Precise control of van der Waals gaps

Pre-adsorption of water molecules on a material surface, followed by assembly of a van der Waals (vdW) structure, provides a vdW water gap with a height that can be precisely tuned through variation of the amount of water adsorbed at the interface. This approach is applicable to different two-dimensional and even three-dimensional homo- and heterojunctions.

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The mission

Within two-dimensional (2D) layered materials, the small angstrom-height gaps between the atomic layers, often referred to as van der Waals (vdW) gaps, can confine molecules or ions, providing a way to tune the material properties and explore microscopic phenomena[1–3]. However, it is difficult to modulate the height of vdW gaps within common vdW materials, as the height mainly depends on the lowest potential of the vdW interaction and the intrinsic properties of the material.

Existing strategies for opening vdW gaps are typically based on electrochemical intercalation techniques, whereby guest molecules or ions are electrochemically driven into the vdW gaps of the host material[4]. However, the introduction of organic macromolecules or alkali metal ions can alter the electronic properties of the host material and reduce its structural stability. Moreover, this method offers limited control of the gap height and can only be applied to specific materials. To date, a universal approach for opening and controlling vdW gaps has not been realized.

The solution

Small vdW gaps form upon the physical assembly of two atomic layers (for example, the vdW gap is 1.8 Å in the case of MoS_2). When small molecules (such as water) are adsorbed at the interface of the atomic layers, the vdW interactions that occur upon physical assembly can confine these molecules while the small molecules directly modulate the height of the vdW gap. Based on this phenomenon, we developed a vdW-gap-engineering approach that involves the pre-adsorption of water molecules on the surface of a material prior to assembly with a second layer to form a 'vdW water gap' (Fig. 1a). By varying the saturation vapour pressure of the water vapour, the level of water molecule adsorption can be modulated and the height of the vdW water gap precisely controlled on the angstrom-scale.

Using 2D MoS_2 as a representative material, we showed that increasing the saturation vapour pressure leads to a monotonic increase in the vdW water gap height of a MoS_2 homojunction from 5.5 Å to 53.6 Å. Characterization of the homojunctions using scanning transmission electron microscopy (STEM) revealed that the vdW water gaps have atomically flat and clean interfaces at different gap heights. Moreover, the water gaps show good stability: the gap height in a MoS_2/gap/MoS_2 junction remained unchanged at room temperature for up to one month and was also stable during thermal annealing at 90 °C.

Importantly, this gap-engineering approach can be extended to different 2D/2D homojunctions as well as 2D/2D heterojunctions, and even to 2D/three-dimensional (3D) and 3D/3D heterojunctions. In addition, different solutions can be used in place of water to produce various molecule or ion gaps. We demonstrated the utility of this gap-engineering approach by preparing complex artificial superlattices (Fig. 1b), in which the height of the vdW water gap between the MoS_2 multilayers could be readily controlled during assembly (from no water gap to gaps of up to 30.6 Å).

Finally, we developed a MoS_2/gap/MoS_2 junction that exhibited gap-dependent diode characteristics, demonstrating the potential of vdW water gaps to modulate carrier transport.

Future directions

This universal approach to controlling the height of vdW gaps offers the freedom to tailor the interlayer coupling, conductivity, chirality and topology of vdW materials. The ability to modify vdW gaps with angstrom-scale precision could also facilitate the study of the effects of nanoconfinement on ions and molecules[5].

In particular, for extremely small vdW gaps (sub-nanometre) with a height less than the diameter of the smallest hydrated ions (such as K^+ and Cl^-), they could be used as selective pores, with potential applications in water filtration, molecular or ion separation, and desalination.

As this gap-engineering approach can be applied to various vdW interfaces, such as semiconductor/semiconductor, dielectric/semiconductor and metal/semiconductor, it could be used to modify the performance and functionality of different devices. Indeed, we are now focusing on the development of electronic and opto-electronic devices based on the proposed vdW-gap-engineering approach.

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EXPERT OPINION

"The authors demonstrate an approach to tune the geometrical nanoconfinement environment in the vdW gap of different 2D materials via pre-adsorption of water to one surface and deposition of a second layer on top; variable spacing is achieved by controlling the amount of pre-adsorbed water through evaporation temperature. The approach should be universally applicable and thus is very interesting for a wide range of applications, where precise control of nanoconfinement channels is desired." **Simon Fleischmann, Helmholtz Institute Ulm, Ulm, Germany.**

FIGURE

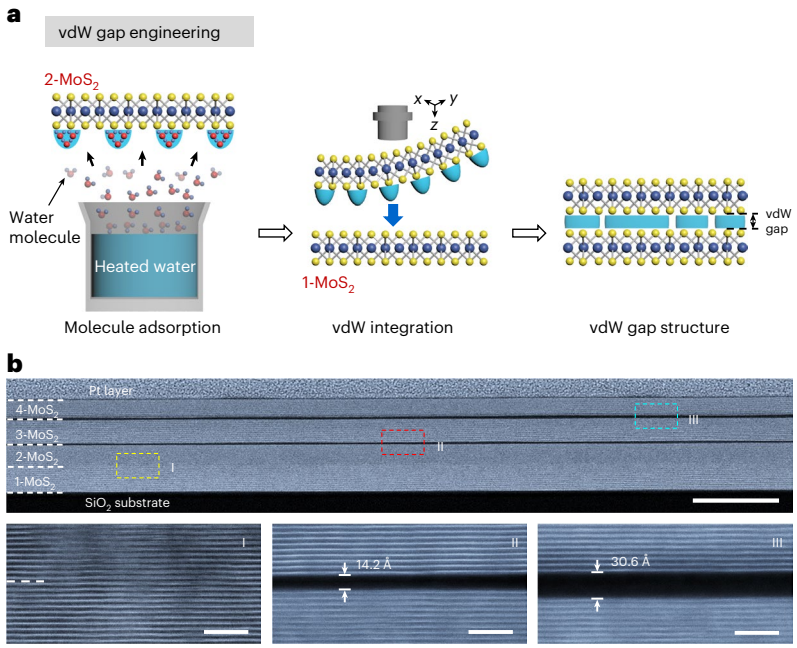

Fig. 1 | vdW gap engineering and proof-of-concept artificial superlattices. a, The vdW-gap-engineering approach developed herein. Water molecules are adsorbed on the surface of a MoS_2 layer (2-MoS_2) by heating ultrapure water to produce saturated water vapour. The 2-MoS_2 layer with the adsorbed water molecules is subsequently assembled with a second MoS_2 layer (1-MoS_2) to form a vdW structure with a vdW water gap. By changing the saturated vapour pressure, and thus the amount of water adsorbed, the height of the vdW water gap can be controlled at the angstrom scale. **b**, vdW gap engineering enabled the fabrication of an artificial superlattice comprising four stacked layers of MoS_2 with a high degree of control of the vdW gaps (top; scale bar, 100 nm). Enlargements of the vdW interfaces, labelled I–III (bottom; scale bar, 5 nm). © 2024, Liu, C. et al.

BEHIND THE PAPER

In 2022, while observing the 2D heterointerfaces of ABC stacks using STEM, C.L. found that the size of the vdW gap at the AB interface was larger than that at the BC interface, which aroused our interest. However, we couldn't explain this phenomenon. After many additional experiments, we found that the gap size seemed to be related to the exposure time of the 2D material to air after peeling. Eventually, we determined that the main cause of this vdW gap is water and were surprised that water could be stabilized between layers. Following this discovery, we aimed to develop a universal approach for creating these angstrom-scale gaps. Finding the answer required perseverance, serendipity and teamwork, and, as Albert Einstein said, "The important thing is not to stop questioning." We believe that vdW gap engineering has diverse applications and look forward to exploring the concept further. **C.L., X.M.Z. & L.L.**

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FROM THE EDITOR

"In their study, the authors present a method to adjust the interlayer spacing between 2D materials. The notable aspect of this approach is its universal applicability, making it highly interesting for a wide range of applications in which precise nanoconfinement control is desired. This capability also opens up possibilities for tailoring material properties and exploring various phenomena on the nanoscale." **Lu Shi, Senior Editor, *Nature Nanotechnology*.**