The construction of atomically precise carbon nanostructures holds promise for developing materials for scientific study and nanotechnology applications. Here, we show that graphene origami is an efficient way to convert graphene into atomically precise, complex nanostructures. By scanning tunneling microscope manipulation at low temperature, we repeatedly fold and unfold graphene nanoislands (GNIs) along an arbitrarily chosen direction. A bilayer graphene stack featuring a tunable twist angle and a tubular edge connection between the layers is formed. Folding single-crystal GNIs creates tubular edges with specified chirality and one-dimensional electronic features similar to those of carbon nanotubes, whereas folding bicrystal GNIs creates well-defined intramolecular junctions. Both origami structural models and electronic band structures are computed to complement analysis of the experimental results. The present atomically precise graphene origami provides a platform for constructing carbon nanostructures with engineered quantum properties and, ultimately, quantum machines.
our STM nano-origami stand out compared with those of structures described in all existing relevant literature (29–34) and open opportunities for further study that cannot be achieved otherwise: (i) The folding operation is spatially localized [i.e., the operation on one GNI has no effect on its neighbors (fig. S1)]. (ii) The folding direction is arbitrary and atomically precise. (iii) There is no size limitation on the GNIs, which makes it feasible to create folded GNIs at different length scales (fig. S2). (iv) no damage or structural defect has been induced during this repeatable process.

The STM-origami GNIs are of high quality and are atomically well defined. Figure 1C shows atomic arrangements of one typical folded GNI, highlighting two different structural features: a 2D bilayer flatland and a 1D tubular structure on the edge. A line profile across the folded GNI is shown in Fig. 1D. The bilayer nature of the GNI is confirmed by the height between the top layer and the substrate, namely ~0.71 nm, which is comparable to the distance between two graphene layers (~0.70 nm) (35). The curved profile of the edge, which is higher than the flat top layer, corroborates its identification as a tubular edge.

We have repeated the folding and unfolding of a GNI along several directions sequentially. The arbitrary folding capability demonstrated in Fig. 1 immediately opens an opportunity to achieve graphene stacking with a tunable twist (Fig. 2A). The twisting angle $\theta$ between the top layer and the bottom layer can be determined by the folding direction (the moving direction of the STM tip for the origami operation) (fig. S3). Figure 2B (bottom) shows three exemplary GNIs with distinct folding orientations from the same GNI (top middle). In addition to bilayer stacking, by sequentially folding multiple times, multilayer stacked GNIs can also be obtained (fig. S4). We have found that even after multiple folding and unfolding steps, the overall morphology of GNI remains the same without the appearance of defects, as determined by comparing high-resolution STM images recorded before and after operations (Fig. 2B). These data suggest that STM origami is a safe and gentle operation that is essential for the construction of high-quality stacked structures.

Direct evidence of stacking with different twist angles is the formation of a tunable moiré superstructure on a folded GNI. Figure 2A (bottom) presents typical high-resolution STM images and corresponding models of two different GNIs formed by folding the same GNI along different directions. The folding angles (fig. S3) used for creating these two GNIs are 0.8° and 27.2° and lead to the resultant $\theta$ of 1.6° and 54.4°, respectively. This estimation of $\theta$ from folding directions shows excellent agreement with the observed moiré superstructures, in which $\theta$ can also be directly determined by measuring the periodicity $d$ of the superstructure ($d = 2a \sin(\alpha/2\theta$), where $a$ is the graphene lattice constant). This cross-referencing of the value of $\theta$ provides a check for the STM-origami operations and confirms the tunability of twisted stacked GNIs by simply varying the folding direction. Figure 2A (top right), which summarizes the different experimental values of $\theta$ that have been achieved in the present work, demonstrates the range and precise control of arbitrary twisting in bilayer graphene made possible by the STM origami.

In addition to the stacked bilayer nanostructures, folding a GNI also generically forms a tubular edge whose chirality depends solely on the folding direction (Fig. 1C). The origami process is essentially the same as the roll-up model of a perfect single-walled CNT from a monolayer graphene except that the as-formed tube is not seamlessly closed in the present work (36). We have, therefore, employed the conventional chiral indices notation $(n,m)$ of a CNT to define the constructed tubular edges, where $n$ and $m$ are integers (fig. S5). Figure 3, A and B, shows atomic configurations of two tubular edges constructed from the same GNI but using two different folding directions. In Fig. 3A, the angle between the folding axis and hexagonal lattice is $\sim 3 \pm 1^\circ$, whereas in Fig. 3B is $19 \pm 1^\circ$. Correspondingly, these two single-walled tubes are (10,8) and (12,3), respectively (a more detailed analysis is shown in fig. S5). The simulated STM images based on the chiral index assignment is also provided and placed underneath its corresponding STM images for comparison. Our simulations of STM images do not consider the tip-convolution effect that often leads to underestimation of tube diameters (37). However, the good agreement between simulated and experimental STM images further confirms our index assignment.

We have also measured $dI/dV$ spectra ($I$, current; $V$, voltage) along as-formed tubular edges and presented the data in Fig. 3C. In contrast with the data acquired from the flat bilayer graphene region, a clear manifestation of van Hove singularity (VHS) peaks is observed on both tubular edges, suggesting that although these tubular edges are not seamlessly closed, they still have 1D electronic characteristics. Our experimental observation of the 1D VHS characteristic from the folded tubes is also corroborated by the density functional theory calculations of electronic structures of both folded tubes and conventional single-wall CNTs (fig. S7) (38). The consistency of the $dI/dV$ spectra acquired along the same tube suggests the delocalized nature of electronic states intrinsic in a 1D structure as well as the
defect-free quality of the tubes created by the STM origami. Although the two tubular edges presented in Fig. 3, A and B, are created from the same GNI, they show different electronic properties. For example, by comparing their spectra, we find that there exists a small energy shift (31 meV) of the VHS gap from the Fermi energy for the tubular edge in Fig. 3A, which can be attributed to interactions between the tubular edge and the substrate because the (10, 8) tube should behave more as a semiconductor, whereas the (12, 3) tube is more metallic (39, 40). These observations highlight the opportunity to investigate effects of the local environment on low-dimensional electronic properties by using the STM origami.

As we have already demonstrated, STM origami is a general technique that is not limited to period 2D GNSs with different chiralities and electronic properties. For example, by comparing their spectra, we find that there exists a small energy shift (31 meV) of the VHS gap from the Fermi energy for the tubular edge in Fig. 3A, which can be attributed to interactions between the tubular edge and the substrate because the (10, 8) tube should behave more as a semiconductor, whereas the (12, 3) tube is more metallic (39, 40). These observations highlight the opportunity to investigate effects of the local environment on low-dimensional electronic properties by using the STM origami.

As we have already demonstrated, STM origami is a general technique that is not limited to period 2D GNSs with different chiralities and electronic properties. For example, by comparing their spectra, we find that there exists a small energy shift (31 meV) of the VHS gap from the Fermi energy for the tubular edge in Fig. 3A, which can be attributed to interactions between the tubular edge and the substrate because the (10, 8) tube should behave more as a semiconductor, whereas the (12, 3) tube is more metallic (39, 40). These observations highlight the opportunity to investigate effects of the local environment on low-dimensional electronic properties by using the STM origami.

As we have already demonstrated, STM origami is a general technique that is not limited to period 2D GNSs with different chiralities and electronic properties. For example, by comparing their spectra, we find that there exists a small energy shift (31 meV) of the VHS gap from the Fermi energy for the tubular edge in Fig. 3A, which can be attributed to interactions between the tubular edge and the substrate because the (10, 8) tube should behave more as a semiconductor, whereas the (12, 3) tube is more metallic (39, 40). These observations highlight the opportunity to investigate effects of the local environment on low-dimensional electronic properties by using the STM origami.

As we have already demonstrated, STM origami is a general technique that is not limited to period 2D GNSs with different chiralities and electronic properties. For example, by comparing their spectra, we find that there exists a small energy shift (31 meV) of the VHS gap from the Fermi energy for the tubular edge in Fig. 3A, which can be attributed to interactions between the tubular edge and the substrate because the (10, 8) tube should behave more as a semiconductor, whereas the (12, 3) tube is more metallic (39, 40). These observations highlight the opportunity to investigate effects of the local environment on low-dimensional electronic properties by using the STM origami.

As we have already demonstrated, STM origami is a general technique that is not limited to period 2D GNSs with different chiralities and electronic properties. For example, by comparing their spectra, we find that there exists a small energy shift (31 meV) of the VHS gap from the Fermi energy for the tubular edge in Fig. 3A, which can be attributed to interactions between the tubular edge and the substrate because the (10, 8) tube should behave more as a semiconductor, whereas the (12, 3) tube is more metallic (39, 40). These observations highlight the opportunity to investigate effects of the local environment on low-dimensional electronic properties by using the STM origami.
switches, amplifiers, and photodetection devices, among others (42). These IMJs have been observed experimentally (43, 44), but growth of such IMJs with desirable structural configurations and properties has presented challenges. We have demonstrated that 1D carbon IMJs between dissimilar tubular edges can be created in a highly controlled manner by performing STM origami on a bicrystal GNI (Fig. 4, A and B). Bicrystal GNIs consisting of two different in-plane graphene domains joined by the well-known 5–7 pair boundary (alternating orange pentagons and purple heptagons) overlay on the STM image for structural assignment. (D) Atomically resolved STM characterization of the IMJ formed by two folded tubular segments with different chirality (green line segments highlight the chiral vectors of the top tubes). (Left) Large-scale view and (right) zoom-in image of the black rectangular area at left. (E) The dI/dV spectra recorded at different locations along the IMJ labeled by the color symbols in (D). The two dotted lines are guides to show the evolution of the first VHS peaks along the junction. The blue arrow highlights the appearance of a defect state in the junction interface, which is clearly absent at the location away from the IMJ interface. Settings for (A) and (B): I = 10 pA; V = −3.0 V. Settings for (C) to (E): I = 100 pA; V = −0.2 V.

Fig. 4E. The energy positions of the first two VHSs and corresponding energy gap (0.19 eV) are almost the same for the two connected (9, 4) and (10, 3) tubular edges. This feature can be understood by the fact that both tubes have the same width, and the VHS gap is mainly determined by the tube diameter for semiconductingCNTs (40). However, in the junction interface, not only a lattice distortion but also a localized (dI/dV) peak at 0.20 eV is clearly observed, which can be attributed to defect states of the 5–7 pairs (44). In Fig. 4E, there is a large asymmetry between the two VHS on one side of the junction but not on the other. Such asymmetries are known to exist in CNTs and have been attributed to a variety of effects ([45] and references therein). Differences in lattice deformations are the likely cause.

The emerging IMJ-like structures enabled by STM origami offer a distinctive set of building blocks for demonstrating innovative physical effects and device concepts. Compared with previous work in which IMJs could only be accidentally observed (42–44), the present method allows for the creation of IMJ-like structures from well-defined 5–7 boundaries, and different combinations of tubular edges can be integrated in a highly selective manner by simply varying the folding direction. Therefore, the present work provides a route to fabricate complex and atomically precise carbon nanostructures with engineered electronic properties that may ultimately lead to the construction of graphene-based quantum machines.

REFERENCES AND NOTES
1. V. Meunier, A. G. Souza Filho, E. B. Barros, M. S. Dresselhaus, Rev. Mod. Phys. 88, 025005 (2016).
2. V. Georgakilas, J. A. Pernan, J. Tucek, R. Zboril, Chem. Rev. 115, 4744–4822 (2015).
3. A. K. Geim, K. S. Novoselov, Nat. Mater. 6, 183–191 (2007).
4. L. A. Ponomarenko et al., Science 320, 356–358 (2008).
5. Y. Chen et al., Nano Lett. 12, 1996–2002 (2012).
6. D. Joung et al., Nano Lett. 17, 1987–1994 (2017).
7. S. R. Peurifoy et al., J. Am. Chem. Soc. 140, 9341–9345 (2018).
8. J. Li et al., Sci. Rep. 4, 5846 (2014).
9. Y. Segawa, H. Itô, K. Itami, Nat. Rev. Mater. 1, 15002 (2016).
10. T. Al-Mulla, M. J. Buehler, Nat. Mater. 14, 366–368 (2015).
11. M. J. Allen et al., Chem. Commun. 41, 6285–6287 (2009).
12. B. Wang et al., Nano Lett. 17, 1467–1473 (2017).
13. B. Wang et al., Adv. Mater. 30, e1707448 (2018).
14. J. Mu et al., Sci. Adv. 1, e1500533 (2015).
15. W. Xu et al., Sci. Adv. 3, e1701084 (2017).
16. N. Patra, B. Wang, P. Král, Nano Lett. 9, 3766–3771 (2009).
17. S. Zhu, T. Li, ACS Nano 8, 2864–2872 (2014).
18. W. J. Hyun, D. O. Park, B. D. Chin, Adv. Mater. 25, 4729–4734 (2013).
19. T. Hallam et al., Nano Lett. 15, 857–863 (2015).
20. Y. Wang, V. H. Crespi, Nano Lett. 17, 6708–6714 (2017).
21. M. Z. Mislin et al., Proc. Natl. Acad. Sci. U.S.A. 115, 466–470 (2018).
22. A. T. Costa, M. S. Ferreira, T. Hallam, G. S. Dueberg, A. H. Castro Neto, Europhys. Lett. 104, 47001 (2013).
23. D. Rainis et al., Phys. Rev. B 83, 165403 (2011).
24. J. Feng, L. Qi, J. Y. Huang, J. Li, Phys. Rev. B 80, 165407 (2009).
25. F. Queisser, R. Schützhold, Phys. Rev. Lett. 111, 046601 (2013).
26. E. Prada, P. San-Jose, L. Brey, Phys. Rev. Lett. 105, 106802 (2010).
27. Y. E. Lee, Y. P. Chen, X. L. Wei, J. X. Zhong, Phys. Rev. B 86, 195426 (2012).
28. H. Terrones, R. Lv, M. Terrones, M. S. Dresselhaus, Rep. Prog. Phys. 75, 062501 (2012).
29. T. W. Ehretse, H. Hira, Adv. Mater. 7, 582–586 (1995).
30. H. V. Roy, C. Kallinger, B. Marsen, K. Sattler, J. Phys. Appl. Phys. 83, 4695–4699 (1998).
31. H. V. Roy, C. Kallinger, K. Sattler, Surf. Sci. 407, 1–6 (1998).
32. L. X. Li et al., Carbon 44, 1544–1547 (2006).
33. H. C. Schneipp et al., ACS Nano 2, 2577–2584 (2008).
34. K. Akius, J. V. Ruitenbeek, arXiv:1812.09501 [cond-mat.mes-hall] (22 December 2018).
35. A. Lucian, G. H. Li, E. Y. Andrei, Solid State Commun. 149, 1151–1156 (2009).
36. M. Duyang, J. L. Huang, C. M. Lieber, Acc. Chem. Res. 35, 1018–1025 (2002).
37. G. I. Márk, L. P. Biró, J. Gyalui, Phys. Rev. B 58, 12645–12648 (1998).
38. Materials and methods are available as supplementary materials.
39. S. M. Bachilo et al., Science 298, 2361–2366 (2002).
40. T. W. Odom, J. L. Huang, N. Kim, C. M. Lieber, Nature 391, 62–64 (1998).
41. L. Cheo, V. H. Crespi, L. X. Benedict, S. G. Louie, M. L. Cohen, Phys. Rev. Lett. 76, 971–974 (1996).
42. D. C. Wei, Y. Q. Liu, Adv. Mater. 20, 2815–2841 (2008).
43. Z. Yao, H. W. C. Postma, B. Balents, C. Dekker, Nature 402, 273–276 (1999).
44. M. Duyang, J. L. Huang, C. M. Cheung, C. M. Lieber, Science 291, 97–100 (2001).
45. L. Meng et al., Phys. Rev. B 87, 205405 (2013).

ACKNOWLEDGMENTS
Funding: This work was financially supported by the National Natural Science Foundation of China (nos. 61888102 and 51872284). National Key Research and Development Projects
of China (2016YFA0202300 and 2018YFA0305800), the Strategic Priority Research Program of the Chinese Academy of Sciences (no. XDB30000000), the CAS Pioneer Hundred Talents Program, the Beijing Nova Program (no. Z181100006218023), and the International Partnership Program of the Chinese Academy of Sciences (no. 112111KYSB20160061). M.O. acknowledges support from the Office of Naval Research (N000141712885) and National Science Foundation (DMR1608720). Work at Vanderbilt University (S.T.P., Y.-Y.Z., and D.-L.B.) was supported by the U.S. Department of Energy (grant DE-FG02-09ER46554) and the McMinn Endowment. Computations at Vanderbilt University were carried out at the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy (contract no. DE-AC02-05CH11231). **Author contributions:** H.-J.G. designed the experiments. H.C., D.W., Y.Q., and W.X. prepared the sample and performed the STM experiments. X.-L.Z., Y.-Y.Z., and D.-L.B. performed the calculations and provided theoretical models and explanations under the guidance of S.D. H.C., Y.-Y.Z., S.D., M.O., S.T.P., and H.-J.G. analyzed the experimental data, plotted the figures, and wrote the manuscript. H.-J.G. and S.D. supervised the project. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** The data presented in this paper can be found in the supplementary materials.

**SUPPLEMENTARY MATERIALS**

science.sciencemag.org/content/365/6457/1036/suppl/DC1

Materials and Methods

Supplementary Text

Figs. S1 to S9

References (46–56)

23 April 2019: accepted 8 August 2019

10.1126/science.aax7864