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Preview

Programing Two-Dimensional Materials in Non-Euclidean Spaces

Shanshan Wang[1,2] and Jin Zhang[1,*]

Recently in *Nature Materials*, the Fu group reported a sphere diameter engineering (SDE) strategy for modulating the band gap of monolayer MoS_2, which exhibited high precision, reliability, uniformity, and flexibility with a tuning range of 360 meV. This work provides new ideas for engineering two-dimensional materials, commonly regarded as flatlands, in curved spaces.

Two-dimensional (2D) materials have attracted immense interest from both the laboratory and industry in the past decade because of their great potential in both fundamental sciences and diverse applications in flexible nanodevices and energy harvesting. Structurally, 2D materials exhibit two primary features: (1) highly ordered atoms arranged in plane, showing planar periodicity similar to that of bulk crystals; and (2) atomic-level thinness, giving considerable freedom to the out-of-plane deformation. Layered 2D materials also adopt dangling-bond-free surfaces, exerting weak forces to neighboring layers. Thanks to these structural characteristics, two special strategies have been developed for programming 2D materials with exotic properties. One is to stack 2D materials vertically with free tuning of the twist angle and the relative displacement between adjacent layers, creating new in-plane periodicity in the vertical heterostructures. Intriguing phenomena such as unconventional superconductivity,[1] novel direct optical band gaps,[2] and chiral properties[3] have been observed.

The other strategy is to engineer 2D materials in curved spaces rather than on flat surfaces. A curved space, also termed a non-Euclidean space, can be understood as a concave or convex surface on which the sum of interior angles of a triangle is no longer 180°. Even though 2D materials are often seen as "flatlands," out-of-plane deformation can be easily introduced because of their atomic thinness and great freedom in the direction perpendicular to the lattice plane. Bending, folding, and crumpling have been applied to 2D materials. The curvature brought by these operations can break the

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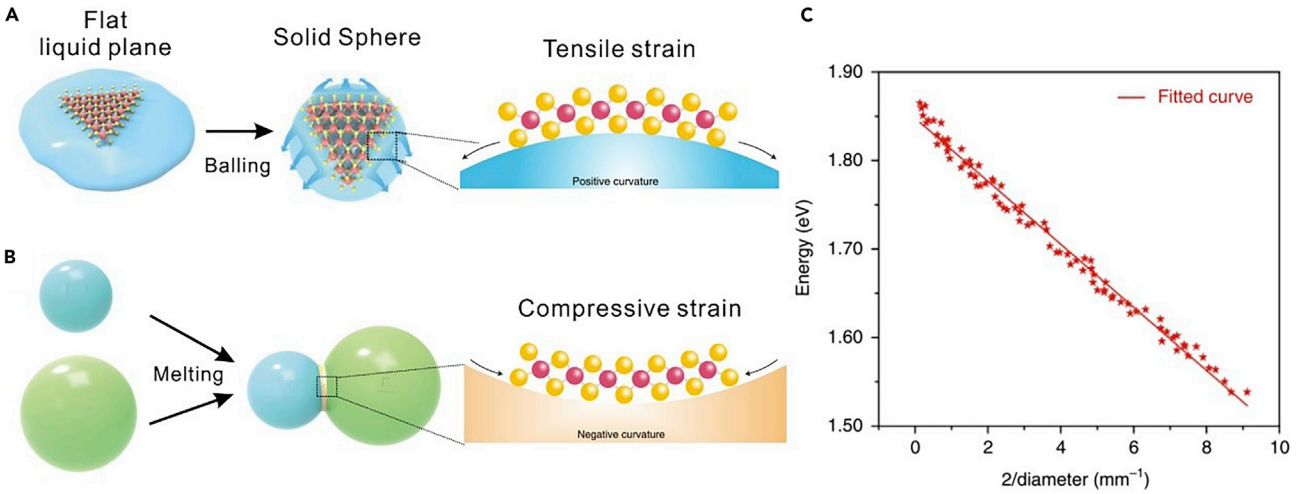

Figure 1. Band-Gap Tailoring of Monolayer MoS_2 by SDE

(A and B) Schematic illustration showing the introduction of tensile strain (A) and compressive strain (B) to the MoS_2 lattice through reshaping of the substrate's curvature.

(C) Linear relationship between the optical band gap and the sphere curvature.

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original lattice symmetry on the flat surface and add strain energy to the material, thus remarkably tailoring physical, mechanical, and chemical functionalities of 2D materials. For example, ripples with controllable height fluctuations were generated in graphene by thermally induced stress, which influenced both the band gap and the electronic transport behavior.[4] Moreover, graphene nano-islands folded to form a one-dimensional tubular structure by atomic-level manipulation led to the transformation of the electronic properties of the nanostructure from graphene to a carbon nanotube.[5] Now, writing in *Nature Materials*, Fu and colleagues have recently developed a sphere diameter engineering (SDE) method that can program monolayer molybdenum disulphide (MoS_2) on both concave and convex surfaces, leading to precise, uniform, continuous, and dual-directional band-gap tuning of MoS_2 with a large range of 360 meV.[6]

Fu and colleagues realized the band-gap tuning of 2D semiconducting materials by first growing high-quality, single-crystalline-monolayer MoS_2 on a flat liquid substrate and then reshaping the liquid substrate to a sphere with a designed diameter (Figure 1A). An isotropic molten substrate not only facilitates the uniformity of MoS_2 when growing but also is suitable for applying isotropic stress on MoS_2 during subsequent solidification molding, leading to the precise tailoring of the band energy. The SDE approach has several advantages for band-gap tailoring. First, the tuning range is as large as 360 meV, surpassing most of the other strain-engineering methods. This derives from an effective transfer of the large, multi-axial strain from the spherical glass surface to the MoS_2 lattice as they form intimate contact during the growth process, avoiding interfacial decoupling under intense strain. Second, the band energy changes linearly with the curvature of the sphere substrate (Figure 1C). One can adjust the slopes of the linear working curve by altering SDE programs so that the band gap can be modulated with diverse precision and range. Third, the strain introduced to MoS_2 by the SDE strategy possesses high spatial homogeneity because of the isotropic nature of the glass sphere throughout its melting and solidification processes. 2D crystals grown on different areas of a glass sphere show a uniform photoluminescence peak position with a relative standard deviation as small as 1.05‰. Finally, the SDE strategy can program the flat 2D crystals not only on a convex surface but also on a concave surface by partially merging two sphere substrates to construct a concave junction (Figure 1B). The concave surface introduces compressive strain to the 2D MoS_2 lattice, leading to a blueshift of the band energy, whereas the convex surface introduces tensile stress to MoS_2 and triggers a redshift of the band gap. The flexibility of shaping the 2D lattice in diverse non-Euclidean spaces enables the dual-directional tuning of the band gap.

This work by Fu and co-workers inspires a number of open questions. From a synthesis perspective, developing new methods to facilitate the engineering of 2D materials in non-Euclidean spaces is required. Currently, the approaches are limited to (1) directly growing 2D materials on curved surfaces,[7] (2) wrinkling or bending planar sheets, and (3) forming nanoscale origami and kirigami. More strategies with high controllability,

reproducibility, and productivity are anticipated. From this aspect, abundant experience accumulated in the research of carbon nanotubes, which can be seen as rolled-up graphene and adopt a naturally curved surface, can be transferable to the investigation of 2D materials in non-Euclidean spaces.[8,9] In addition, how to find suitable applications for 2D materials programmed in the non-Euclidean space is another significant open question. Fu and colleagues directly employed their monolayer MoS_2 grown on glass spheres with a tunable band gap in the application of surface-enhanced Raman scattering to increase the detection sensitivity of some molecules with specific energy levels. However, more versatile applications are required. Moreover, for applications wherein material transfer is needed, developing a non-destructive transfer method that can preserve the structure and properties obtained in the non-Euclidean space is also important.

A plethora of new opportunities will arise when we study 2D materials in non-Euclidean spaces. The curvature will change our common understanding applicable in the Euclidean space, endowing basic geometric concepts, such as parallel lines, with new definitions and generating disparate principles for the packing of atoms. All these variations in the fundamental mathematics could have an impact on 2D material research, such as enriching the connotation of "epitaxy" and creating novel defects different from those in "flat" 2D or bulk crystals.[10] Therefore, the growth behavior, band structures, chemical stability, and catalytic activity might be altered. It can be envisioned that programming 2D materials in curved spaces will give new life to the property modulation of many 2D materials. It will also establish a closer connection between these "flatlands" and tubule or cage structures, including carbon nanotubes and fullerenes.

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