations to occur in a continuous crystal lattice. A single crystal of a simple metal such as aluminium, for example, is homogeneously metallic throughout. But, in the manganites, valence electrons associated with manganese can become mobile and spin-aligned in some regions of a crystal, yet immobile and anti-aligned with each neighbour in other nearby regions of the same crystal. Consequently, within the same crystal there can be regions that are conducting and ferromagnetic, juxtaposed with regions that are insulating and antiferromagnetic. When the distances over which such variations occur is somewhat below a micrometre, this behaviour is referred to as phase coexistence (much like the coexistence of water and ice at 0 °C). But, when these variations occur over much smaller distances, measured in nanometres, such



**Figure 1** Three ways of creating nanoscale features. **a**, In a top-down process, material is removed from a monolithic entity resulting in the nanostructure. The example shown relates to a lithographically patterned resist mask that protects parts of a thin film during ion-milling. When the mask is later dissolved, the protected regions of the film remain. **b**, In a bottom-up process, building-blocks organize to form the nanostructure. The example shown relates to functionalized molecules coming out of solution to bind with a lithographically defined template such as gold. **c**, In a 'Third Way' process, the nanostructure is created within a homogeneous medium. The example shown describes how one might write patterns by locally addressing a film with electromagnetic radiation. This is reasonable given that an X-ray beam can alter the magnetic and electronic structure of a manganite<sup>9</sup>.

behaviour represents mesoscopic texture within a single thermodynamic phase.



**Figure 2** Magnetic, electronic and structural textures occur in manganites over a wide range of length scales, and may be probed using a wide range of techniques. **a**, Scanning tunnelling microscope image ( $0.61\ \mu\text{m} \times 0.61\ \mu\text{m}$ ) of the local electronic structure of a strained epitaxial  $(\text{La,Ca})\text{MnO}_3$  film (from ref. 3). The lighter regions are insulating and the darker regions are metallic. **b**, Magnetic force microscope image ( $6\ \mu\text{m} \times 6\ \mu\text{m}$ ) of ferromagnetic (dark) and non-ferromagnetic (light) regions in an epitaxial  $(\text{La,Pr,Ca})\text{MnO}_3$  film (from ref. 4). **c**, Dark-field transmission electron microscope image of a thinned  $(\text{La,Pr,Ca})\text{MnO}_3$  sample showing bright submicrometre regions that possess a structural modulation not present in the dark regions (from ref. 5). **d**, Scanning tunnelling microscope image of a  $(\text{Bi,Ca})\text{MnO}_3$  single crystal (adapted from ref. 6) suggesting that structurally modified unit cells (pink peaks, on the left) are associated with the current–voltage ( $I$ – $V$ ) characteristics of an electrical insulator, whereas unmodified unit cells (purple peaks, on the right) are associated with the  $I$ – $V$  characteristics of a metal. The boundary between the two regimes is atomically sharp and, in addition, it is mobile.

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The interest in mesoscopic texture in the manganites is more than academic. To continue to miniaturize transistors beyond the limitations of silicon for the computers of tomorrow, it is necessary to look at nanostructures based on alternative materials to silicon. The manganites provide an interesting test-bed for this purpose, because by controlling the mesoscopic textures one can dream of a nanotechnology in which self-organized functional structures are fabricated within homogenous media. This approach would contrast existing top-down and bottom-up syntheses (Fig. 1).

The model constructed by Ken Ahn and colleagues captures a key aspect of manganite physics by creating an energy landscape based on spatially varying short- and long-range strain fields that are explicitly coupled to each other. Tracking the evolution of various initial strain-field configurations (towards lower-energy states) yields a rich tapestry of behaviour in which distorted regions coexist with undistorted regions. The electronic structure of the system can be plausibly

inferred from this energy landscape, with distorted regions being electrically insulating and undistorted regions being metallic. Moreover, the length scales spanned by these coexisting regions can be controlled to match those observed experimentally.

In any given run of the computer simulations of Ahn *et al.*, the length scale of the resultant texture is controlled by varying an elastic constant in the expression for the energy landscape. This varies the depth of the local energy minimum associated with the locally undistorted state. If the elastic constant is small, then the locally undistorted state occupies a shallow minimum resulting in mesoscopic texture, as seen experimentally using scanning tunnelling microscopy (Fig. 2a)<sup>3</sup>. However, if the elastic constant is larger, the locally undistorted state will occupy a deeper minimum resulting in submicrometre texture, as seen experimentally using magnetic force microscopy (Fig. 2b)<sup>4</sup> and transmission electron microscopy (Fig. 2c)<sup>5</sup>. In this latter scenario, phase coexistence was not automatically forthcoming in the simulation by Ahn and colleagues because of a lack of nucleation events. This may be a consequence of the theorists' crystals being too clean in comparison with real-world samples, which always contain some impurities that can seed nucleation events.

Intriguingly, the images generated by the strain-based model bear striking similarities to their experimental counterparts. The atomically sharp phase boundaries generated by the simulations are seen in scanning tunnelling microscope images<sup>6</sup> of a single crystal of  $(\text{Bi,Ca})\text{MnO}_3$  (Fig. 2d). And the nanoscale droplet pairs with opposing strain fields that arise during nucleation are reminiscent of the micrometre-sized magnetic domain pairs seen in epitaxial  $(\text{La,Pr,Ca})\text{MnO}_3$  films using magnetic force microscopy (private communication, A. de Lozanne, University of Texas, Austin, USA).

A key assumption made by Ahn *et al.*<sup>2</sup> is that the language of elasticity is sufficient to encapsulate the quintessential physics of the manganites. The fact that this simplification enables them to predict structural textures over the wide range of length scales that are observed experimentally is impressive. This coherent picture is a direct advance over previous models<sup>7</sup>, which separately ascribe short-range (nanoscale) texture to coulombically expensive charge fluctuations, and long-range texture (phase coexistence) to uncontrollable chemical disorder.

However, the model is only a beginning, because two parts of the jigsaw are missing. First, the magnetic and electronic textures are considered slave to the strain textures. A more complete picture should represent all three textures using interdependent dynamical variables. This interrelation could be realized through microscopic theory. Second, the present model does not yet make an explicit link to chemical composition<sup>8</sup> and other important experimental parameters such as magnetic field. Nevertheless, the model forms a sound basis for understanding and ultimately manipulating the textures seen in the manganites. In time, it should enable scientists to build a full understanding of the manganites, while those with a more applied bent contemplate a Third Way of generating nanotechnology.

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## BIOMIMETIC POLYMERS

## Tough and smart

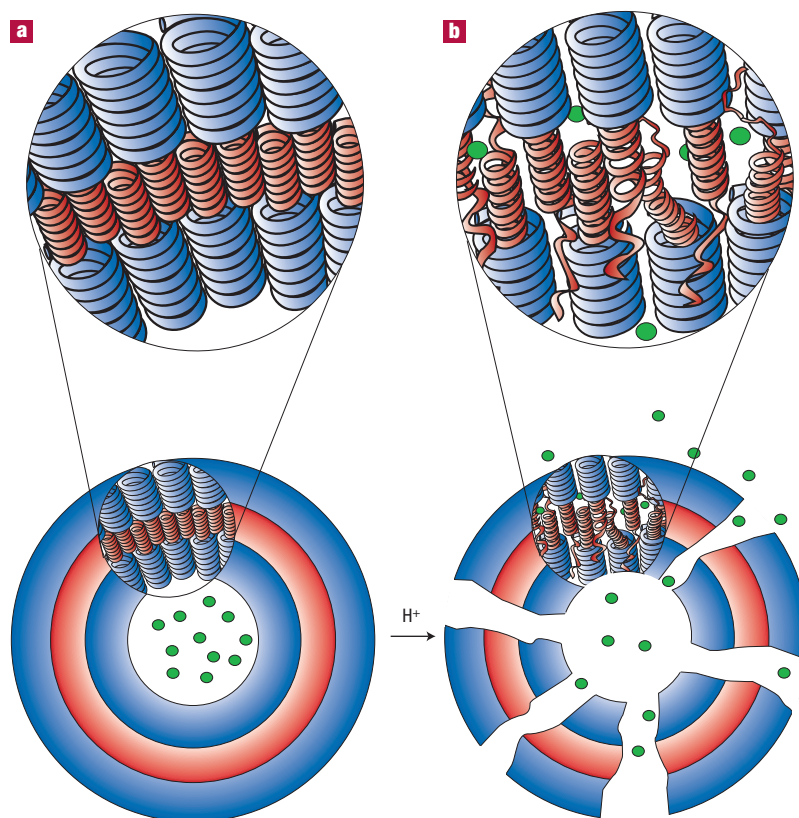
Vesicles for drug delivery should ideally be robust and able to release their cargo at the desired moment. A new type of vesicle, made of block copolypeptides, has exactly these characteristics.

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**H**ow do you make a parcel on a nanoscale, wrapping a molecule up in a robust package that will somehow unwrap itself when the molecule is needed? This is a trick that would be very useful for drug and gene delivery. As is often the case, nature has perfected some impressive ways of doing this, not always with benign results. For example, in viruses, delicate nucleic acids are wrapped up in a robust protein coat, which releases them at the correct moment to infect cells. In this issue of *Nature Materials*, Enrico Bellomo *et al.* report a synthetic approach to molecular delivery that mimics some aspects of these biological mechanisms<sup>1</sup>.

The starting point for synthetic molecular delivery systems are the liposomes — the prominent selling-point of many implausibly expensive beauty creams and lotions. The building unit for a liposome, or lipid vesicle, is a lipid bilayer. Lipids are amphiphilic molecules like soaps, in that one end of the molecule is hydrophobic, with the other end hydrophilic. The geometry of a lipid molecule is such that they self-assemble into bilayer sheets. A liposome is the roughly spherical bag that is obtained when a lipid bilayer folds back on itself to make a closed surface. The water inside the closed surface is completely cut off from the outside world, and a molecule trapped inside the liposome is effectively isolated.

Lipid vesicles are well known, and relatively easy to make from cheap ingredients (despite what cosmetics companies would have us believe). But they are not very robust; their walls are as thin and insubstantial as a soap bubble. An altogether more useful product is obtained if the lipid is replaced by a block copolymer<sup>2</sup>. A block copolymer is the polymeric analogue of a lipid, with two or more blocks having different water affinities covalently linked together: if the architecture is correct, copolymers will self-assemble, like lipids, into sheets,



**Figure 1** Smart drug carriers. **a**, The block copolypeptides synthesised by Bellomo *et al.*<sup>1</sup> self-assemble into a trilayer vesicle structure made of hydrophilic helices (in blue) exposed to the water outside and inside the vesicle, and hydrophobic helices (in red) in the middle. If the pH is lowered, the hydrophobic groups become positively charged and they change their conformation from helical to random coil. **b**, This perturbs the close packing of the vesicle wall and disrupts it, allowing drug molecules (the green spheres) to escape. Drug release can therefore be easily controlled through a change in pH.

and these sheets can be persuaded to fold over into bags or vesicles. The walls of these polymer vesicles