LETTER

# Twisted graphene stabilized by organic linkers pillaring

To cite this article: Chengyuan Liu *et al* 2022 *Nanotechnology* **33** 26LT01

IOP Publishing Nanotechnology
Nanotechnology 33 (2022) 26LT01 (6pp) https://doi.org/10.1088/1361-6528/ac6008

Letter

# Twisted graphene stabilized by organic linkers pillaring

**Chengyuan Liu[1,*], Wenlian Li[2], Lin Xue[1,*] and Yuying Hao[1,*]**

[1] College of Physics and Optoelectronics, Taiyuan University of Technology, Taiyuan 030024, People's Republic of China
[2] State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics Fine Mechanics and Physics (CIOMP), Chinese Academy of Sciences, Changchun 130033, People's Republic of China

E-mail: 553505626@qq.com (Chengyuan Liu), xpw896@163.com (Lin Xue) haoyuyinghyy@sina.com

Received 12 December 2021, revised 18 March 2022
Accepted for publication 22 March 2022
Published 7 April 2022

**Abstract**

Twisted graphene, including magic angle graphene, has attracted extensive attentions for its novel properties recently. However, twisted graphene is intrinsically unstable and this will obstruct their application in practice, especially for twisted nano graphene. The twist angles between adjacent layers will change spontaneously. This relaxation process will be accelerated under heat and strain. To solve this problem, we propose a strategy of pillaring twisted graphene by organic linkers in theory. The necessity and feasibility of this strategy is proved by numerical calculation.

Keywords: twisted, graphene, stabilized, organic, linkers

(Some figures may appear in colour only in the online journal)

## 1. Introduction

Few-layer graphene has been intensively studied for its variable electronic properties in recent years. AB stacking is the most stable and natural arrangement mode in two-layer graphene. All other structures are metastable and unstable. Graphite and multi-layer graphene are generally ABA (Bernal) or ABC (rhombohedral) stacked, in which the former is stable and the later one is metastable structure.

Relative rotation between graphene layers is quite common and it usually results in twisted graphene [1]. A remarkable feature of twisted graphene is two-dimensional Moiré superlattice, what appares periodic arrangement of AA, AB and BA stacking regions, shown as figure 1(b). Twisted bilayer graphenes with twist angles of 0° and 60°, illustrated as figures 1(a) and (c), are equivalent to AB and AA stacked bilayer graphenes, respectively. Energy band structure of twisted bilayer graphene tuned by interlayer coupling was numerically studied by J M B L Dos Santos *et al* [2]. Then R Bistritzer *et al* predicted theoretically in 2010 that twisted bilayer graphene with twist angles taking a series of very small particular values will emerge some unknown properties [3]. This prediction was confirmed by Yuan Cao *et al* experimentally for the first time in 2018 by discovering low-temperature superconductivity of this material [4, 5]. This twisted graphene is specially named as magic angle graphene. Twisted bilayer graphene has many unique physicochemical properties and corresponding applications, such as correlated insulating and superconducting states, ferromagnetic state [6], enhanced optical absorption [7], tunable bandgap [8], and lithium intercalation and diffusion [9]. Haoxin Zhou *et al* reported superconductivity in rhombohedral trilayer graphene [10]. Unconventional superconductivity in magic-angle twisted trilayer graphene was prove by Ammon Fischer *et al* [11].

Up to now, researches on twisted graphene or twisted Van der Waals heterojunction materials are mostly on the bulk properties of macro materials, instead of the properties of nanoscale materials or edges. Experiment and theoretical calculation show that the edge of twisted graphene has metallic transport and the bulk is insulating [12, 13].

* Authors to whom any correspondence should be addressed.

 

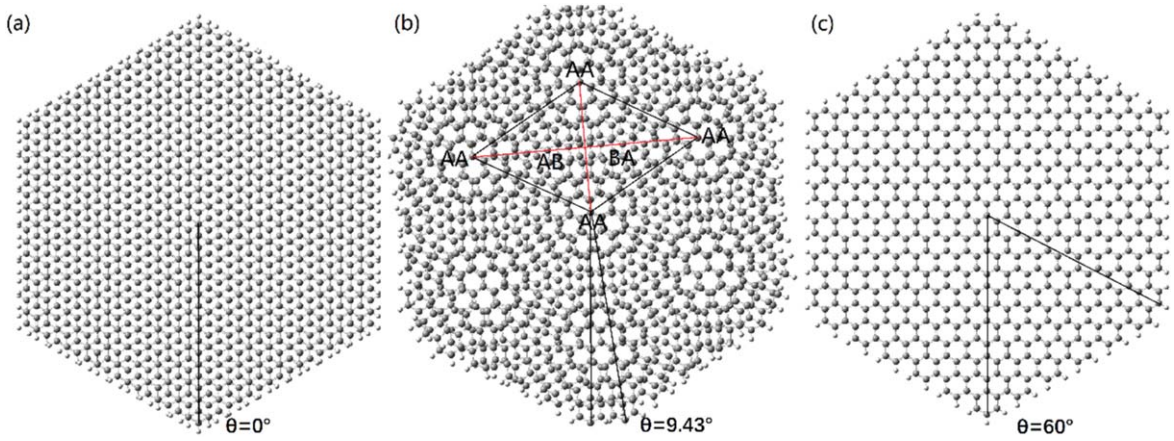


**Figure 1.** Schematic diagrams of AB (a), AA (c) stacked bilayer nano graphene and twisted bilayer nano graphene (b).

Sumandeep Kaur *et al* revealed by calculation that graphene-based nanoflake heterostructures has potential in photonics and quantum technologies [7]. Twisted nano graphene may have more abundant and adjustable properties.

## 2. Instability of twisted nano graphene

Graphene layers are linked together by very weak Van der Waals interactions. This leads to the relative translation and rotation between graphene layers very easily under heat and strain. The easy sliding property between graphene layers is called superlubricity, which has been proved by a large number of experiments and theories [14, 15]. Thermal and strain instability of twisted graphene have been proved by many experiments. Rotation of graphene flakes on graphite was demonstrated both experimentally and theoretically by A E Filippov *et al* in 2008 [16]. Xiaofeng Feng *et al* found that graphene nano flakes show facile translational and rotational motions at temperature as low as 5 K [17]. Soumendu Bagchi *et al* study the rotational stability of twisted bilayer nano graphene of different size under different temperature with large-scale molecular dynamics simulations using LAMMPS. They proved in theory that nano graphene is easy to rotate on graphene under heat and strain. The potential barriers decrease gradually with the size of nano graphene increase. But the rotational dynamics process is slowed down by the increased number of atoms, resulting in slower rotational relaxation [18]. Andrea Silva *et al* calculated energy per atom as a function of the twisted angle, proving unstability of twisted Van der Waals heterojunctions [19].

The structure of twisted bilayer nano graphene was optimized by numerical calculation, with its internal energy obtained in the same time. Twisted graphene always translate into stable (AB stacking) or metastable states as long as degrees of freedom are all opened in locally structural optimization. Therefore, locally relaxation of atoms in plane directions of the graphene layers is forbidden in following calculations, just as literature [20]. Models of hexagonal nano graphene sheets with armchair edges saturated with hydrogen atoms are used here. Each layer of the twisted nano graphenes contains 13, 61, 145, 265, 421 and 613 carbon atoms, respectively. We use the semi-empirical self-consistent-field method PM6-D3H4 as implemented in the quantum chemistry code 'MOPAC 2016' [21, 22]. Formation heat per atom is defined as final heat of formation of the system divided by number of all the atoms, including carbon and hydrogen atoms. Material with high energy will release heat and translate into low energy structure. In this relaxation process, a certain lattice deformation barrier of graphene needs to be overcome. Figures 2(a)–(f) shows relationship curves of formation heats per atom of twisted bilayer nano graphene to twist angles ranging from 0° to 60°, with corresponding schematic diagrams of single-layer graphene shown in the background. As can be seen from figure 2, twisted nano graphene with twisted angle varies from 0° to 60° has no translational symmetry as macro graphene, and the shape and edge will also introduce symmetry destruction, which leads to in-plane asymmetry and angle asymmetry. Relationship curves with twist angles of over 60° are symmetrical to the curves between 0° and 60°. It can be concluded from figure 2 that twisted graphene has one stable state when the twist angle is 0° (AB stacking), with several metastable states characterized by low energy barriers in the same time. Energy barrier is the potential energy that the system needs to overcome from metastable to steady state. Formation heats per atom of these AB stacked twisted nano graphenes are 23.25 kJ $mol^{-1}$, 14 .06 kJ $mol^{-1}$, 11 .72 kJ $mol^{-1}$, 10 .54 kJ $mol^{-1}$, 9.82 kJ $mol^{-1}$ and 9.33 kJ $mol^{-1}$, respectively. Maximum potential barrier of the corresponding twisted graphenes with different twist angles are 1.03 kJ $mol^{-1}$, 0.09 kJ $mol^{-1}$, 0.08 kJ $mol^{-1}$, 0.07 kJ $mol^{-1}$, 0.06 kJ $mol^{-1}$ and 0.05 kJ $mol^{-1}$, respectively. Above data indicated larger twisted nano graphenes are more stable. Smaller changes of formation heat leads to slowly relaxation process of lattice structure in graphene layer while the twist angle varies. This caused mistaken of some experimental researchers to insist that twist graphene is stable. In fact, twist angles will change significantly in long term storage, especially under thermal condition and strain. This annealing process is especially fast for small sized twisted graphene nanoflakes.

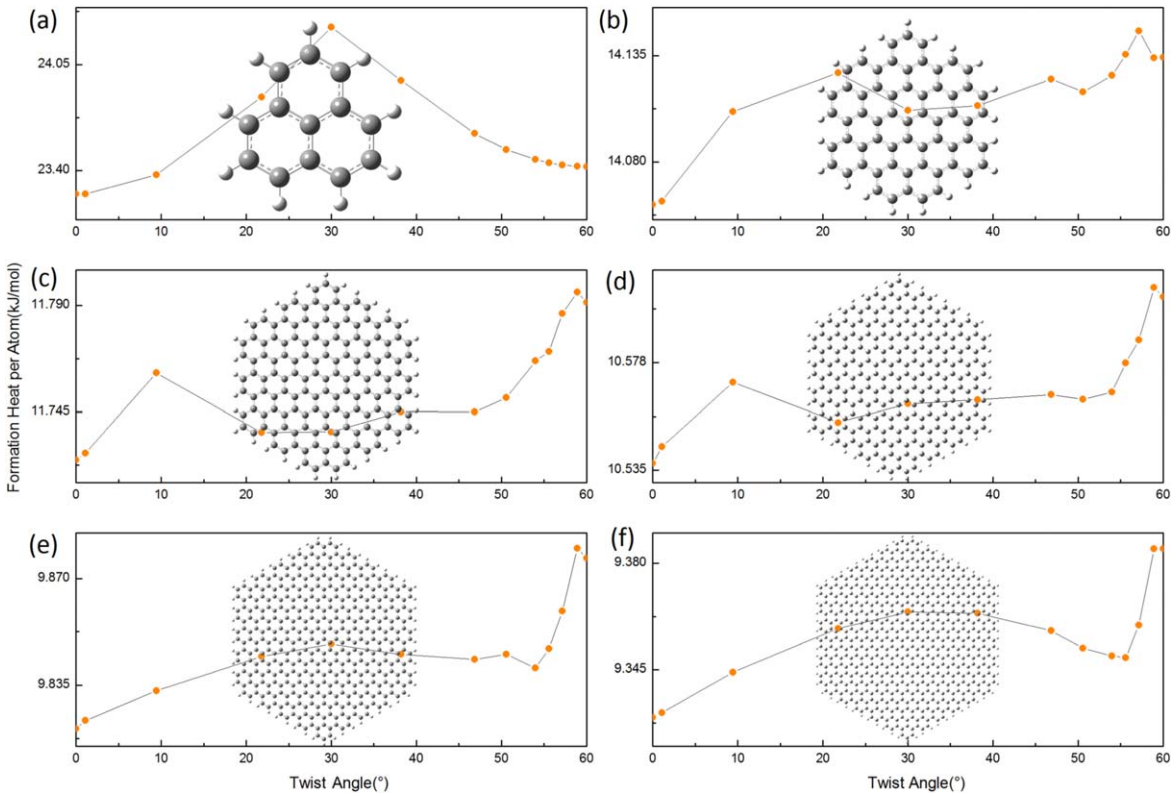


**Figure 2.** Formation heat per atom of twisted bilayer nano graphene containing 22 (a), 82 (b), 178 (c), 310 (d), 478 (e) and 682 (f) atoms each layer as a function of twist angle. Schematic diagrams of the nano graphenes are shown as background in each diagram.

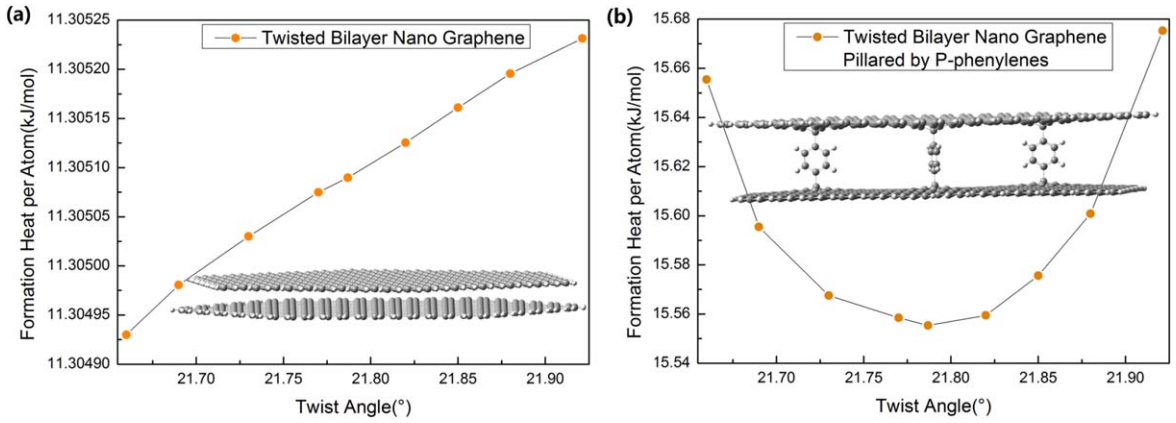


**Figure 3.** Formation heat per atom as a function of twist angle of twisted graphene without (a) and with (b) p-phenylenes pillaring. Schematic diagrams of the twisted nano graphenes are shown as background in each diagram.

## 3. Stability of twisted nano graphene pillared by organic linkers

As early as 2010, Taner Yildirim *et al* prepared graphene frameworks pillared by organic linkers for hydrogen storage [23]. A variety of organic linkers pillared graphene and graphite materials have been developed and discussed in theory since then. These materials are generally called pillared graphene [24].

Here, we suggest the strategy of graphene pillared by organic linkers can be introduce to twisted graphene for long term thermal and strain stabilities.

We calculated formation heat per atom of twisted bilayer nano graphene without and with organic linkers pillaring. The twist angle is 21.79° and each layer is comprised of 613 carbon atoms and 69 hydrogen atoms. Three p-phenylenes are perpendicular to graphene layers at symmetrical AA stacking sites. It is easy to be inferred from figure 3(a) that twisted graphene with a twist angle of 21.79° will spontaneously decrease its twist angle. In contrast, twist angle of twisted graphene pillared by p-phenylenes is unchangeable. External energy disturbances, both heat and strain, will not change it. It will cause elastically deformation of the covalent bonds connecting the organic linkers and graphene layers whether

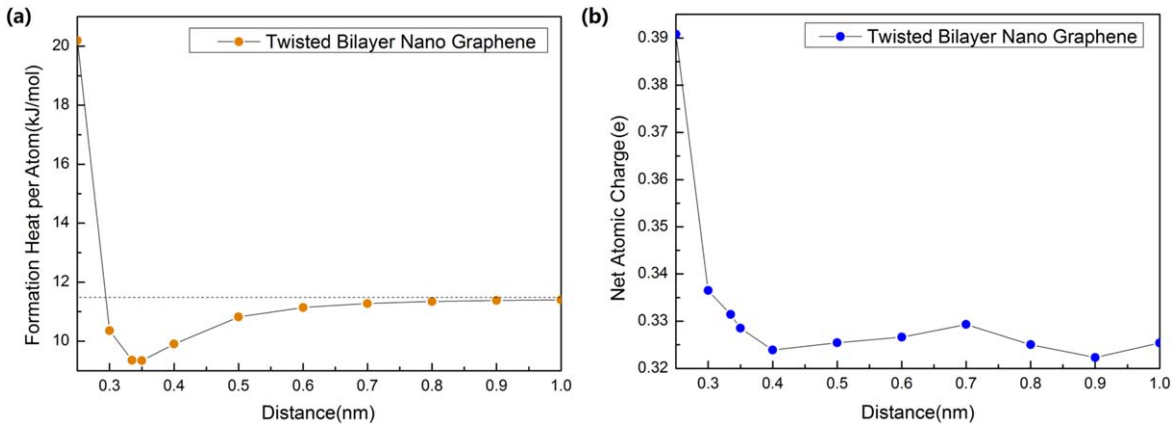


**Figure 4.** Formation heat per atom (a) and net charge of AA stacking carbon atom (b) as a function of interlayer distance of twisted bilayer nano graphene with twist angle of 21.79°.

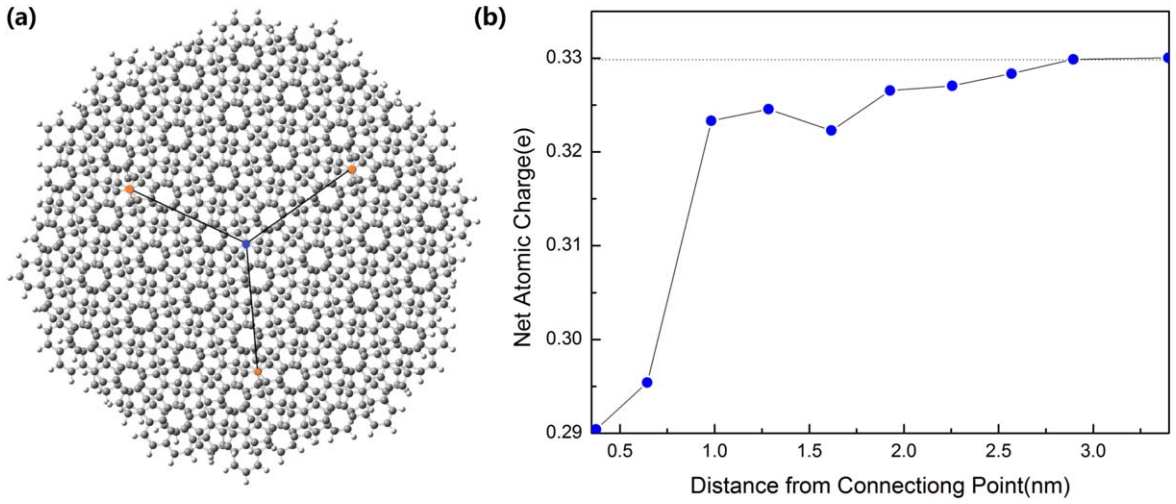


**Figure 5.** (a) Positions of center carbon atom (blue colored) and connecting points (orange colored) of graphene and p-phenylenes. (b) Net charge of center carbon atom changes with its distance from connecting points.

increase or decrease the twist angle. Energy per atom of twisted graphene varies with the angles, as shown in figure 2. Zhang *et al* proved this experimentally [25]. As shown in figure 3, formation heat per atom increases 0.1 kJ $mol^{-1}$ when twisted angle of twisted nano graphene pillared by three p-phenylenes reduced from 21.79° to 21.65°. When it comes to unpillared twisted nano graphene, formation heat per atom decreases 0.0002 kJ $mol^{-1}$. The former is 500 times of the latter. This means that the deformation energy of the three p-phenylenes is enough to compensate for the energy loss of rotation of twisted nano graphene with an area 500 times of ones in figure 3. In other words, three p-phenylenes can stable twisted graphene with diameter of 105 nm.

It should be noticed that pillaring twisted graphene by organic linkers will increase spacing between graphene layers and therefor weaken the interlayer coupling. Interlayer distance of twisted bilayer nano graphene with three p-phenylenes pillaring are 0.77 nm, while natural interlayer distance of twist graphene is only 0.34 nm. Fortunately, interlayer coupling of twisted graphene has a wide range of interaction distance. In 2018, an experiment showed that the interlayer coupling distance of twisted bilayer graphene reached up to at least 1.66 nm [26]. Interlayer coupling of twisted graphene has strong robustness in distance.

Analysis of electronic distribution and electronic properties of magic angle graphene by local charge density is performed by Yuan Cao *et al* [4]. The calculated local density of states, or local charge density in another word, obtained by numerical calculations are consistent with the TEM images. The electron density of one graphene sheet is strongly concentrated in the regions with AA stacking and depleted in the AB and BA stacked regions.

Net atomic charge of each atom of the former studied twisted nano graphene is calculated by MOPAC 2016. Properties of materials are the functional of its electron density in density functional theory. While charge density in turn is a function of the atomic net charge distribution. Schematic diagrams of the twisted nano graphene are shown in figure 3(a). Distribution of net atomic charges is consistent with literatures [4], that is charge density of AA stacking regions is greater than

AB and BA stacking regions. Formation heat per atom and net charge of AA stacking atom in the center of nano graphene as functions of interlayer distance of twisted bilayer nano graphene are shown in figures 4(a) and (b), respectively. Total energy of twisted graphene changes slowly when distance between graphene layers is around 1 nm. It indicated Van der Waals interaction between graphene layers has become very weak at this distance. But net atomic charge of the center carbon atom still changes obviously, as shown in figure 4(b), indicating strong interlayer coupling of electrons.

It can be seen from figure 5 that organic linkers will affect electron distribution of twisted graphene. Organic linkers will change local graphene structure around connecting points of them and graphene sheets. Besides, different organic groups have different characters of donating or withdrawing electrons [27]. Besides, the edge of graphene will also change the charge distributions [12, 13]. The effect on net atomic charges is weak enough to be ignored when the distance from connection points is longer than 3 nm.

## 4. Conclusion and future perspective

In this paper, the intrinsic instability of twisted graphene is proved by numerical simulation, and it is discovered that small-size twisted nano graphene is more instable. Twisted graphene can be pillared by organic linkers to solve the problems of long-term instability, thermal instability and strain instability, while retaining interlayer coupling of electrons. This makes application of twisted graphene, especially for twisted nano graphene, in practice possible.

P-phenylene was chosen here to prove the feasibility of stabilizing twisted graphene by organic linkers. Many other groups can be used to stabilize twisted graphene through covalent bond, hydrogen bond or coordination bond. Hydroxyl-functionalized graphene, as a common kind of graphene oxide, can be used to prepare twisted graphene. Twisted graphene linked by hydrogen bonds between hydroxyls will be stable enough under heat and strain. Only the case that the organic linkers are perpendicular to the graphene layers is calculated here. In fact, as long as the lengths and angles of organic pillars meet a certain symmetry or conform to Gaussian distribution, their influence on the twisted graphene would offset each other, keeping the twisted graphene parallel and stable. This condition will be met naturally for twisted graphene large enough.

The above demonstration of the feasibility of organic linkers pillared twisted bilayer graphene can be extended to the cases of twisted multilayer graphene and Van der Waals heterojunction. Twisted bilayer Van der Waals heterojunction is comprised of two layers of different material, such as one graphene flake pasted on a hexagonal boron nitride sheet, combined by Van der Waals interaction with a twist angle. It has some novel properties, and is also thermal, strain unstable just like twisted bilayer graphene [28, 29]. Organic linkers pillaring will also work on twisted Van der Waals heterojunction in the same way.

Organic linkers pillaring enables Van der Waals homojunction or heterojunction to exist and work stably in solution under high temperature and complex mechanical environments for long term. Besides, high tunability of interlayer spacing increases the tunability of properties and range of applications. Many materials can be inserted between layers [9], expanding the possible properties, applications and tunable range. Main disadvantages of organic linkers pillaring is organic linkers will disturb electron distribution of 2D materials within a certain range. The connection process is also difficult.

## Acknowledgments

This research work was supported by National Natural Scientific Foundation program of China (62074108, 61274056), NSFC-Joint Foundation program of Shanxi Coal Based Low Carbon Nurturing Project (U1710115), Major special projects of Shanxi Province in science and technology (20201101012), Key Research and Development (International Cooperation) Program of Shanxi (201603D421042), Platform and Base Special Project of Shanxi (201605D131038, 201805D131012-3), The Natural Science Foundation of Shanxi Province (201901D211115), The Science and Innovation Project of Higher Education Institutions of Shanxi Province (2020L0078).

## Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

## Author contributions

Liu, C Y designed the project, carried out the calculations and wrote the paper. Hao, Y Y; Xue, L and Li, W L provided guidance, and supervision. All authors contributed to discussions of the results.

## Competing interests

The authors declare no competing interests.

## ORCID iDs

Lin Xue https://orcid.org/0000-0001-7934-5682
Yuying Hao https://orcid.org/0000-0002-1245-2325

## References

[1] Kuwabara M, Clarke D R and Smith D A 1990 Anomalous superperiodicity in scanning tunneling microscope images of graphite *Appl. Phys. Lett.* **56** 2396

[2] Lopes Dos Santos J M B, Peres N M R and Castro Neto A H 2007 Graphene bilayer with a twist: electronic structure *Phys. Rev. Lett.* **99** 256802

[3] Bistritzer R and MacDonald A H 2011 Moiré bands in twisted double-layer graphene *Proc. Natl. Acad. Sci. USA* **108** 12233

[4] Cao Y, Fatemi V, Fang S, Watanabe K, Taniguchi T, Kaxiras E and Jarillo-Herrero P 2018 Unconventional superconductivity in magic-angle graphene superlattices *Nature* **556** 43

[5] Cao Y *et al* 2018 Correlated insulator behaviour at half-filling in magic-angle graphene superlattices *Nature* **556** 80

[6] Bultinck N, Chatterjee S and Zaletel M P 2020 Mechanism for anomalous Hall ferromagnetism in twisted bilayer graphene *Phys. Rev. Lett.* **124** 166601

[7] Kaur S, Pandey R and Karna S P 2021 Enhanced nonlinear optical response of graphene-based nanoflake Van der Waals heterostructures *RSC Adv.* **11** 5590

[8] Liu J B *et al* 2015 Observation of tunable electrical bandgap in large-area twisted bilayer graphene synthesized by chemical vapor deposition *Sci Rep.* **5** 1

[9] Larson D T, Carr S, Tritsaris G A and Kaxiras E 2020 Effects of lithium intercalation in twisted bilayer graphene *Phys. Rev.* B **101** 075407

[10] Zhou H, Xie T, Taniguchi T, Watanabe K and Young A F 2021 Superconductivity in rhombohedral trilayer graphene *Nature* **598** 434

[11] Fischer A, Goodwin Z A H, Mostofi A A, Lischner J, Kennes D M and Klebl L 2022 Unconventional superconductivity in magic-angle twisted trilayer graphene *npj Quantum Mater.* **7** 1

[12] Debopriya D, Annabelle O, Oded H and Elad K 2020 The scaling laws of edge versus bulk interlayer conduction in mesoscale twisted graphitic interfaces *Nat. Commun.* **11** 1

[13] Wang Y M, Herzog-Arbeitman J, Burg G W, Zhu J H, Watanabe K, Taniguchi T, MacDonald A H, Bernevig B A and Tutuc E 2022 Bulk and edge properties of twisted double bilayer graphene *Nat. Phys.* **18** 48

[14] Dong Y, Tao Y, Feng R, Zhang Y, Duan Z and Cao H 2020 Phonon dissipation in friction with commensurate–incommensurate transition between graphene membranes *Nanotechnology* **31** 285711

[15] Dong Y, Duan Z, Tao Y, Wei Z, Gueyea B, Zhang Y and Chen Y 2019 Friction evolution with transition from commensurate to incommensurate contacts between graphene layers *Tribol. Int.* **136** 259

[16] Filippov A E, Dienwiebel M, Frenken J W M, Klafter J and Urbakh M 2008 Torque and twist against superlubricity *Phys. Rev. Lett.* **100** 046102

[17] Feng X F, Kwon S, Park J Y and Salmeron M 2013 Superlubric sliding of graphene nanoflakes on graphene *ACS Nano* **7** 1718

[18] Bagchi S, Johnson H T and Chew H B 2020 Strain-controlled dynamic rotation of twisted 2D atomic layers for tunable nanomechanical systems *ACS Appl. Nano Mater.* **3** 10878

[19] Silva A, Claerbout V E, Polcar T, Kramer D and Nicolini P 2020 Exploring the stability of twisted Van der Waals heterostructures *ACS Appl. Mater. Inter.* **12** 45214

[20] Lucignano P, Alfè D, Cataudella V, Ninno D and Cantele G 2019 Crucial role of atomic corrugation on the flat bands and energy gaps of twisted bilayer graphene at the magic angle $\theta \sim 1.08^{\circ}$ *Phys. Rev.* **99** 195419.1

[21] Stewart J J P MOPAC 2016 (http://OpenMOPAC.net)

[22] Landgraf W 2014 *Electronic Structure of Twisted Graphene Nanoflakes and Nanoribbons* 10701502 (Germany: Friedrich-Alexander-Universitaet Erlangen-Nuernberg) (https://www.proquest.com/openview/98713295543a65496cf58a971d44d86a/1?pq-origsite=gscholar&cbl=2026366)

[23] Burress J W, Gadipelli S, Ford J, Simmons J M, Zhou W and Yildirim T 2010 Graphene oxide framework materials: theoretical predictions and experimental results *Angew. Chem. Int. Ed.* **49** 8902

[24] Yuan K *et al* 2016 Straightforward generation of pillared, microporous graphene frameworks for use in supercapacitors *Adv. Mater.* **27** 6714

[25] Hou Y, Dai Z H, Zhang S, Feng S Z, Wang G R, Liu L Q, Xu Z P, Li Q Y and Zhang Z 2021 Elastocapillary cleaning of twisted bilayer graphene interfaces *Nat. Commun.* **12** 5069

[26] Jeon J W, Kim H, Kim H, Choi S and Kim B H 2018 Experimental evidence for interlayer decoupling distance of twisted bilayer graphene *AIP Adv.* **8** 075228

[27] Dong X, Fu D, Fang W, Shi Y, Chen P and Li L J 2009 Doping single-layer graphene with aromatic molecules *Small* **5** 1422

[28] Wang D *et al* 2016 Thermally induced graphene rotation on hexagonal boron nitride *Phys. Rev. Lett.* **116** 126101

[29] Ribeiro-Palau R, Zhang C J, Watanabe K, Taniguchi T, Hone J and Dean C R 2018 Twistable electronics with dynamically rotatable heterostructures *Science* **361** 690