2D materials

https://doi.org/10.1038/s44160-024-00686-3

Metallic nanosheets fill the gap

Xiaoxi Li & Zheng Vitto Han

Grain boundary engineering, by electrodeposition and demoulding of elemental metal from a van der Waals gap, gives rise to nanosheets with high electrical anisotropy.

Anisotropic conductivity, preferably tunable via electrostatic gating or other means, in 2D materials has recently become a popular area of research. This interest stems from the ability of transistors with anisotropic conductance to form device architectures for application in nanoelectronics, such as directional memories and multi-level output switches. Large conductance anisotropy, with anisotropic ratios up to a few thousand, can be achieved in 2D systems, exhibiting gate-tunability in some cases[1–3]. For example, anisotropic effective masses along different crystallographic directions can be found by exploring exotic band structure in 2D semiconductors[2] or by symmetry engineering in interfacially-coupled systems of an anisotropic 2D dielectric insulator and a 2D semiconducting channel[3].

However, candidate materials for such applications are so far largely limited to a few semimetals or semiconductors, while metallic 2D thin films or nanosheets are seldomly reported with any significant in-plane anisotropic electrical properties. 2D materials often demonstrate characteristics unattainable in their bulk forms, due to the confinement of the *z* dimension. It is expected that 2D nanomaterials may display surprising figure-of-merits (such as unconventional dielectric, switching, or anisotropy) if their microstructure is carefully engineered. The challenge is therefore how to experimentally develop novel methods for the confined growth or assembly of 2D materials with distinctive properties from the bulk.

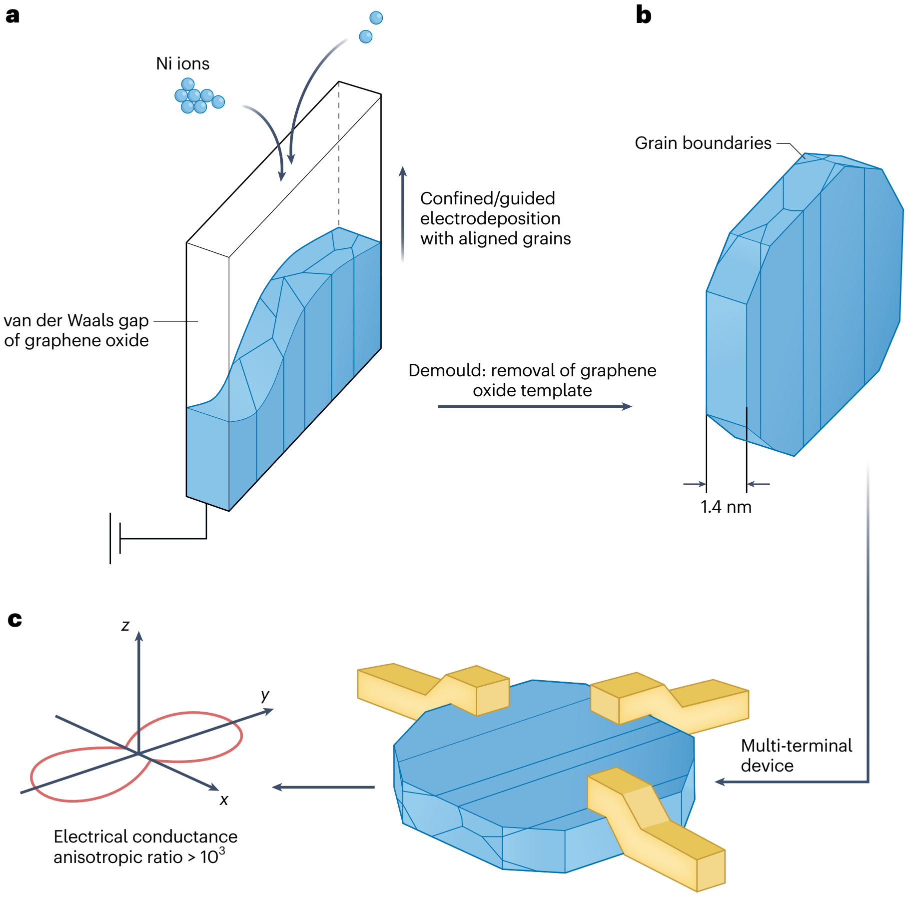

Fig. 1 | Growth of 2D anisotropic metallic nanosheets confined by a van der Waals gap. a, The electrochemical deposition of metallic 2D nanosheets in the interlayer gap of graphene oxide templates. **b**, Schematic of elemental metal nanosheets demoulded from the van der Waals gap with highly aligned domains. **c**, Illustration of the anomalous anisotropic conductivity in the elemental metal nanosheets, and possible application in multi-terminal logic-like devices.

Now, writing in *Nature Synthesis*, Shim and co-workers report an electrodeposition method for synthesizing 2D elemental metal nanosheets with highly aligned grain orientations, resulting in remarkably high in-plane electrical anisotropies of over three orders of magnitude[4]. The nanosheets are grown within the nanoscale gap of the van der Waals material, graphene oxide. Graphene oxide serves as a template and is removed after the growth of the metal nanosheets. This resembles the well-established moulding and demoulding process, but occurs at the nanoscale in 2D, and the metallic nanosheets are fabricated by electrodeposition.

Shim and co-workers' method relies on the heterogeneous nucleation and assembly of metal atoms at the cathode within a channel of several angstroms in width. The template comprising the graphene oxide layers is confined to epoxy and glass and placed in a Watts bath, and one end of the graphene oxide film is connected to the cathode electrode. The Ni nanosheets subsequently grow by electrodeposition in the 2D confined environment, initiating from the cathode. These nanosheets are grain-boundary-free along the growth direction, while grain boundaries are not forbidden at the bottom of the nucleation channel (Fig. 1a). Using molecular dynamic simulations, several key energy barriers are accessed, and the electrodeposition process is confirmed by tracking a single Ni ion (Ni^{2+}) during the growth process. The Ni^{2+} ion is tracked from its entry into the interlayer space between the graphene oxide layers, during diffusion through the van der Waals gap, and finally to the reduction of Ni^{2+} at the cathode. The results suggest that, despite the larger size of hydrated ions in the electrolyte compared with the interlayer spacing (δ) of graphene oxide, the Ni^{2+} ions may undergo dehydration and enter the internal pathways of the template by the external electric field, leading to the directed grain orientations of the as-prepared elemental metal nanosheets (Fig. 1a).

The graphene oxide moulds are then sacrificed by a calcination procedure at 350 °C, to obtain pristine Ni nanosheets (Fig. 1b). This demoulding of the Ni nanosheets is optimized to minimize damage to the metal during the removal of the graphene oxide. The typical thickness of assembled 2D Ni nanosheets is 1.4 nm, which is about four times the lattice parameter of face-centred cubic Ni. The average lateral size of the as-prepared Ni nanosheets is, however, limited to less than 2 µm owing to the nonuniformity of the graphene oxide template.

Cross-sectional scanning transmission electron microscopy confirms that the 2D Ni nanosheets show highly anisotropic microstructures, with grains oriented along the growth direction (y-axis in Fig. 1c), and a random network of grain boundaries is seen in the cross-section of the x–z plane in the nanosheets. These grain boundaries serve as scattering centres in electrical transport, yielding a high-resistivity-state (HRS) and low-resistivity-state (LRS) when measuring electrical conductivity along the x (longitudinal) and y (transverse) directions, respectively. This behaviour is a direct consequence of the anisotropic microstructure of the metallic nanosheets. Notably, the maximum anisotropic ratio of HRS and LRS in the current system can reach above 10^3 (Fig. 1c), in stark contrast to the rather isotropic electrical conductance of the conventional elemental metal thin films obtained by methods such as physical deposition or sputtering.

Based on the high in-plane electrical anisotropy, Shim and co-workers design an all-metal three-terminal switching device that exhibits an on–off switching ratio exceeding 10^4. Unlike the conventional logic transistors which take advantage of the change of carrier density in the channel, this proposed electrical switch device uses the differentiate-voltage between the transverse and longitudinal drain terminals as a control parameter. The source current is therefore modulated as a result of the anisotropically-grown grain boundaries, mimicking a transistor-like performance. Logic operations (such as AND, OR, NAND) are also demonstrated using the three-terminal all-metal switching devices.

This 2D synthesis via electrodeposition and demoulding within a confined van der Waals gap, together with a peculiar grain boundary alignment, is unique and shown to be specifically suitable to form metallic nanosheets. It differs from other known 2D confined growth routes for nanomaterials, usually realized by chemical vapour deposition or by thermal recrystallization, such as recently reported graphene nanoribbons or bismuthene grown in the layer spacing of hexagonal boron nitride[5,6]. Although limited by the small lateral sizes of the prepared anisotropic Ni nanosheets and relatively low homogeneity in the graphene oxide templates, the method of Shim and co-workers may be expanded to various metals by reselecting combinations of electroplating baths and 2D nanoscale moulds, shedding light on the future development of 2D materials for unconventional nanoelectronics.

Xiaoxi Li [1,2] ✉ **& Zheng Vitto Han** [1,2,3] ✉
[1]State Key Laboratory of Quantum Optics and Quantum Optics Devices, Institute of Opto-Electronics, Shanxi University, Taiyuan, China. [2]Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan, China. [3]Liaoning Academy of Materials, Shenyang, China.
✉e-mail: xiaoxili1987@sxu.edu.cn; vitto.han@gmail.com

References

1. Zhao, S. et al. *Nanoscale Adv.* **2**, 109–139 (2020).
2. Wang, H. et al. *Nat. Commun.* **10**, 2302 (2019).
3. Li, Z. et al. *Nat. Commun.* **14**, 5568 (2023).
4. Kim, T. et al. *Nat. Synth.* https://doi.org/10.1038/s44160-024-00669-4 (2024).
5. Chen, L. et al. *Nat. Mater.* **23**, 741–746 (2024).
6. Lyu, B. et al. *Nature* **628**, 758–764 (2024).

Competing interests

The authors declare no competing interests.