TWO-DIMENSIONAL MATERIALS

Polyphony in B flat

Early theories suggested the possibility of atomically thin boron layers, but electron-deficient boron favours multicentre bonds and assembles into various polymorphs, making the synthesis of such layers challenging. Now, in two independent experiments, the deposition of atomic boron has offered this long-sought material on a silver platter.

Zhuhua Zhang, Evgeni S. Penev and Boris I. Yakobson

Flat is in vogue. Since carbon made it so famously as graphene, other chemical elements and blends have rushed to follow suit; boron nitride, transition metal dichalcogenides, phosphorus, silicon and tin have all shown 2D forms that are nearly one atom thin, and have provoked a rush of attention in materials research. Boron, positioned just one to the left of carbon in the periodic table, combines properties of both metals and non-metals. A rich variety of bonding configurations can form between boron atoms, ranging from the expected two-centre two-electron bonds up to seven-centre two-electron bonds[1]. This leads to extreme bonding complexity in boron, boranes and boron-rich solids, which include a large number of allotropes.

Is there room for boron in the vigorously explored flatland? How would boron atoms assemble if confined to two dimensions? What new properties could such materials bring? These questions are particularly pertinent in light of the fact that boron clusters of up to tens of atoms do favour planar conformations with similar electronic structures to aromatic molecules. Recently, the similarities between boron and carbon were further extended by the experimental evidence of a cage-like B_{40} cluster[2]. If you unfolded its hypothetical sibling, a B_{80} buckyball, onto a plane it would lead to a boron α-sheet[3] (Fig. 1a) — one of the most stable sheets predicted theoretically, due to optimal filling of its orbitals.

In contrast to the well-defined lattices of graphene or hexagonal boron nitride (h-BN, also known as white graphene) the boron sheet has been predicted to be polymorphic[4]: within a narrow range of energies near the ground state, numerous lattices can exist that are set apart by the pattern of hexagon holes (or vacancies) in a reference triangular grid (Fig. 1a). In addition, 2D boron has been shown to adopt a structure that depends on which substrate the boron atoms are landing on[5] — a behaviour that has not been observed for other 2D crystals. This inherent polymorphism, further fine-tuned by the substrate, has rendered the experimental realization of 2D boron rather challenging.

In further contrast to most 2D materials (such as graphene, h-BN and phosphorene) for which the layered form is the natural ground state, boron's 3D bulk solid is lower in energy than any of its flat polymorphs. How then can the atoms be enticed into choosing the 2D route despite its ultimate thermodynamic disadvantage? A sufficiently 'sticky' substrate can selectively suppress the 2D nucleation barrier (all n atoms of a B_n sheet being attracted to the substrate, instead of only ~$n^{2/3}/6$ in the case of a 3D nucleus). Once this path has been chosen, boron is kinetically protected from converting into a 3D form (Fig. 1b) and just keeps growing in a planar manner. In light of this, detailed theories have suggested using metal substrates[5,6], such as Ag or Cu, to guide the synthesis of 2D boron.

Acting along these lines, two recent studies have now made spectacular advances in realizing the elusive 2D boron. Writing in *Nature Chemistry*, a team led by Kehui Wu has now described the successful synthesis
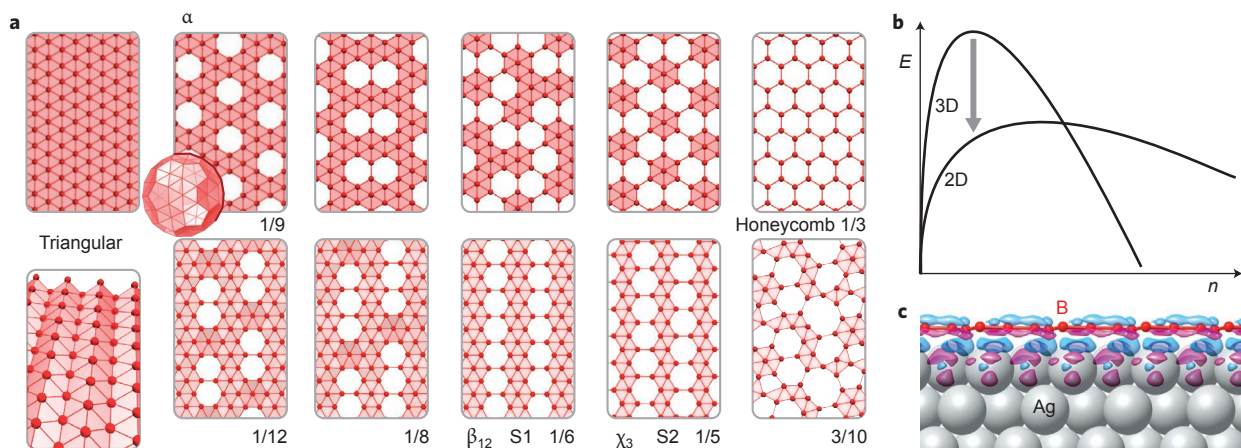

Figure 1 | Models of the structures and growth mechanism of boron sheets. **a,** The free-standing boron monolayer can have polymorphs featuring multiple patterns (a small selection is shown), from the close-packed triangular, to the familiar honeycomb. The numbers at the bottom right of each model mark the hole density, S1 and S2 are the observed phases[7], and the other labels (α, $β_{12}$, $χ_3$) are the identifiers given to the structures, as discussed in the text. **b,** The energies of the growing nuclei versus the number of atoms, $E(n)$, show how the substrate steers the synthesis towards the 2D route by suppressing the nucleation barrier (downward arrow). **c,** Computed charge density shows how the Ag surface donates electrons (from pink to blue) to the boron layer and provides just the right level of interaction[5,6], and also endows boron with a somewhat 'carbon character' that favours higher hole fractions.

of two 2D boron sheets, which are both one-atom thin and tens of nanometres wide[7]. This comes on the heels of the description[8] in *Science* by Andrew Mannix and co-workers, of very similar materials. A few months earlier, chemical vapour deposition of boron sources on copper foils had produced boron nanofilms of finite thickness[9], showing that the growth of atom-thin boron would require more delicate control. In their recent experimental realizations of 2D boron sheets, both teams[7,8] used molecular beam epitaxy, directly evaporating a pure boron source on a clean single-crystal Ag(111) surface.

The Wu group observed the formation of two sheets, referred to as S1 phase and S2 phase, which were characterized by scanning tunnelling microscopy (STM). This not only showed that the materials were indeed monoatomic layers, but also led the team to independently deduce for the S1 phase the same atomic structure that had been predicted by theory, for deposition of boron on the same Ag(111) substrate, just a few months earlier[5]. This atomic structure (known as the β_{12}-sheet) is a rectangular lattice displaying parallel rows of hexagonal holes (Fig. 1a) — in agreement with the common view that such holes are needed to stabilize 2D boron. The β_{12}-sheet structure for the S1 phase is supported by simulated STM images, as well as by an estimation of the density of boron atoms.

An experimental testimony to the predicted polymorphic subtle fabric of 2D boron is that the S1 phase could only be synthesized at ~570 K. At just a few degrees below, clusters and disordered boron were produced instead, whereas raising the growth temperature to 680 K yielded the S2 phase, apparently consisting of parallel rows of protrusions. The S2 phase was also obtained by annealing the S1 phase above 650 K. High-resolution STM images of the S2 phase seemingly reveal parallel atomic rows, in a similar manner to S1 yet with shorter inter-row distances and alternating bright segments. Those segments are organized in a regular brick-wall pattern, which is attributed to inhomogeneous electronic interactions with the substrate. This phase is proposed to have atomic structure known as the χ_3-sheet. The observation of two different phases coexisting at very similar conditions further corroborates the polymorphic nature of 2D boron. We also note that, relative to the α-sheet (hole density $\eta = 1/9$), both the β_{12} and χ_3 phases that formed on the electron-donating metal (Fig. 1c) are more sparse ($\eta = 1/6$ and 1/5, respectively), shifting the preference

of the boron arrangement towards a honeycomb structure ($\eta = 1/3$) — in a way, this is as if adding electrons gradually made electron-deficient boron 'more like carbon' (the extreme example of this is the boron honeycomb layer in the magnesium diboride, MgB_2).

In addition to the temperature, the boron deposition rate is important to the final product. In their study, using essentially the same growth method involving molecular beam epitaxy on Ag(111), Mannix and co-workers independently realized[8] two forms of atomically thin boron that exhibited different morphologies depending on the deposition rate. A low rate favoured a 'striped' phase consisting of a rectangular lattice that closely resembles the S1 phase described by Wu and co-workers in terms of measured lattice constants and STM images. Yet, rather than the β_{12}-sheet structure, a close-packed triangular pattern was proposed for this phase, on the basis of simulated STM images. This raises a question regarding the true atomic structure of the 2D boron sheets. *Ab initio* calculations show that the β_{12}-sheet is a better lattice match to Ag(111) (~1% mismatch) than the triangular one (~3% mismatch) and is also considerably more stable (lower in energy) on a substrate. One cannot exclude, however, the possibility that the growth dynamics may produce structures that are not global energy minima. Further structural characterization and exploration of the growth mechanism are warranted to reach a firm conclusion on the atomic makeup of this sheet.

The second phase observed by Mannix and co-workers, referred to as the homogeneous phase, appeared on STM images as periodically protruding atomic chains. Despite some differences in the details — owing to the different bias voltages used for STM imaging — this sheet does resemble the S2 phase described by the Wu group. Both show short-ranged rhombohedral patterns with the same periodicity, and so the two forms are likely to stem from the same atomic structure. However, Mannix and co-workers found that lowering the temperature and/or increasing the growth rate favours the growth of the homogeneous phase, and suggests that the homogenous phase is metastable relative to the striped one, whereas the Wu team observed that the S2 phase is preferred at higher temperature and concluded that the S2 phase is more stable than S1. Although Wu and co-workers propose a structural model for the S2 phase, these discrepancies show that — in the same way as for the S1 phase — the precise

arrangement of the boron atoms and holes in this polymorph is also far from settled and calls for further study. A better understanding of the growth kinetics and the inherent interplay between temperature and deposition rate is also needed.

In any case, the two reports agree that the boron layers are made of strong covalent bonds, leading to high in-plane stiffness (the β_{12}-sheet's stiffness is somewhat below that of graphene's high 340 N m^{-1}, but that of the triangular sheet is even higher, along its ridges). For out-of-plane bending, however, the β_{12}-sheet is fivefold softer than graphene, allowing for easy buckling undulations. Such undulations are very limited with the triangular structure, which is much harder to bend across the ridges. The mechanical robustness of the sheets may prove helpful in lifting the boron layers from their substrates, but such separation and transfer is a challenge yet to be dealt with, as is their protection from deteriorating in an ambient environment.

The boron sheets appear to be rather inert to oxidation in the short-term, perhaps owing to their planarity. Some oxygen was detected in the samples exposed to air, but this oxidation was mostly attributed to the edges of the boron islands, although the lattice remained intact. Certainly, 2D boron cannot compete with graphene's chemical inertness and gets contaminated upon long-term exposure to air, highlighting the need for its encapsulation in any air-stable devices. Mannix and co-workers demonstrated that the oxidation of 2D boron was greatly impeded by a silicon/silicon oxide capping layer. One can imagine that an ideal way to protect 2D boron would be to sandwich it between two very inert, thermally stable and atomically smooth h-BN sheets.

Despite the discrepancies between the proposed atomic structures, both reports also described the boron layers as metallic, in agreement with earlier electronic-structure calculations[3,4]. Combined with mechanical robustness, this invites a plethora of applications in nano-electromechanical devices and flexible electronics. With unambiguous metallicity and high carrier density independent of Fermi level, the boron layers are expected to exhibit intrinsic plasmonic properties and allow novel manipulation of light. In particular, it opens the possibility to extend the plasmon frequency into near-visible range, to complement graphene whose gate-controlled plasmons are in the infrared range. The intrinsically metallic boron layer, which accommodates 2D electron gas, should motivate the studies of quantum Hall

effect in strong magnetic fields, or serve as a flexible transparent electrode.

Last but not least, both metallicity and light atomic weight are typical prerequisites for phonon-mediated superconducting behaviour, possibly rendering boron an attractive test bed for exploring the 2D limit of conventional superconductivity[10]. Phenomena such as possible charge density waves will also attract physicists — and judging by the Fermi surface topology, charge density waves should not be unexpected[10].

Although a number of tantalizing properties and even applications come to mind, understanding the atomistic structure of 2D boron offers in itself an unusual intellectual challenge. The current impression that a few regular, distinctly different atomic arrangements can indeed form and develop at the same time looks like true polyphony in materials chemistry. ❑

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SURFACE SPECTROSCOPY

Between a rock and a soft place

The critical step in water splitting is the formation of a peroxo bond; the mechanism, thought to involve oxyl radical formation, remains elusive. Now, experiments reveal a distinct bond vibration directly connected to an oxyl radical that is simultaneously coupled to both the semiconductor electronic states and the motion of the surrounding water.

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The prospect of generating a seemingly endless supply of chemical fuels from sunlight and water makes photocatalytic water-splitting one of the grand challenges within catalysis and alternative energy conversion research[1]. Solar energy is the only alternative energy source with the capacity to replace fossil fuels for current and projected global energy demands, but due to the Sun's transient nature over the course of 24 hours, an efficient storage platform is needed[2,3]. The most efficient way to store the Sun's energy is in chemical bonds, which is the process nature achieved billions of years ago with photosystem II.

Creating solar fuels in the form of hydrogen or simple hydrocarbons involves splitting water and the formation of O–O bonds[2]. Water splitting is a highly complex process that requires the rearrangement of four electrons and four protons, and a considerable amount of effort has been devoted to investigating both biological and abiological water-splitting with the ultimate aim of developing new catalysts to promote the reaction[4]. The critical step in water oxidation is the formation of an O–O bond to produce O_2 (refs 4,5). This bond formation is thought to go through an intermediate oxyl radical, but despite the importance, such oxyl intermediates have not previously been detected. Now, Cuk and co-workers, writing in *Nature Chemistry*, present data from both
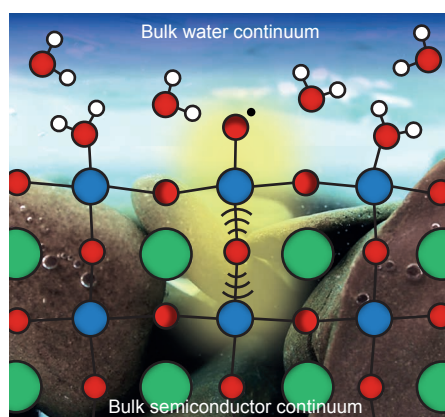

Figure 1 | An interfacial vibrational mode for monitoring water splitting. The sub-surface Ti–O vibrational mode in n-SrTiO$_3$ reports on the oxyl radical at the surface, while being coupled to the solvent librational and semiconductor electronic state continua. Monitoring the changes of this vibration on ultrafast timescales opens the door for studying the water oxidation reaction *in situ*. Colour scheme for atoms: white, hydrogen; red, oxygen; blue, titanium; green, strontium.

ultrafast vibrational spectroscopy and theoretical calculations that identify a unique sub-surface vibration that directly reports on the elusive oxyl radical[6]. The ability to track oxyl radicals through this newly discovered sub-surface vibration opens the door to study the mechanism of

photocatalytic water-splitting in greater detail than previously possible.

Cuk and co-workers study water splitting driven by UV excitation of a Nb-doped $SrTiO_3$ single-crystal in contact with water using femtosecond time-resolved infrared spectroscopy. Doping $SrTiO_3$ with Nb results in an n-type semiconductor and such n-$SrTiO_3$ crystals exhibit high photon-to-O_2 evolution efficiency under UV radiation. Following UV excitation Cuk and colleagues observe a distinct vibrational mode around 800 cm^{-1} exhibiting the peculiar 'Fano resonance' lineshape that is associated with a discrete state coupled to a continuum of states[7]. Through theoretical calculation, they assign the discrete state to a sub-surface vibrational mode within the $SrTiO_3$ lattice involving the stretching of the Ti–O bonds directly below the photo-generated oxyl radical (Fig. 1). This mode only exists at the surface and is decoupled from the bulk Ti–O phonon modes by the formation of the oxyl radical. The continuum of states that the vibration is coupling to comprises both the bulk electronic states of the semiconductor and the water librations (hindered rotations) of the surface water in contact with the $SrTiO_3$. This is verified by the large modulation of the Fano resonance when either changing the doping level of the semiconductor (altering the frequency of the bulk semiconductor plasmonic modes) or replacing the water with heavy water (altering the frequency of the solvent