

DNA NANOTECHNOLOGY

A metamaterial with memory

DNA can be used to create a very soft gel with liquid-like properties that can return to a preset solid shape when water is added.

Ju Li and Liyuan Bai

In the film *Terminator 2: Judgment Day*, the robot assassin T-1000 — a liquid metal nanomorph — can flatten under gravity, flow through a narrow opening and then reconstitute itself into a solid shape. Writing in *Nature Nanotechnology*, Dan Luo and colleagues now report a gel with very similar properties¹. The gel is made from water and DNA molecules, and has a very low elastic modulus (~10 Pa, which is less than 1/100th the elastic modulus of human muscle). The material is so soft that it completely collapses under its own weight if without water and can conform to the shape of a container. The waterless gel puddle it forms can also be easily manipulated and could, for example, be made to flow through the narrow opening beneath a door. Then, once on the other side, the puddle can spring up and morph into a preset solid shape just by adding water.

The researchers — who are based at Cornell University, the University of Seoul, Hiroshima University, Samsung Advanced Institute of Technology, and Suzhou Institute

of Nano-Tech and Nano-Bionics — describe their gel as a mechanical metamaterial. Metamaterials have internal structures designed to give properties — in this case mechanical properties — not often found in nature^{2,3}. They are typically made of inorganic materials such as silicon and have unusual electromagnetic or acoustic properties. However, the unusual properties of this organic metamaterial are more closely related to shape-memory polymers.

Shape-memory polymers are well known and are used in applications such as biomedical implants and dry adhesives^{4,5}. The significant difference between the DNA gel of Luo and colleagues and shape-memory polymers is that the so-called temporary shapes of the gel are not fixed. Therefore, instead of solid shape-to-solid shape transitions, the gel provides an arbitrary liquid shape (that of the container or an 'amoeba' shape if unconfined) to solid shape transition. The liquid-like shape multiplicity of the material should give it an advantage in transporting through narrow

channels. Furthermore, the researchers show that the material can be used in electrical switch applications — the gel becomes electrically conductive after it is doped with gold nanoparticles — and the shape conformity of the liquid-like state should be able to provide better electrical contacts.

The DNA metamaterial is formed by using a polymerase enzyme to extend and weave long strands of DNA into a non-covalently bonded 'physical' gel. With the help of electron microscopy, a structural unit is identified that looks like a bird's nest of woven DNA and has a diameter of 0.3 to 2.3 μm . Similar to the hierarchical DNA packaging inside a eukaryotic cell nucleus (nucleosome→solenoid→fibre), the gel also seems to be hierarchically structured: to be visible under the electron microscope, the sheet-like constituents of the 'bird's nest' must be much larger than a single DNA molecule. The analogy with eukaryotic DNA packaging only goes so far, however, because the artificial gel seems to pack much less DNA per volume, and is also a bulk-scale material.

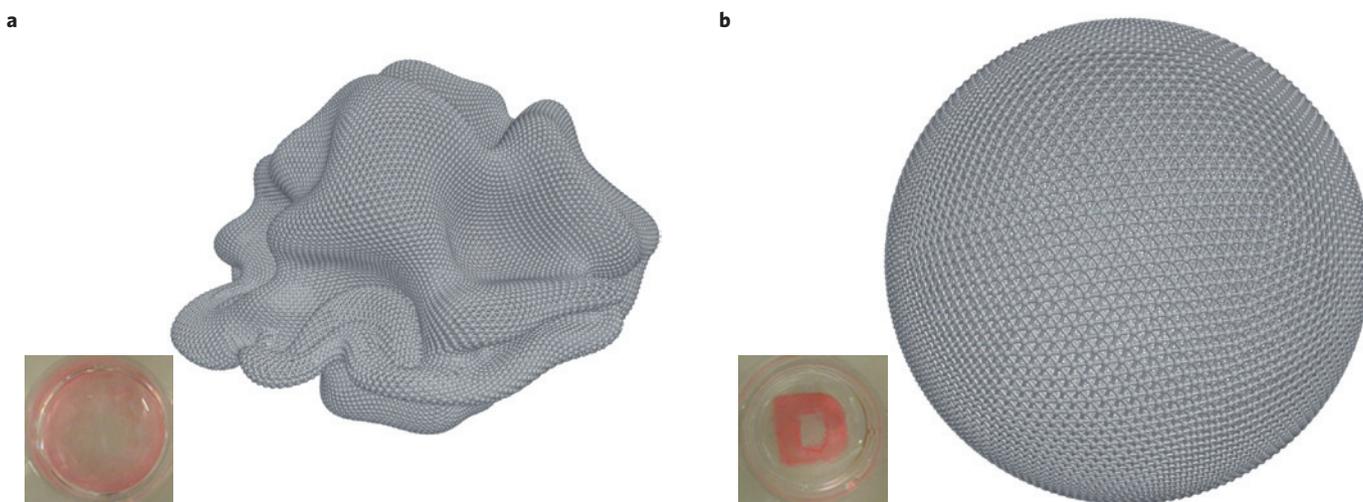


Figure 1 | A potential mechanism for the liquid- and solid-like properties of the DNA metamaterial. **a,b**, The metamaterial has a very open network structure, which can be compared to a fishing net. An empty fishing net (**a**) can freely morph into numerous shapes, and under gravity will take the shape of its container (liquid-like). When swollen (**b**), however, the same fishing net can take only one shape (solid-like). Although this inflation mechanism is, in principle, infinitely repeatable, in order for the network to deploy rapidly it is important that it does not get heavily entangled and stuck. The photographs show the equivalent state of the DNA gel: liquid-like when without water (**a**) and solid-like when in water (**b**). Note, the exact structural origins of these properties are still unclear and therefore this analogy is only a speculative illustration.

The exact structural origins of the properties of the gel are still unclear, and further characterization and modelling will be required to clarify this relationship. Nevertheless, it is possible to speculate about its memory mechanism. Similar to the structure of shape-memory polymers, the solid-like shape of the DNA metamaterial must be fixed by a network of connectivities that persist with or without water, and encode and preserve the memory of the shape. The spatial density of the fixed connectivities must be very low in comparison with materials such as vulcanized rubber in order to explain the very low elastic modulus, and the gel, therefore, must be a very open network.

Without water, the open network is in a collapsed state⁶. In this form, the material can take on many configurations with similar energies (Fig. 1) and this shape multiplicity can be used to rationalize its

liquid-like behaviour. When volumetrically swollen, however, the shape multiplicity is removed, and a unique solid-like shape is created. Note that the entropy–volume relation of open networks seems to be quite different from that of gases or metals, where higher volume usually means higher entropy (multiplicities); here it is just the opposite.

The architect of this strange metamaterial is the DNA polymerase of a bacteriophage, $\Phi 29$, that arose out of natural selection and has now been exploited by Luo and colleagues. It weaves a material that perhaps has no evolutionary value in the past, but may have some industrial value in the future. In a similar vein, viruses have recently been exploited for photovoltaics⁷ and electrochemical energy storage⁸. As for the building material itself, DNA is a very special polymer with defined rules of engagement and a wealth of structural potential. Therefore, the gel developed by

Luo and colleagues could belong to a range of bulk organic metamaterials that offer a higher degree of design and control^{9,10} compared with traditional materials. □

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DILUTED MAGNETIC SEMICONDUCTORS

Copper joins the family

Magnetic circular dichroism on quantum dots doped with a small percentage of copper ions show the typical features of diluted magnetic semiconductors.

Jacek Kossut

In a diluted magnetic semiconductor (DMS), the substitution of a small amount of cations with transition metal ions enhances the magnetic properties of the weakly or non-magnetic host material. The transition metal ions have an incompletely occupied electronic *d* shell. This leads to a finite magnetic moment, which can be due either to the orbital momentum of the *d* electrons or to their spin momentum, or even a combination of both. The interaction of the conduction band electrons (mostly *s*-like in character) or valence band holes (primarily *p*-like) with these localized magnetic moments changes the magnetic properties of the whole material, usually leading to an increased spin splitting of the conduction and valence bands. In extreme cases, like in manganese-doped GaAs, the electrons or holes even mediate the magnetic interaction between different localized ions giving rise to ferromagnetism.

Manganese has traditionally been the favourite transition metal in DMSs, because it substitutes very neatly inside the host semiconductors, particularly group II–VI, for example CdTe, and because its *d* electrons have zero orbital momentum but a very stable 5/2 spin that interacts with *s*- and *p*-type

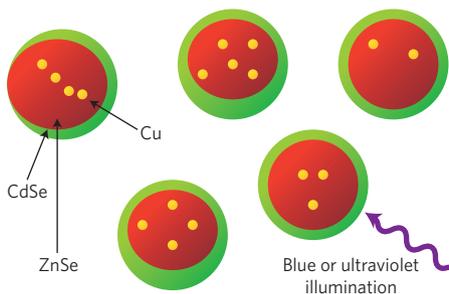


Figure 1 | Diluted magnetic semiconductor quantum dots studied by Pandey *et al.* have ZnSe cores (red) and CdSe shells (green) that exert additional stretching strain on the cores. Within the cores there are few copper ions (yellow) in a $3d^9$ configuration. Some of these carry localized spin $\frac{1}{2}$. Their magnetization induced by a magnetic field maybe increased in a persistent way by blue or ultraviolet illumination.

electrons in a simple and efficient way¹. This is not necessarily the case for other magnetic ion species where *L* is not equal to zero. Cobalt, iron and chromium were also shown to lead to sizeable *s*–*d* and *p*–*d* coupling. Now writing in *Nature Nanotechnology*,

Pandey *et al.*² show that a tiny amount of copper introduced in ZnSe–CdSe core–shell quantum dots effectively creates DMS quantum dots (Fig. 1). Previous attempts to use copper had been largely unsuccessful, regardless of whether bulk or nanostructures had been examined.

The amount of copper substituted in the dots by Pandey *et al.* is minute, estimated as four copper ions per dot. The same team had had previous indications that these types of nanostructures show DMS characteristics³.

Now they show it directly using magnetic circular dichroism measurements that reflect the *s*–*d* or *p* interaction in the dots. The researchers believe that the CdSe outer shell has a fundamental role in defining the magnetic properties. On the one hand the shell allows the copper ions to stay confined in the core. More importantly, the shell modifies the electronic structure of the dots so that the electrons in the copper ions are in a $3d^9$ configuration and have spin $\frac{1}{2}$. The shell also has an effect on the strength of the exchange interaction as it determines the extent to which the wavefunction of electrons and holes overlap with the $3d^9$ electrons localized in the copper ions.