INTO THE FOURTH DIMENSION

An Australian institute is designing and printing objects that can shapeshift after they're made. Forget next-gen – **Denise Cullen** reports from the next dimension.

Materials scientist Liwen Zhang dips a pair of tweezers into a beaker of iced water (0°C) and plucks out a small grey object the shape of a lotus flower in full bloom.

He plunges it into a second beaker filled with tepid water (15°C). When Zhang retrieves it after a few seconds, the flower has flattened out to form a disc shaped like a picture-book sun.

This demonstration, unfolding during my tour of The University of Queensland's Australian Institute for Bioengineering and Nanotechnology (AIBN), may seem simple, but it's an example of the remarkable and pioneering field of four-dimensional (4D) printing.

This emerging process – which is how the shapeshifting object was made – has profound implications for a range of fields, from manufacturing and medicine to fashion and furniture.

The AIBN's Group Leader, Senior Research Fellow and NHMRC Emerging Leadership Fellow, Ruirui Qiao, explains that 4D printing is an extension of three-dimensional (3D) printing.

"3D printing is the technology – 4D printing is just the process," she says. "The fourth dimension is actually time – these structures can change their shape over time."

STEELCASE

MIT's Skylar Tibbits (below) highlighted the essential weakness in 3D printing in a 2013 TED talk: once fabricated, 3D-printed objects couldn't be altered. 4D printing would correct that flaw, he said.

There's no such thing as a 4D printer. Rather, items assume the mantle of 4D by the way in which specific ingredients are combined to give the finished product useful qualities and abilities. Using a readily available 3D printer purchased for about $300, Qiao and Zhang turn out solid objects with the capacity to morph into different forms when exposed to stimuli such as heat, water or light.

4D printing is already in use in the medical device sector to create coronary stents, artificial muscles and other devices that adapt and change shape inside the body.

But having the ability to customise and shape materials after printing opens up the possibility of broader manufacturing breakthroughs and consumer innovations, from self-healing plumbing pipes to clothes that react to weather. And in good news for anyone who's ever struggled to put together an IKEA cabinet, 4D printing might also lead to self-assembling furniture.

"4D printing is a rapidly evolving field that is really only limited by imagination," Qiao says.

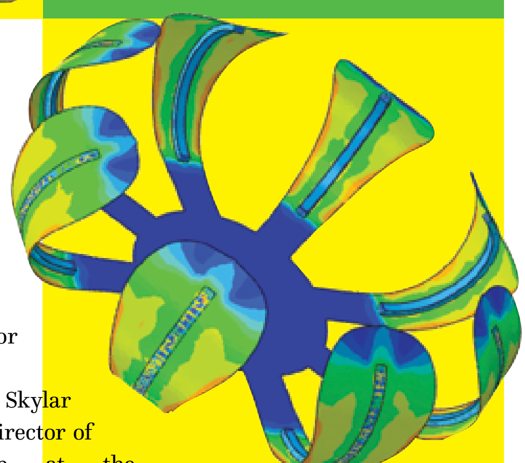
THE FOURTH DIMENSION

It's been almost five decades since the advent of 3D printing.

Sometimes called additive manufacturing, 3D printing creates three-dimensional objects layer by layer, using a digital file. This permits the creation of complex structures with minimal waste.

The two most commonly used techniques are fused deposition modelling – where molten material is deposited on a bed layer by layer using a heated nozzle – and stereolithography (SLA), which uses a UV laser to

UQ materials scientists Liwen Zhang (above, at right) and Ruirui Qiao (left) are among the 4D printing leaders in Australia. Qiao says the field is limited only "by imagination".



selectively cure a polymer resin and thus build successive layers.

A range of objects, from architectural models to dental crowns, can be built by printing successive layers in plastic, metal, resin or other materials.

In a 2013 TED talk, Skylar Tibbits – founder and co-director of the Self-Assembly Lab at the Massachusetts Institute of Technology (MIT) – highlighted the flaw inherent in 3D-printed objects: they were static, inanimate and unable to change their form or function after they were made.

"Imagine if water pipes could expand or contract to change capacity or change flow rate, or maybe even undulate like peristalsis to move the water themselves," he said.

In his eight-minute presentation, he unveiled a new concept called 4D printing, in which objects printed using "programmable" or "smart" materials could transform from one shape to another directly on their own "like robotics without wires or motors". He brought the concept to life by dipping a 4D-printed single strand structure into water to reveal how it changed shape into the letters MIT; meanwhile, a different strand self-folded into a cube.

Tibbits didn't tell the audience exactly how he worked this magic. However, the authors of a 2021 review in the journal *Polymer* noted that it was done by using a moisture-responsive material over plastic. On contact with water, the material expanded due to the formation of a hydrogel. It worked, but there was only a 30% expansion, and the structure gradually degraded over successive folding and unfolding cycles.

TRIGGER POINT

Despite these early limitations, the idea of 4D printing caught on quickly.

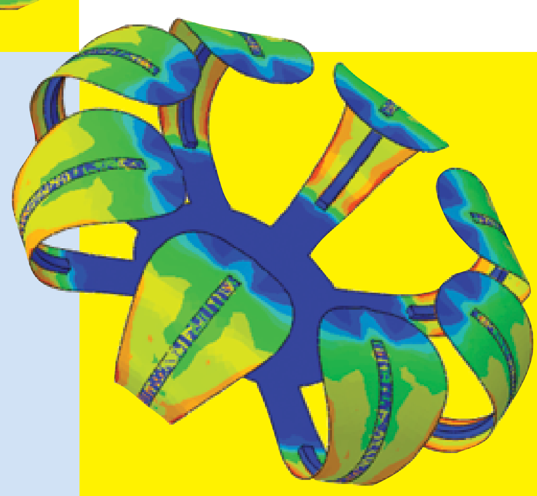
In 2015, US doctors treated three infants with a potentially fatal airway condition by implanting 3D-printed splints that changed shape as the children grew.

Writing in *Science Translational Medicine*, they explained that the splints – hollow, porous tubes – were stitched over the affected airways to provide scaffolding, improving the children's breathing.

Made with a "bioabsorbable" material known as polycaprolactone (PCL) that dissolves in the body over time, the splints stayed in place until the airway cartilage naturally strengthened with age and the associated risks of cardiopulmonary arrest abated.

An MRI follow-up in one patient at 38 months post operation showed fragmentation and degradation of the splint "with no problems related to the device". According to paediatric otolaryngologist and co-author Glenn Green, the splints were gone within four years.

His subsequent 2021 paper, and another published in *RadioGraphics* in 2022, reports that the same procedure has been since used in other children and adults.



TOP: AIBN. FLOWERS: *4D PRINTING SELF-MORPHING STRUCTURES*, MATERIALS 2019.

How 4D-printed objects react to stimuli like temperature, light or moisture depends on the intrinsic properties of the materials they are made from. A jacket made from polymers with "shape memory" properties could stiffen to provide extra insulation during cold weather and then revert to a more flexible, breathable state in warmer weather. Drug-delivery patches or implants based on hydrogels can swell in response to moisture (releasing medication) and contract in dry conditions (reducing the release of medication).

But a gamechanger arrived in 2017, with the introduction of nanoparticles to 4D printing.

INTO THE NANO-VERSE

Nanoparticles are tiny materials ranging in size from one to 100 nanometres. (As a point of comparison, a single human hair is approximately 80,000 to 100,000 nanometres wide.) Their size gives them unique physical, chemical and biological properties. Integrating nanoparticles into polymers or other materials for 3D printing allows creators to exercise enhanced control over how these materials respond to stimuli, without the challenges posed by other materials including stability and compatibility.

"WHEN YOU HAVE THE MICRO YOU CAN BUILD A FAR MORE INTRICATE PATTERN"

By enabling more precise and efficient shape changes, the integration of nanoparticles paves the way towards more complex and functional 4D-printed structures.

AIBN's director Alan Rowan likens it to the difference between working with the big clunky Lego Duplo sets versus the much smaller Nanoblocks.

"When you have the micro, you can build a far more intricate pattern," he says.

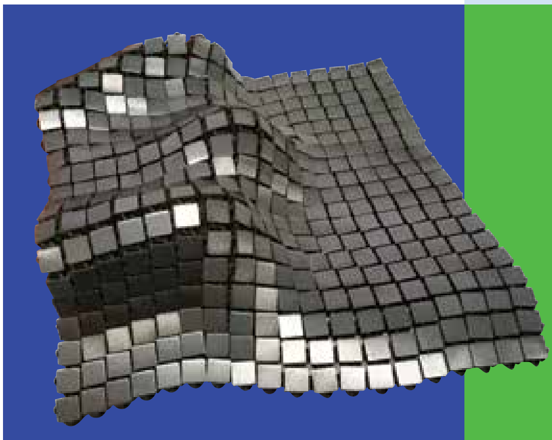
One conventional way to incorporate nanoparticles into 4D printing is to synthesise the nanoparticles and then immerse them in the resins, or "ink". However, writing in *Nature Communications* late last year, Qiao, Zhang and colleagues explained that blending nanoparticles directly into a molten polymer matrix didn't always imbue the 4D-printed materials with the desired shapeshifting capabilities.

Mixed in, the liquid metals tended to clump together or expel themselves during the printing process, and they were susceptible to oxidation. These factors detrimentally altered the properties of the printed materials.

So Zhang, Qiao and colleagues developed a method that is breaking new ground for 4D printing. They take small organic molecules responsible for controlling growth – called reversible addition-fragmentation chain-transfer polymerisation (RAFT) agents – and graft them onto liquid metal nanoparticles. They then synthesise nanoparticles into a polymer matrix during the polymerisation process, which improves the dispersal of liquid metal nanoparticles in solutions and prevents surface oxidation.

Qiao says the spherical liquid metal nanoparticles are created from bulk liquid metals. A bulk alloy of gallium and indium is added to 3D printing liquid resins; the metals are then directly reduced to nanosized liquid metal particles through the application of high-frequency sound waves (ultrasound) in a process known as sonication.

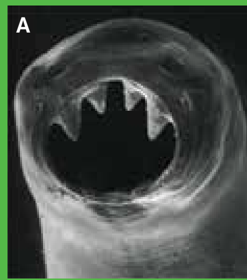
Finally, the liquid is placed in the 3D printer's resin tank and printed using the stereolithography method, in which a laser solidifies or cures the liquid resin with ultraviolet light.



SPACESHIP MATERIALS **NASA is creating a foldable, shapeshifting fabric that could be useful for large antennas and other deployable devices. The material could one day be used to shield a spacecraft, make astronaut spacesuits, or capture objects on the surface of another planet. One side of the fabric reflects light, while the other absorbs it, acting as a means of thermal control, the space agency reports.**

4D-PRINTED FASHION **In his book *Things Fall Together: A Guide to the New Materials Revolution* (Princeton University Press, 2021) Tibbits documented his team's experimentation towards a self-assembling shoe that sprung into shape when released from a rigid plate. He also explored climate-adaptable clothes, the fibres of which would expand or contract based on external temperature or moisture change.**

FROM TOP: NASA / JPL-CALTECH. MIT SELF ASSEMBLY LAB.



DRUG DELIVERY 4D-printed devices can release drugs when the target environment provides the correct stimulus. These scanning electron microscopy images show one such device: a thermo-responsive "theragripper" (B), which changes shape to latch onto mucosal tissue in the gastrointestinal tract and then release an encapsulated drug. The design of its sharp microtips is based on the teeth of a hookworm (A).

Ruirui Qiao's team have created a "soft gripper" (centre x 3) that can grasp and release small objects. 4D-printed objects may have application in fields as diverse as robotics and medicine.

FROM TOP: HUMAN PARASITOLOGY, 4TH ED. QI (KEVIN) GE / SUTD.

Like the lotus flower I saw, the resulting objects have shape memory properties. This means that they can return from an altered state (the flower) to their original shape (the sun) when induced by an external trigger – in this case, shifting from a chilled to a tepid beaker of water.

Unlike Tibbits' 2013 demonstration, Qiao, Zhang and colleagues found that their 4D-printed materials remained "unaffected" through at least 25 cycles of programming.

In real-life medical and other applications, though, the trigger would not be water but a laser – near-infrared light irradiation, which increases temperature due to the excitation of molecules. So what it is about the shift in temperature that causes the object to change shape?

Qiao explains that this is due to a fundamental property of polymers. At a critical temperature threshold, they transition from a rigid, glassy state to a more flexible, rubbery state, due to the movements of the carbon chains polymers are composed of. Polymers are often chosen for applications based on their capability to be both rigid and flexible.

Incorporating nanoparticles into polymer matrices allows researchers to further tailor the glassy-to-rubbery transition behaviour.

Other stimuli that can induce change in 4D-printed objects include moisture, magnetism, UV light, electrical energy, pH value, glucose and enzymes. The mechanisms of change are similarly diverse, potentially including an expansion in mass due to absorption (as in Tibbits' shapeshifting strands), thermal expansion, molecular transformation or organic growth – though it depends upon the precise combination of materials used.

A NEW ERA

While I saw a lotus flower, Qiao and her team have also designed a claw, or soft gripper, capable of grasping a cap and then releasing it. In much the same way, other 4D structures can be coaxed into performing a range of different mechanical tasks with infrared lasers – meaning they can bend, grasp, lift and release items five times their weight.

Zhang says this method allows the researchers to produce objects that can be customised, shaped and prompted to change over time without the need for wires or circuits. "This is a new era for robotics applications and a gamechanger for additive manufacturing," he says.

There is also huge potential for the use of such devices in the medical field.

"For example, you could print a stent structure, and you could put it in the vascular [system] and use light to trigger a change in shape which causes the stent to expand [inside the blood vessel]," says Qiao.

While further research is required to develop a stent with sound biocompatibility and the right level of responsiveness, Qiao anticipates that this research will be in market within two years.

She's also planning to upgrade the laboratory's $300 printer. While most 3D printers can incorporate nanoparticles into 4D printed composites, cheaper models have limitations in terms of the intricacy of the structures they can create, and the maximum size of the object.

Such a printer may cost in the ballpark of $20,000 – a massive upgrade. What will they make with it? In time, I'll have to come back and see.

DENISE CULLEN is based in Brisbane. Her story on the Mandela effect appeared in Issue 99.