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PERSPECTIVE

Stacking control in graphene-based materials: A promising method for fascinating physical properties

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Graphene, defined as a single atomic plane of graphite, is a semimetal with a small overlap between the valence and conduction bands [1]. The stacking of graphene up to several atomic layers can lead to diverse physical properties, depending on the stacking method. Bilayer graphene is also a semimetal, adopting the AB-stacked (or Bernal-stacked) structure or the rare AA-stacked structure [2]. Trilayer or few-layer graphene (FLG) can be semimetals or semiconductors, depending on whether they adopt Bernal (ABA) stacking or rhombohedral (ABC) stacking.

Compared with these ideal stacking structures, the stacking structure in most graphene multilayers is actually more complex. Twinning is a common feature, where different stacking configurations coexist and are connected by discrete twin boundaries [3]. Twisted multilayers, where one layer is rotated relative to another, have also been observed experimentally. These complex structures usually lead to more advantageous or even unique physical properties. It has recently been reported in 2018 that a small twist angle of 1.1° induced unconventional superconductivity [4] — a feature which can be employed in superconducting transistors made of graphene for quantum devices.

Owing to the possibility of different stacking configurations, controlling the stacking structure of graphene materials is vital to realizing specific properties and/or novel functional devices. In early 2018, Japanese scientists reported the success in the selective fabrication of pure ABA and ABC trilayer graphene [5]. Their methods involved heat treatment at high temperatures up to 1510 °C under pressure or high vacuum (ca. 10^{-7} Torr). They reported that precise temperature and pressure control is the key to selective fabrication [5]; however, this will pose a limitation to the application of their methods.

Very recently, Latychevskaia *et al.* [6] presented two mild approaches to control the stacking via local transition from ABC stacking to ABA stacking. One approach is Joule heating by passing high currents through hBN/ABC FLG/hBN heterostructures, where hBN is the hexagonal boron nitride, and the fraction of the ABA stacking can be controlled by tuning the applied voltage. This approach has a spatial resolution of ca. 1 μm for the initial transition, and is a more effective way to fabricate many graphene-based electronic devices with different stacking structures. The second approach is illumination by laser pulses to trigger the transition in the laser-focused zone.

In Joule heating, the high-temperature-induced stress was thought to be the driving force for the transition. However, a high-density direct current can also induce significant stress or structural change due to strong electron-lattice couplings [7, 8]. It would be more promising to explore the possibility of using large currents to tune the stacking. An electropulsing technique [8], which employs a high-density direct current and generates less heat, can be used for this purpose. With high-density electric pulses, it is possible to bind two separate FLGs and produce twisted layers or numerous interesting stacking configurations.

Latychevskaia and coworkers employed laser pulses of 790 nm wavelength to initialize the transition in a focused zone of ca. 20 μm in the second method. The stacking transition is triggered by the laser illumination the focused zone. With the short-wavelength UV light (10–400 nm), which generates much higher energy, a smaller focused zone for the stacking transition can be realized. This method will allow customized design of the stacking structure on a scale of nanometers by controlling the pathway of the pulsing beam like stereolithography, which expands the feasibility of preparing novel graphene-based functional devices.

Although nanospot angle-resolved photoemission spectroscopy is powerful for characterizing the local stacking structure [9], many researchers cannot access this technique due to the limited availability of such synchrotron facilities. Latychevskaia and coworkers demonstrated that a convergent beam electron holographic technique allows the characterization and reconstruction of the stacking and defects (e.g., misorientation, strain, and ripples) at a sub-nanometer spatial resolution [10, 11]. Qualitative information on these defects can also be extracted from the obtained patterns or images using the technique, which enables further optimization of controlled stacking structures.

The above techniques to control and characterize the stacking structure can also be applied to other 2D or layered materials, which makes it possible to introduce more exciting properties or solve structural mysteries. One example is graphitic C_3N_4 (g-C_3N_4), the most stable allotrope of carbon nitrides and a fascinating 2D semiconductor. In past decades, numerous efforts to prepare g-C_3N_4 yielded mainly graphitic s-heptazine-based C_3N_4 (gh-C_3N_4), containing a small amount of H [12]. The successful synthesis of graphitic s-triazine-based C_3N_4 (gt-C_3N_4), i.e., the final condensation form of gh-C_3N_4, was reported in 2014, and only triple layers were obtained by exfoliation in the work [13]. Despite these efforts, the 3D stacking structure of these g-C_3N_4 has still not been elucidated. Now, it will be possible to uncover and modify the stacking, which will open new possibilities for post-silicon electronic devices.

With the rapid development of graphene-based materials, these techniques for stacking control can be used for more complex structure to fulfill fascinating properties and devices. However, challenges still lie ahead, e.g., encapsulation of the heterostructure, precise control of heating effects, and mechanical performance of devices. To tackle these challenges, in-depth understanding is required not only on these techniques but also on the structure-properties relationships of graphene-based materials, which also leads to better structural design. Compared with the extensive studies in structure and electronic behaviors, less attention was paid to mechanical properties of graphene-based materials and functional devices. From the perspective of practical application, the mechanical properties are also very important and therefore significant efforts are needed to be devoted [14]. Theoretical investigations based on first-principle calculations will provide a simple and effective way to design the desirable structure for verifying the performance on demand [15], and meanwhile utilize the multi-physics simulations further to optimize the technical parameters [16]. It is worthwhile pointing out that it is a matter of time when these challenges will be overcome. It can be postulated that more fascinating 2D graphene-related materials with a well-controlled van der Waals 2D heterostructures will be available soon, which would not only exhibit extremely exciting physical phenomena but also stimulate superior functional devices for various applications.

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