

# Versatile strategy for making 2D materials

Wei Sun Leong

Two-dimensional materials have potential uses in flexible electronics, biosensors and water purification. A method for producing air-stable 2D materials on an industrial scale, now reported, is a key step in bringing them to market. **See p.492**

Modern materials science relies on a deep understanding of defects – interruptions to regular atomic arrangements in crystalline solids. Although ‘defects’ brings to mind imperfections and blemishes, they often make a material more useful than it otherwise would be. For example, metal impurities such as chromium and iron atoms in corundum (a crystalline form of aluminium oxide) are responsible for the colours of rubies and sapphires. Moreover, the addition of impurities to silicon has enabled the current era of computing and robotics. On page 492, Du *et al.*<sup>1</sup> report a method for producing a variety of technologically useful two-dimensional materials that contain deliberately introduced impurities, solving a fabrication problem for next-generation devices.

Transition-metal chalcogenides (TMCs) are emerging materials that hold great promise for their incorporation into a wide range of applications, from batteries and flexible electronics to biosensors and water-purification systems. They are composed of a transition metal such as molybdenum or tungsten and a chalcogen (an element in group 16 of the periodic table) such as sulfur, selenium or tellurium. The properties of TMC monolayers change greatly if the metallic element is altered. In particular, these structures can change from being normal metals to semiconductors, or even superconductors.

In the past few years, many researchers<sup>2–4</sup> have focused on making ultrathin electronics that have superior properties to those of existing silicon devices, by combining different TMC monolayers into a single object known as a heterostructure, using a technique called chemical-vapour deposition. Other researchers<sup>5</sup> have produced functional devices using a single TMC in which different regions of the material have different properties, such as being metallic or semiconducting. However, although these techniques are good for fabricating prototype devices, they are not practical enough for real-world applications.

The long-standing problem in incorporating

TMC monolayers into a functional device has been the lack of a metallic-phase TMC monolayer that is stable in ambient conditions for more than a month<sup>6</sup>. Du and colleagues overcame this challenge, and made metallic-phase TMC monolayers that they show can exist in such conditions for about a year. The authors achieved this feat by introducing a technology based on a process known as doping.

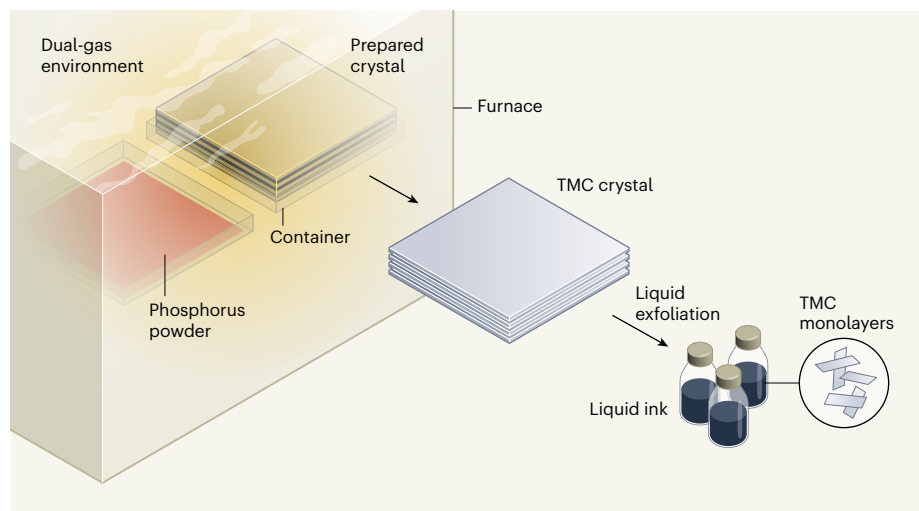
Doping has shaped the digital revolution – the shift from analog to digital electronics that began in the second half of the twentieth century. The process involves changing the electrical conductivities of semiconductors such as silicon by adding impurities. Eighty years ago<sup>7</sup>, dopant atoms of boron and phosphorus were added to pure silicon to produce materials called p-type and n-type silicon, respectively; these form p–n junctions, the basis of computing. This doping technology

continues to be useful today, and is found in our everyday electronics. Du and co-workers’ doping technology for 2D materials is also expected to have a long-term impact on the field.

The authors produced TMC monolayers in three steps (Fig. 1). First, they prepared a crystal that contained two different transition metals (one of which provided impurity atoms for TMC doping), an element in group 13 or 14 of the periodic table, and carbon. Second, they heated the crystal at high temperatures (873–1,373 kelvin) for 4 hours in an environment that contained two gases. One of these was a chalcogen-containing gas that supplied chalcogen atoms for the TMC; the other gas was phosphorus, which provided further impurity atoms for TMC doping. Third, the authors used a process called liquid exfoliation to convert the resulting TMC crystal into TMC monolayers in the form of liquid inks.

Du *et al.* used this three-step dual-doping technology to make, for example, metallic-phase TMC monolayers of tungsten disulfide that were doped with both yttrium and phosphorus atoms. They also produced undoped TMC monolayers by preparing layered crystals that contained one type of transition metal, rather than two, and removing the source of phosphorus gas. In total, the authors made six doped and seven undoped TMC monolayers, demonstrating the remarkable versatility of their approach for producing 2D materials.

One major advantage of Du and colleagues’ method is that the final 2D materials are in the form of liquid inks. There is clearly a shift in this field towards making high-quality monolayer



**Figure 1 | Method for producing air-stable transition-metal chalcogenides (TMCs).** Du *et al.*<sup>1</sup> demonstrate a technology for making monolayers of materials called TMCs that they show can remain stable in ambient conditions for about a year. They first prepare a crystal that contains two different transition metals, an element in group 13 or 14 of the periodic table, and carbon. They then place the crystal in a container and heat it in a furnace for 4 hours, in an environment containing two gases. One of the gases contains a chalcogen (an element in group 16 of the periodic table) and the other is phosphorus gas produced by heating phosphorus powder in a separate container in the furnace. The result of this process is a TMC crystal. Finally, the authors use a process called liquid exfoliation to convert the crystal into TMC monolayers in the form of liquid inks.

inks for commercialization<sup>8,9</sup>, rather than films produced by techniques such as epitaxial growth or chemical-vapour deposition. Such films require a process known as delamination to separate them from their growth substrates, which deteriorates the material's quality and necessitates further processing<sup>10,11</sup>. By contrast, monolayer inks can be readily deposited on arbitrary substrates using techniques such as inkjet printing or spin coating, and so are easily integrated into 3D systems<sup>12,13</sup>.

From a scientific standpoint, 2D materials need to be stable and usable in our immediate surroundings. Du and colleagues' findings are promising for the field because they show that the presence of a low quantity (less than 1%) of impurity atoms can stabilize TMC monolayers. This result suggests that materials researchers should start to explore the use of chemical elements to stabilize 2D materials that would otherwise degrade in ambient conditions within hours, rather than using encapsulation layers, which complicate the monolayer systems.

The next steps will be for theorists to predict suitable 'impurity stabilizers' for TMC monolayers, and for experimentalists to investigate the use of elements that are abundant on Earth. In the meantime, it should still be possible to build advanced machines for precise and reliable dual doping of TMCs, because only a low quantity of relatively rare yttrium and phosphorus is needed to stabilize TMC monolayers. Du and colleagues' work demonstrates that, whatever new materials are discovered, it is crucial that we understand, manipulate and use their atomic-level defects. Every atom matters.

**Wei Sun Leong** is in the Department of Materials Science and Engineering, National University of Singapore, 117575 Singapore. e-mail: weisun@u.nus.edu

- Du, Z. *et al. Nature* **577**, 492–496 (2020).
- Sahoo, P. K., Memaran, S., Xin, Y., Balicas, L. & Gutiérrez, H. R. *Nature* **553**, 63–67 (2018).
- Leong, W. S. *et al. J. Am. Chem. Soc.* **140**, 12354–12358 (2018).
- Zhang, Z. *et al. Science* **357**, 788–792 (2017).
- Kappera, R. *et al. Nature Mater.* **13**, 1128–1134 (2014).
- Lin, H. *et al. Nature Mater.* **18**, 602–607 (2019).
- Hey, T. & Pápay, G. in *The Computing Universe: A Journey through a Revolution 123* (Cambridge Univ. Press, 2014).
- Lin, Z. *et al. Nature* **562**, 254–258 (2018).
- Pan, K. *et al. Nature Commun.* **9**, 5197 (2018).
- Shim, J. *et al. Science* **362**, 665–670 (2018).
- Leong, W. S. *et al. Nature Commun.* **10**, 867 (2019).
- McManus, D. *et al. Nature Nanotechnol.* **12**, 343–350 (2017).
- Sivan, M. *et al. Nature Commun.* **10**, 5201 (2019).

## Microbiology

# Meet the relatives of our cellular ancestor

Christa Schleper & Filipa L. Sousa

Microorganisms related to lineages of the Asgard archaea group are thought to have evolved into complex eukaryotic cells. Now the first Asgard archaeal species to be grown in the laboratory reveals its metabolism and cell biology. **See p.519**

Complex life forms including plants, animals and fungi are known as eukaryotes. These organisms are composed of cells that contain membrane-bound internal compartments such as nuclei and other organelles. Imachi *et al.*<sup>1</sup> report on page 519 that a type of microorganism called an Asgard archaeon, which might shed light on how early eukaryotic cells evolved, has finally been cultured in the laboratory. The achievement will enable detailed metabolic and cellular investigation of microbes that represent the closest Archaeal relative of eukaryotes cultured so far.

It is thought that eukaryotes arose when two types of single cell merged, with one engulfing the other. A cell from the domain archaea is proposed to have engulfed a bacterial cell of a type known as an alphaproteobacterium, and the engulfed bacterium evolved into eukaryotes' energy-generating organelles – mitochondria.

However, the nature of the ancestral cell that engulfed this bacterium is unclear. Genomic analyses have strengthened the idea that this cell traces back to archaea because many archaeal genes involved in central biological processes such as transcription, translation and DNA replication share a common ancestry with (are phylogenetically related to) the corresponding eukaryotic genes. Was the alphaproteobacterium engulfed by a bona fide archaeal cell, or by an archaeal cell that had already acquired some eukaryotic characteristics, such as a nucleus? No fossils have been found that could shed light on the early eukaryotic ancestors. However, investigation of archaeal lineages has offered a way forward.

Since 2015, on the basis of genomic and phylogenetic analyses<sup>2</sup>, archaea of a newly discovered phylum termed Lokiarchaeota (after the Norse god Loki) have been proposed as the closest living relatives of the ancient archaeal host cells from which eukaryotes are thought to have evolved. Subsequent genomic research revealed yet more such lineages, for which other Norse gods have provided names (Thor, Odin, Heimdall and Hel)<sup>3,4</sup>, and which are now

grouped together with Lokiarchaeota into what are collectively termed Asgard archaea (Fig. 1). Intriguingly, all of these lineages contain an unprecedentedly large number of genes that encode what are called eukaryotic signature proteins (ESPs), which are usually found only in eukaryotes<sup>2,3,5,6</sup>. Heimdallarchaeota currently represent the predicted closest Archaeal relative of eukaryotes on the basis of phylogenetic analysis and the ESP content of their genomes<sup>3,7</sup>. However, all members of the Asgard archaea were previously identified, and their metabolism predicted, solely by their DNA sequences, and thus their cellular features have remained unknown until now.

Imachi and colleagues report that they have cultured in the laboratory an Asgard archaeon from the Lokiarchaeota phylum that they propose to call 'Prometheoarchaeum syntrophicum', which was obtained from deep-ocean sediments. The unusual shape and metabolism of Prometheoarchaeum prompt the authors to propose a new model for the emergence of the first eukaryotic cell. This event, predicted<sup>8</sup> to have occurred between 2 billion and 1.8 billion years ago, is one of the key cellular transitions in evolutionary biology, and is also a major biological mystery.

More than six years before Asgard archaea were even identified, Imachi and colleagues had already started to generate enrichment cultures of microorganisms found in deep marine sediments<sup>9</sup>. Their original goal was to find organisms that could degrade methane, and the authors searched for such microbes at a site about 2.5 kilometres below the ocean surface off the coast of Japan.

Imachi *et al.* set up a flow bioreactor device that mimicked the temperature (10 °C) and the low-oxygen and low-nutrient conditions at this underwater site. Within five years of starting this bioreactor work, a highly diverse consortium of active bacteria and archaea, including Lokiarchaeota, were obtained. Small subcultures were then used to gradually enrich for cultures in which archaeal cells were the dominant component, and