

Birth of a class of nanomaterial

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Nearly 30 years ago, a simple chemical principle was reported that enabled the synthesis of a plethora of porous materials – some of which might enable applications ranging from biomedicine to petrochemical processing.

In 1992, Kresge *et al.*¹ reported a breakthrough in materials science. They described multimolecular templates that guide the assembly of ordered mesoporous molecular sieves – materials that contain uniform, regularly arranged pores with mesoscopic diameters (between 2 and 50 nanometres). Their findings triggered an explosion of research into mesoporous materials, which have since been intensively studied for applications as diverse as catalysis, molecular adsorption, drug delivery and molecular separations using membranes.

When Kresge and colleagues published their work, materials known as zeolites – crystalline aluminosilicate compounds with uniform pores usually less than 2 nm in diameter – had long been used as catalysts in petroleum refining and for molecular separations. However, large molecules, such as those found in the heavy fractions of crude oil, were unable to diffuse through the small pores of these molecular sieves, and so could not be processed efficiently. There had been many attempts to obtain zeolite-like materials with enlarged pores and ordered structures, but the large-pore materials commonly available at that time all had a broad

distribution of pore diameters, making them unsuitable for many applications.

In 1990, it was reported² that the spaces between the layers of a silicate material called kanemite could be expanded by adding organic molecules containing long hydrocarbon chains to a suspension of kanemite powder in water. This process could generate pores of up to 4 nm in diameter, but worked only with kanemite.

Enter Kresge and colleagues, whose method for making mesoporous materials began with the formation of layers of silica, a few nanometres thick, in between the surfaces of cylindrical supramolecular assemblies called micelles (Fig. 1). The micelles consisted of numerous detergent-like molecules, known as surfactants, that were packed together to form a liquid-crystal structure reminiscent of a honeycomb. Once silica layers had formed between the micelles, the researchers heated the resulting material in air to remove the surfactant, thereby producing a silica product that retained a honeycomb-like array of nanometre-scale pores. The researchers named their material Mobil Composition of Matter No. 41 (MCM-41), after the oil company that they worked for.

The most impressive feature of Kresge and

colleagues' strategy was that the diameter, shape and connectivity of the pores could, in principle, be controlled by manipulating the structure and size of the surfactant molecules. The authors demonstrated only a few examples of this: they showed that the pore diameter could be controlled within a narrow range of about 3–10 nm. Nevertheless, their approach was later shown to be applicable to the full range of mesopore sizes³.

Researchers in the field initially regarded Kresge and colleagues' work as simply extending the pore sizes of the existing family of molecular sieves. However, it soon became apparent that the surfactant-based strategy could be used to synthesize many types of ordered mesoporous material, including ones made from metal oxides⁴, organic polymers⁵ and even transition metals⁶. Having the ability to make a variety of mesoporous materials that contain highly ordered arrangements of pores opened up many avenues of research for nanoscience.

A key development in 1998 was the use of polymeric surfactants⁷, which increased the size of mesopores that could be made to 30 nm. Polymeric surfactants used in the synthesis of such large-pored materials, as well as other organic surfactants (including the one used to make MCM-41) are now classified as soft templates, which reflect the somewhat deformable nature of the micelles that act as the mould. An advantage of using soft templates is that mesoporous materials can be made in solution at relatively low temperatures. Moreover, the porous structure of the resulting material can easily be controlled by making simple modifications to the template molecules.

Another breakthrough, reported in 1999, was the discovery of hard templating (also known as nanocasting)^{8,9}. In this process, mesoporous materials are fabricated from precursor molecules using another solid mesoporous material as a mould, in a manner analogous to the casting of concrete pipes or bricks. Nanocasting has two somewhat cumbersome requirements:

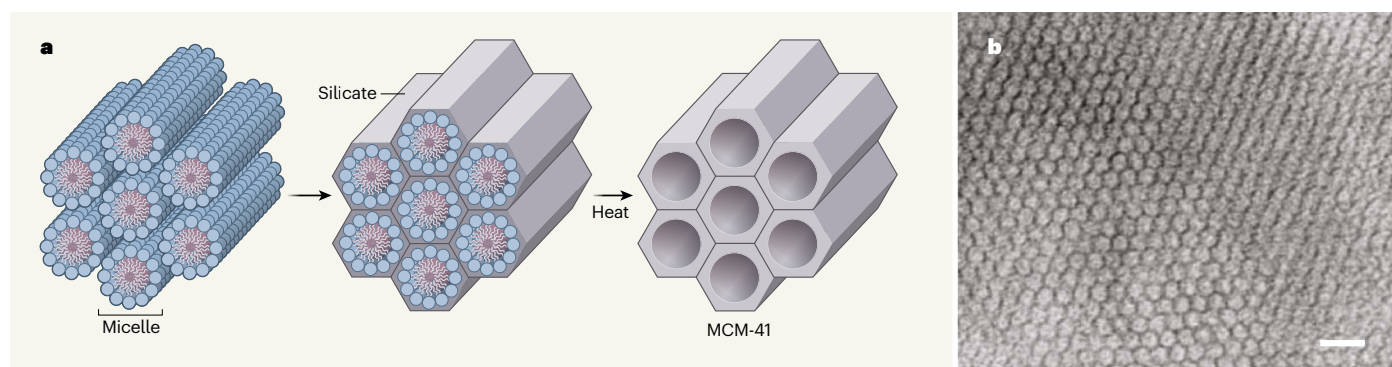


Figure 1 | Synthesis of the porous solid MCM-41. In 1992, Kresge *et al.*¹ reported the use of cylindrical molecular aggregates, called micelles, as templates for the synthesis of porous materials. **a**, In the first step, they formed a silicate layer between micelles stacked in a hexagonal array; the individual molecules in the micelles are shown as blue spheres with 'tails' attached. The authors then

destroyed the micelles using heat, thereby producing the porous silicate MCM-41. **b**, This micrograph¹ of MCM-41 reveals its uniform, honeycomb-like porous structure. Kresge and colleagues' template-based strategy has since enabled the synthesis of a wide range of potentially useful materials that contain ordered pores of 2–50 nanometres in diameter (mesopores). Scale bar, 100 ångströms.

the precursors must infiltrate the pores of the mould uniformly, without accumulating on the external surface; and the precursors must convert completely into the desired product. The method does, however, work particularly well when high temperatures (of the order of 500 °C or more) are needed to synthesize a mesoporous material. This contrasts with the use of surfactant-based soft templates, which typically decompose at temperatures above 200 °C.

Nanocasting was first used to make ordered mesoporous carbon⁸, but has since been developed as a general approach for synthesizing nanowires and nanoporous materials of various compositions, including metal oxides, organic polymers and metals¹⁰. Mesoporous carbons have garnered much interest because of their high electrical conductivity¹¹, and because they can accommodate a large volume of guest atoms, molecules or particles inside the mesopores. For this reason, mesoporous carbons are considered to be particularly attractive candidates for electrode materials in chemical sensors¹², supercapacitors¹³ and high-performance batteries¹⁴.

Mesoporous materials are also gaining attention for biomedical applications such as drug or gene delivery^{15,16}. Mesoporous silicas, in particular, can be synthesized in various shapes and sizes, are often biocompatible and spontaneously degrade in human tissues – a property that could be used to release drugs trapped in the silica. Moreover, the ability to accurately control the diameters of mesopores in silica is expected to provide tremendous advantages in biomedical applications, because the pore sizes directly affect the loading and release kinetics of drugs in delivery systems.

The main uses envisaged for mesoporous materials include as adsorbents in industrial processes for separating chemicals, and as catalysts in petrochemical refinery processes. Indeed, the original motivation for Kresge and colleagues' MCM-41 research was to synthesize catalytic materials for petroleum refining¹⁷. But although MCM-41 had sufficiently large pores for this purpose, its glass-like amorphous framework showed poor catalytic activity.

Ever since, enormous efforts have been made to synthesize mesoporous materials that contain crystalline, microporous, zeolite-like frameworks, which exhibit high catalytic performance. A breakthrough was made ten years ago, with the report of a specially designed surfactant molecule that enables the synthesis of such materials^{18,19}. The catalytic properties of the resulting mesoporous zeolites have not been fully explored for industrial processes, because the required surfactant is costly and not yet commercially available. However, I expect that mesoporous zeolites will trigger the next explosion of research in this field, by opening up many opportunities for catalytic applications.

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Palaeontology

Evolutionary insights from *Australopithecus*

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In 1925, a *Nature* paper reported an African fossil of a previously unknown genus called *Australopithecus*. This finding revolutionized ideas about early human evolution after human ancestors and apes split on the evolutionary tree.

Australian-born Raymond Dart had barely started his job as chair of the anatomy department of the University of the Witwatersrand in Johannesburg, South Africa, when he made a momentous discovery. Using his wife's knitting needles, he painstakingly extracted a fossil (Fig. 1) from a chunk of rock found in Taungs (now known as Taung), South Africa. As he recalled¹, “the rock parted ... What emerged was a baby's face, an infant with a full set of milk teeth ... I doubt if there was any parent prouder of his offspring than I was of my 'Taungs baby' on that Christmas of 1924.” Better yet, the fossil fitted neatly with another type of fossil, called an endocast, formed from sediments accumulated inside the skull. The endocast reflects brain-surface details stamped on the braincase's inner walls. These fossils revealed a combination of ape-like and human-like features never previously reported together.

Convinced that the specimen, called the Taung Child, represented an extinct link between humans and our ape ancestors, Dart dispatched a report² to *Nature* by mail boat. He probably felt some trepidation because several fellows of the Royal Society in London, who had mentored and taught with him, considered the human forerunner to be the British specimen known as Piltdown Man (which was later exposed as a hoax). Piltdown Man's human-sized brain and ape-like jaw contrasted with the Taung Child's ape-sized brain and

human-like jaw and teeth. In Dart's view, the Taung Child looked more primitive and older than the main existing candidates for the earliest ancestral human relative – Piltdown Man and Java Man (*Homo erectus*) from Indonesia. Dart therefore described the Taung Child as a ‘man-ape’ rather than an ‘ape-man’, like Java Man, and named the species *Australopithecus africanus*, which means southern ape from Africa.

Dart declared that humankind's cradle was not in Indonesia or Britain as his contemporaries thought, but was instead in Africa, as Charles Darwin had previously suggested³. The comfortable habitats favoured by African chimpanzees and gorillas in Dart's time were more than 3,200 kilometres north of where the Taung Child dwelled, and Dart suggested in his 1925 *Nature* paper that intense competition for limited resources in harsh southern African landscapes “furnished a laboratory such as was essential to this penultimate phase of human evolution”. In the paper, he also reasoned that “enhanced cerebral powers possessed by this group ... made their existence possible in this untoward environment”, attributing intelligence based on his interpretation of human-like brain convolutions at the back of the specimen's endocast.

When the paper appeared, the Taung Child and 32-year-old Dart became world famous overnight. Yet not everyone was receptive to new ideas about human evolution. Indeed,