

Teng Zhang
School of Engineering,
Brown University,
Providence, RI 02912

Huajian Gao
School of Engineering,
Brown University,
Providence, RI 02912
e-mail: Huajian_Gao@brown.edu

Toughening Graphene With Topological Defects: A Perspective

The low fracture toughness of graphene has raised sharp questions about its strength in the presence of crack-like flaws. Here, we discuss a number of recent studies that suggest some promising routes as well as open questions on the possibility of toughening graphene with controlled distributions of topological defects. [DOI: 10.1115/1.4030052]

Keywords: graphene, toughness, topological defects

It has been claimed that graphene, with the elastic modulus of 1 TPa and theoretical strength as high as 130 GPa, is the strongest material [1]. However, from an engineering point of view, it is the fracture toughness that determines the actual strength of materials, as crack-like flaws (i.e., cracks, holes, notches, corners, etc.) are inevitable in the design, fabrication, and operation of practical devices and systems. Recently, it has been demonstrated that graphene has very low fracture toughness, in fact close to that of ideally brittle solids [2]. These findings have raised sharp questions and are calling for efforts to explore effective methods to toughen graphene.

Nanoscale defect engineering in the form of introducing grain boundaries and twin boundaries have been widely employed to improve the mechanical properties of many types of materials including metals [3,4], ceramics [5], and diamond [6]. Nanotwinned cubic boron nitride [5] and diamond [6] exhibit higher hardness and toughness than their defect-free counterparts. Recent studies have also shown that nanoscale defects can be utilized to enhance the fracture toughness of graphene. Zhang et al. [7,8] investigated the properties of a sinusoidal graphene ruga¹ containing periodically distributed disclination quadrupoles and found from molecular dynamics (MD) simulations that the mode I fracture toughness of the selected sinusoidal graphene is around 25.0 J/m², about twice that of the pristine graphene [8]. Jung et al. [10] demonstrated that the fracture toughness of polycrystalline graphene with randomly distributed grain boundaries could be 50% higher than that of the pristine graphene.

The above studies are suggesting that topological defects could toughen graphene. Some fundamental questions could be immediately asked. (1) Why and how do defects toughen graphene? (2) Is there an optimum distribution of defects that leads to the toughest graphene? (3) Is it possible to fabricate graphene structures that contain deliberately designed defect patterns?

On the first question, it appears that there exist at least three mechanisms contributing to the toughness enhancement in graphene, i.e., dislocation shielding, stress reduction by out-of-plane deformation and atomic-scale crack bridging. As illustrated in Fig. 1(a), the compressive stress induced by a dislocation in graphene may significantly alleviate the stress concentration near a crack tip. The out-of-plane deformation induced by defects could also reduce the stress intensity at the crack tip, as shown in Fig. 1(b) [8,10]. Also, as graphene with topological defects tends to fail at bonds with high prestresses (usually in a heptagon ring near a crack tip), the distributed defects could lead to discrete rupture events ahead of the main crack, leading to atomic-scale crack

bridging [8]; see Fig. 1(c). While all three mechanisms can contribute to the observed toughness enhancement, a detailed, quantitative investigation has not been performed. At present, there is still a general lack of understanding on various toughening mechanisms and their interactions in graphene.

On the second question, it will be extremely interesting to find out if there indeed exists an optimum distribution of defects that leads to the toughest graphene. To address this question, presumably one will need to solve a highly nonlinear optimization problem with multiple design variables including the type, position, density, and spatial pattern of defects. In addition, simulations involving bond failures will be needed to determine graphene toughness under given distributions of defects. Thus, it seems nearly impossible to employ conventional gradient type methods to search for the optimal solution. Perhaps only by fully understanding the toughening mechanisms can one acquire the capability of systematically optimizing the toughness of graphene through controlled topological defects. At the moment, it seems more feasible to probe some locally optimal configurations for specific families of defect patterns. For example, the toughness of sinusoidal graphene [7,8] may be further enhanced by tuning the aspect ratio between undulation amplitude and wavelength. One should not underestimate the challenge even for this simplified problem, as the defect pattern required to generate a prescribed 3D configuration of graphene is generally unknown. To address this issue, Zhang et al. [8] proposed a design methodology combining the so-called phase field crystal method [11] and atomistic simulations (Fig. 2), which can serve as a basis for optimizing the toughness of graphene for specific families of 3D configurations. As an extreme case of “defective” graphene, a recent calculation based on the density functional theory has suggested the existence of the so-called penta-graphene composed entirely of carbon pentagons following the Cairo pentagonal tiling [12]. The penta-graphene has no special cleavage planes and may exhibit higher fracture toughness than the pristine graphene.

On the third question, it will be extremely interesting to develop techniques to fabricate graphene structures with deliberately designed defect patterns. Currently, chemical vapor deposition (CVD) [13,14], a popular method to grow large scale graphene, can only produce samples with randomly distributed defects. A recent study has explored using irradiation to control the types and positions of defects in graphene [15], which provides a promising way to make tailored graphene structures. Topological defects, once formed in graphene, can seldom move owing to the strong covalent bonding between carbon atoms. Another possibility is to grow graphene on a curved template with CVD. For example, 3D porous graphene made of curved graphene has been created with the aid of nickel foam [16]. Recent progress in fabricating 3D crystalline metallic structures with ultrasoft nanoscale surface patterns [17] might further facilitate the design of

¹The Latin word ruga is used to refer a large-amplitude state of wrinkles, creases, ridges, or folds [9].

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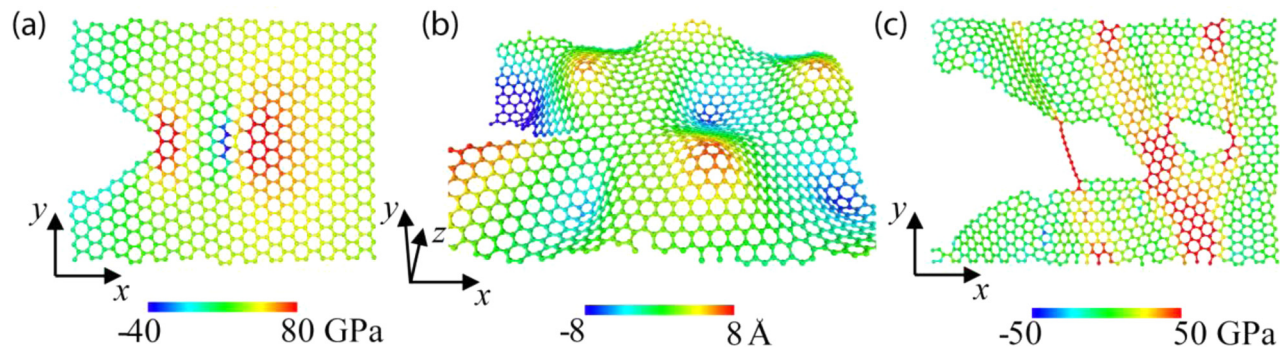


Fig. 1 Toughening mechanisms induced by topological defects in graphene. (a) Dislocation shielding; (b) stress reduction by out-of-plane deformation; and (c) atomic-scale crack bridging. The color represents normal stress σ_{yy} in (a) and (c) and out-of-plane deformation in (b). Figure adapted from Ref. [8].

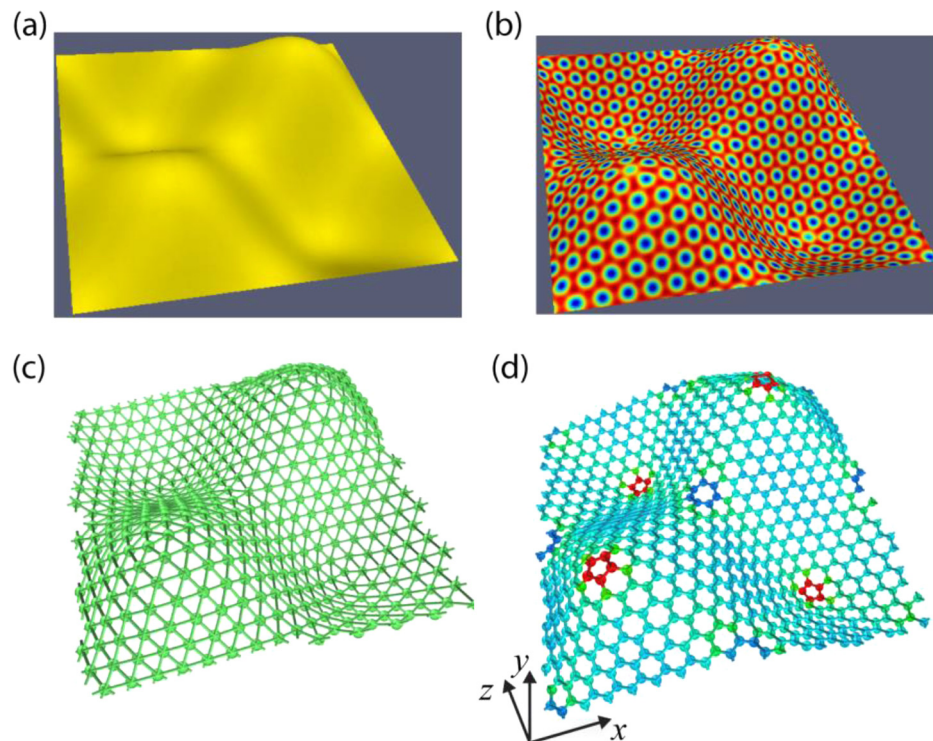


Fig. 2 A general methodology to design an arbitrary 3D curved graphene structure through controlled distributions of topological defects. (a) The target curved surface. (b) A continuum triangular pattern of density waves on the target curved surface generated by a phase field crystal method. (c) A discrete triangular lattice network from the continuum density waves. (d) The full-atom structure generated from a Voronoi construction from the triangular network, followed by equilibration through MD simulations. Figure adapted from Ref. [8].

graphene with desired 3D topology, as it could be potentially used as templates for CVD growth of graphene or as supporting substrates for graphene under irradiation.

It should be cautioned that the introduction of topological defects is a double-edged sword, as dislocations and grain boundaries are also known to reduce the strength of graphene [18,19]. Similar to most other materials, there will be a tradeoff between strength and toughness. For metals, it has been recognized that a special type of hierarchical nanostructure with high densities of twin boundaries embedded in polycrystalline grains can lead to simultaneously high strength, high ductility and superior toughness [4,20,21]. Extending this concept to two-dimensional nanomaterials, it might also be possible to manipulate topological defects in graphene to achieve high strength and high toughness, and a systematic investigation of this issue is expected to have

far-reaching impact on exploring ultrastrong and tough two-dimensional materials for broad applications ranging from flexible electronics, water desalination devices, tissue scaffolds, protective skins/coatings, to novel composites.

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References

- [1] Lee, C., Wei, X., Kysar, J. W., and Hone, J., 2008, "Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene," *Science*, **321**(5887), pp. 385–388.

- [2] Zhang, P., Ma, L. L., Fan, F. F., Zeng, Z., Peng, C., Loya, P. E., Liu, Z., Gong, Y. J., Zhang, J. N., Zhang, X. X., Ajayan, P. M., Zhu, T., and Lou, J., 2014, "Fracture Toughness of Graphene," *Nat. Commun.*, **5**, p. 3782.
- [3] Kumar, K., Van Swygenhoven, H., and Suresh, S., 2003, "Mechanical Behavior of Nanocrystalline Metals and Alloys," *Acta Mater.*, **51**(19), pp. 5743–5774.
- [4] Lu, K., Lu, L., and Suresh, S., 2009, "Strengthening Materials by Engineering Coherent Internal Boundaries at the Nanoscale," *Science*, **324**(5925), pp. 349–352.
- [5] Tian, Y., Xu, B., Yu, D., Ma, Y., Wang, Y., Jiang, Y., Hu, W., Tang, C., Gao, Y., and Luo, K., 2013, "Ultrahard Nanotwinned Cubic Boron Nitride," *Nature*, **493**(7432), pp. 385–388.
- [6] Huang, Q., Yu, D., Xu, B., Hu, W., Ma, Y., Wang, Y., Zhao, Z., Wen, B., He, J., and Liu, Z., 2014, "Nanotwinned Diamond With Unprecedented Hardness and Stability," *Nature*, **510**(7504), pp. 250–253.
- [7] Zhang, T., Li, X., and Gao, H., 2014, "Defects Controlled Wrinkling and Topological Design in Graphene," *J. Mech. Phys. Solids*, **67**, pp. 2–13.
- [8] Zhang, T., Li, X., and Gao, H., 2014, "Designing Graphene Structures With Controlled Distributions of Topological Defects: A Case Study of Toughness Enhancement in Graphene Ruga," *Extreme Mech. Lett.*, **1**(1), pp. 3–8.
- [9] Diab, M., Zhang, T., Zhao, R., Gao, H., and Kim, K.-S., 2013, "Ruga Mechanics of Creasing: From Instantaneous to Setback Creases," *Proc. R. Soc. A*, **469**(2157), p. 20120753.
- [10] Jung, G., Qin, Z., and Buehler, M. J., "Molecular Mechanics of Polycrystalline Graphene With Enhanced Fracture Toughness," *Extreme Mech. Lett.* (in press).
- [11] Elder, K., Katakowski, M., Haataja, M., and Grant, M., 2002, "Modeling Elasticity in Crystal Growth," *Phys. Rev. Lett.*, **88**(24), p. 245701.
- [12] Zhang, S., Zhou, J., Wang, Q., Chen, X., Kawazoe, Y., and Jena, P., 2015, "Penta-Graphene: A New Carbon Allotrope," *Proc. Natl. Acad. Sci. U.S.A.*, **112**(8), pp. 2372–2377.
- [13] Li, X., Cai, W., An, J., Kim, S., Nah, J., Yang, D., Piner, R., Velamakanni, A., Jung, I., and Tutuc, E., 2009, "Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils," *Science*, **324**(5932), pp. 1312–1314.
- [14] Huang, P. Y., Ruiz-Vargas, C. S., van der Zande, A. M., Whitney, W. S., Levendoff, M. P., Kevek, J. W., Garg, S., Alden, J. S., Hustedt, C. J., and Zhu, Y., 2011, "Grains and Grain Boundaries in Single-Layer Graphene Atomic Patchwork Quilts," *Nature*, **469**(7330), pp. 389–392.
- [15] Robertson, A. W., Allen, C. S., Wu, Y. A., He, K., Olivier, J., Neethling, J., Kirkland, A. I., and Warner, J. H., 2012, "Spatial Control of Defect Creation in Graphene at the Nanoscale," *Nat. Commun.*, **3**, p. 1144.
- [16] Ito, Y., Tanabe, Y., Qiu, H. J., Sugawara, K., Heguri, S., Tu, N. H., Huynh, K. K., Fujita, T., Takahashi, T., Tanigaki, K., and Chen, M., 2014, "High-Quality Three-Dimensional Nanoporous Graphene," *Angew. Chem. Int. Ed.*, **53**(19), pp. 4822–4826.
- [17] Gao, H., Hu, Y., Xuan, Y., Li, J., Yang, Y., Martinez, R. V., Li, C., Luo, J., Qi, M., and Cheng, G. J., 2014, "Large-Scale Nanoshaping of Ultrasoft 3D Crystalline Metallic Structures," *Science*, **346**(6215), pp. 1352–1356.
- [18] Grantab, R., Shenoy, V. B., and Ruoff, R. S., 2010, "Anomalous Strength Characteristics of Tilt Grain Boundaries in Graphene," *Science*, **330**(6006), pp. 946–948.
- [19] Wei, Y., Wu, J., Yin, H., Shi, X., Yang, R., and Dresselhaus, M., 2012, "The Nature of Strength Enhancement and Weakening by Pentagon–Heptagon Defects in Graphene," *Nat. Mater.*, **11**(9), pp. 759–763.
- [20] Li, X., Wei, Y., Lu, L., Lu, K., and Gao, H., 2010, "Dislocation Nucleation Governed Softening and Maximum Strength in Nano-Twinned Metals," *Nature*, **464**(7290), pp. 877–881.
- [21] Wei, Y., Li, Y., Zhu, L., Liu, Y., Lei, X., Wang, G., Wu, Y., Mi, Z., Liu, J., Wang, H., and Gao, H., 2014, "Evading the Strength–Ductility Trade-Off Dilemma in Steel Through Gradient Hierarchical Nanotwins," *Nat. Commun.*, **5**, p. 3580.