In-situ observations of novel single-atom thick 2D tin membranes embedded in graphene

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ABSTRACT

There is ongoing research in freestanding single-atom thick elemental metal patches, including those suspended in a two-dimensional (2D) material, due to their utility in providing new structural and energetic insight into novel metallic 2D systems. Graphene pores have shown promise as support systems for suspending such patches. This study explores the potential of Sn atoms to form freestanding stanene and/or Sn patches in graphene pores. Sn atoms were deposited on graphene, where they formed novel single-atom thick 2D planar clusters/patches (or membranes) ranging from 1 to 8 atoms within the graphene pores. Patches of three or more atoms adopted either a star-like or close-packed structural configuration. Density functional theory (DFT) calculations were conducted to look at the cluster configurations and energetics (without the graphene matrix) and were found to deviate from experimental observations for 2D patches larger than five atoms. This was attributed to interfacial interactions between the graphene pore edges and Sn atoms. The presented findings help advance the development of single-atom thick 2D elemental metal membranes.

KEYWORDS

in-situ transmission electron microscopy, Sn atoms, planar cluster, graphene, vacancy

1 Introduction

The isolation of graphene from graphite has inspired research into other van der Waals (vdW) layered two-dimensional (2D) materials, such as hexagonal boron nitride (hBN) and transition metal dichalcogenides (TMDs) [1-11]. These freestanding single-layer materials, which can be stacked vertically or laterally, mainly rely on lamellar structures that ensure the stability of their few or even single-layer formations through their strong intra-layer chemical bonding and weak inter-layer interaction [12]. In contrast to van der Waals materials, metal atoms have a strong preference for three-dimensional (3D) close-packed structures. Hence, monolayer free-standing metallic structures with numerous unsaturated atoms are difficult to stabilize and their synthesis has been challenging [13]. Recently, researchers have shown that metal (and metalloid) elements that do not adopt a layered structure in their bulk form can exist as a 2D single-atom-layer thick structure. Examples include stanene [14-16], silicone [17, 18], germanene [19-21], antimonene and plumbene [22, 23]. However, these examples have only been demonstrated on a support (substrate). It can be argued that a valid single-atom thick 2D layered material should be sufficiently stable to exist as a freestanding structure, as is the case for graphene, h-BN, TMDs, and MXenes. Over the past few years, the use of a lateral support structures to exploit the potential of metals and metal oxides has been developing, in particular, using in-situ transmission electron microscopy (TEM). To date, the most successful development uses pores or holes in mono-layer graphene as a system to suspend a novel material as a 2D single-atom thick membrane. Examples include freestanding single-atom thick Fe and graphene-like ZnO and CuO membranes [24-26]. Suspended Au and Mo monolayer membranes have also been formed in an Au-Ag alloy and MoSe₂, respectively [27, 28]. Thus, the principle of an atomic monolayer material suspended in a support can also be used to explore whether exotic supported 2D monolayers, such as stanene, can exist as freestanding structures. Freestanding metals and metalloids are of interest for two reasons: the necessity of decoupling their support on their physical properties and the development of novel properties that may expand their utility. The different monolayer 2D material examples and strategies discussed are provided in Fig. 1.

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Figure 1 Examples of various of 2D single-atom-thick layer or membrane formations. (a) Van der Waals freestanding mono-atomic 2D layer. (b) Mono-layer 2D metal on a support (substrate). (c) Freestanding single atom thick membrane suspended in graphene. (d) Illustration of how freestanding 2D materials found on supports (e.g. stanene or alternatives) might be observed in a graphene pore.

This work explores the potential of Sn atoms to form in graphene pores and form freestanding stanene or alternate 2D single-atom thick membranes. Stanene has attracted considerable interest due to its unique properties as both a 2D topological insulator (TI) with very large band gaps (as proposed by firstprinciples calculations) and an amplifier of thermoelectric performance, topological superconductivity, and the near-roomtemperature quantum anomalous Hall (QAH) and quantum spin Hall (QSH) effects [16, 29–33]. While we did not obtain stanene, we did discover the ubiquitous formation of novel 2D single-atom Sn patches embedded in graphene vacancies or anchored to defects.

2 Results and discussion

To evaluate the potential of forming free-standing stanene or novel 2D Sn membranes, a previously developed technique in which Sn material is deposited over a graphene mono-layer was used [34]. This was achieved by the sublimation and decomposition of tin acetylacetonate over the graphene (on a standard Lacey carbon Mo TEM grid) in vacuum (ca. 10^{-6} mbar) at an elevated temperature (300 °C). After the deposition process, the specimen was loaded into the TEM and exposed to a beam shower for 5–30 min (dose ca. 1×10^{-4} A/m²). Further details are provided in the Methods section. Energy dispersive spectroscopy (EDS), as well as visual inspection of the specimen before and after the deposition process, confirmed the presence of Sn atoms on the graphene, as can be seen in Fig. S1 in the Electronic Supplementary Material (ESM).

Detailed visual examination of the specimen showed that, in addition to Sn atoms deposited on the mono-layer graphene surface, small groups of Sn atoms could be observed in vacancies and pores. Remarkably, the structural configuration of the atoms in the graphene was reproducible over large areas for many of the 2D embedded patches. These clusters/patches varied from 1 to 8 atoms and were mostly planar (as confirmed through image simulations, which are discussed further on). To distinguish whether Sn atoms are embedded in the graphene plane or absorbed on-top of the graphene, relative intensity analysis for one atom in and on graphene was performed, and the results are shown in Fig. S2 in the ESM. Clearly, the experimental data (red curve) has a better fit in the case of one atom in graphene as compared with the case of one atom on graphene. Most 2D patches (from 2-7 atoms) showed two types of structural configurations as shown in Fig. 2, rows a and b. Single Sn atoms were found to reside in either single or double vacancies in the graphene, similar to the formations observed in Cr and Fe embedded graphene systems [34, 35]. Two Sn atoms embedded in the graphene occurred either in small pores comprising several vacancies (Number 2, row a) or in a single graphene vacancy with their axis perpendicular to the graphene plane (Number 2, row b). This double-atom configuration led to a darker relative contrast (normalized to the graphene contrast) as compared to a single atom. This was confirmed through normalized relative intensity measurements from micrographs and image simulations, as shown in Fig. S3 in the ESM.

In the case of three-atom 2D clusters, two configurations, a tri-star (Number 3 row a) and a line, were again observed, as shown in Fig. 2. For four Sn atoms the first arrangement (Number 4, row a) is again a tri-star configuration; however, unlike the three-atom case, a fourth atom is located in the centre of the tri-star configuration. In the second configuration, the four atoms form a close packed or diamond arrangement. Indeed, these two configurations (star and close-packed) form in all remaining atom 2D patches, except in the case of eight atoms, where no close-packed cluster was observed. No cluster formations with greater than eight atoms were observed. To better comprehend the cluster structures we conducted image simulations to compare to the experimental data, as shown in Fig. 2, rows II, III, and IV. In some patches with more atoms, a slight difference is observed between the contrasts of some experimental and simulation images, as multiple images were captured over a period of time for the imaging of a cluster. Since the image capture process takes a finite (approximately half a second) artefacts because atom movement can occur. This can lead to slight differences between the experimental micrographs and the image simulations.

The stability of the clusters under electron irradiation, as well as the frequency for each cluster type, was also examined (Fig. 3), where the typical dose was 1.8×10^6 A/m². With regards to the stability, it was determined that the larger planar cluster were more susceptible to electron irradiation before collapsing. Between the different types of structures (a and b) the trends are less clear; however, still suggest a competition between the graphene pore shape/size and the Sn atom structural configuration. Single Sn atoms were embedded in both monovacancies and divacancies. Monovacancy-based Sn atom embedding was found to be more stable and prevalent, which is in agreement with studies investigating Cr and Fe atoms embedded in graphene [34, 35]. With two atoms, the more frequent and stable configuration involved two Sn atoms embedded in-plane with the graphene next to each other. The instability (and low frequency) of both atoms anchoring was attributed to a strong preference for single atom anchoring in a monovacancy.



Figure 2 The observed in-plane single-atom thick 2D Sn patches found embedded in graphene. These clusters varied from 1 to 8 atoms and were mostly planar, two types of (2D) structural configurations, rows Ia and Ib, were found for most patches. (Ia and Ib) HRTEM images, image simulations (IIa and IIb), top-view stick-and-ball models (IIIa and IIIb), and side-view stick-and-ball models (IVa and IVb) for different forms of clusters.



Figure 3 Sn cluster stability for two types of structural configuration ((a), (b) from Fig. 1) under electron beam irradiation. (a) Plot of the experimentally observed frequency. (b) Observed frequency for the different forms of clusters. A total of 76 videos (each video contains 200 images) were selected to calculate the stability and frequency of the different types of atom cluster. The *x*-axis denotes the longest time that a cluster takes to stabilize in graphene, based on the videos that we randomly selected. The frequency indicates the number of images containing different atom clusters divided by the total number images selected.

With three atoms, the tri-star configuration was energetically favourable, since it was a close-packed form and the graphene pore was more circular than elongated. With four atoms, the close- packed formation is more prevalent than the star configuration as there is little difference in the pore morphology required between the two structures. However, with five atoms or more, the star-based 2D structures tend to be more stable and more frequently observed. This difference is attributed to the graphene pore shape being more circular and therefore, inadequate for the close-packed clusters, which require faceting due to a higher energy configuration.

To confirm that the clusters were Sn atoms, electron energy loss spectroscopy (EELS) and normalized relative intensity measurements were employed (Fig. 4). EELS measurements over many clusters showed signals for Sn around 485 eV (Figs. 4(a) and 4(b), and Fig. S4 in the ESM). Weak oxygen signals around 532 eV were also found; however, were collected on bare pristine graphene (Figs. 4(c) and 4(d)) and were attributed to adsorbed O or H₂O species on the graphene. For single-atom clusters, EELS signals proved challenging due to low signal to noise ratios and limited stability. However, to better examine the patches we also obtained EELS spectra in a probe corrected TEM. Figure 4(f) shows the EELS data for the blue dot area of patch shown in Fig. 4(e); the results show a patch comprising pure Sn as indicated by the Sn $M_{4,5}$ edge at 485 eV and no oxygen peaks (as would be present from tin oxide) [36]. This observation was true for other planar clusters embedded in graphene as for example the upper and middle EELS spectra in Fig. 4(g). We also examined some nano-particles on the surface of the graphene and these showed clear oxygen K1 edges, indicating they are tin oxide. In addition, relative intensity measurements for single-atom Sn, Si, and Cu (with Si and Cu being the two most likely contaminants) were conducted from image simulations [37], as presented in Figs. 4(k), 4(l), and 4(m). The data indicates that the atoms were Sn.

We now turn to the dynamic aspects of the Sn clusters under electron irradiation. Two dynamic aspects were observed as the Sn atoms were ejected from a graphene vacancy. First, when the Sn atom was ejected, the vacancy remained behind (Figs. 5(a) and 5(b)). In some instances, the vacancy was filled again (Figs. 5(c) and 5(d)) due to the vacancies being efficient traps for diffusing atoms (and clusters) on the graphene surface



Figure 4 EELS studies from different areas and relative-intensity analysis for Si, Cu and Sn atoms embedded in graphene. (a) HRTEM images of several-atom 2D patches embedded in graphene. (b) EELS spectra of the square area in image (a). (c) HRTEM images of clean graphene. (d) EELS spectra of the square area in image (c). (e) HRTEM images of Sn patch embedded in graphene. (f) EELS spectra of the area of Sn patch represented by the blue dot in image (e). (g) EELS spectra from additional Sn cluster areas and particles on the surface of the graphene (the inset (h), (i), (j) on the right side of image g shows HRTEM images of the measurement locations; orange, purple, and green dots indicate the specific position measured. (k) Experimental TEM image of a single Sn atom in a graphene vacancy. (l) Image simulation for Sn, Cu, and Si atoms embedded in graphene vacancies. (m) Comparison of the normalized intensity profiles across the single metal atom at a vacancy between the simulations and experiments.



Figure 5 Dynamic activity of single Sn atom in graphene vacancies under electron beam irradiation. (a)–(d) A series of HRTEM images of single Sn atom being ejected and leaving a graphene vacancy. ((e), (f)) and ((g), (h)) Two series of HRTEM images of single Sn show catalytic healing of Sn embedded graphene. All scale bars are 5 Å.

[38]. Second, when an Sn atom was ejected the vacancy healed, it suggests that perhaps Sn atoms have a catalytic ability similar to Cr and Fe [34, 39]. Examples of this healing are provided in Figs. 5(e)-5(h).

Occasionally, the star-structured clusters (with 6–7 atoms) anchored to the surface of the graphene would rotate under the electron beam. An example is provided in Fig. 6; panels (a)–(c) show the three positions that the six-atom star cluster adopts at t = 0, 1.5, and 2.5 s, respectively. Immediately below the star cluster, a pair of defects in the graphene was observed and used for spatial identification of the anchor atom of the

cluster, viz. the atom bound the graphene. The rotation angles are shown in the schematic in panel (d). Another example of a six-atom star cluster was seen rotating through 180°. Further examples are provided in Fig. S5 in the ESM. With extended irradiation, eventually the clusters would either detach and instantaneously disappear from view, leaving a vacancy, healed vacancy, or if only part of the cluster was released, a smaller cluster embedded in the graphene. A fuller demonstration of the dynamic character of the star clusters anchored to graphene can be seen in Movies ESM1–ESM4.

The initial aim of this study was to determine if stanene could



Figure 6 Dynamic behaviour of anchored star 2D single-atom thick cluster on graphene. (a)–(d) Sequences of HRTEM images show the flip/rotate activities that prove the clusters can form in free space. (e)–(h) Sequences of HRTEM images show the flip/rotate activities an insertion of an atom (from 6 atoms to 7 atoms) forming the 2D star cluster. All scale bars are 5 Å.

exist as a freestanding membrane suspended in a pore-like Fe and graphene-like ZnO and CuO [24–26]. In this study, Sn atoms were successfully deposited on graphene, where they became embedded in vacancies or pores and formed ordered planar clusters (or small membranes). Clusters of three or more atoms would adopt either a star-like or close-packed structural configuration. Planar clusters comprising more than eight atoms were not observed. Hexagonal crystal structures as found with stanene [14–16, 30] were not observed and nor was a predicted vertical zigzag structure [33, 40]. This suggests freestanding or suspended stanene may not be able to exist under these conditions. Moreover, the observation of anchored (2D) planar star clusters on graphene highlights the importance of the structural commensurability of the support in the formation of stanene.

As such, this section will discuss the driving forces necessary to form highly ordered and reproducible single-atom-thick planar clusters embedded in graphene. Pores in 2D materials are often suitable for the stabilization of metal atoms. 2D clusters are stabilized when the interaction between the metal atoms and the pore edge is exothermic and appropriately directional [41]. This requirement is fulfilled by graphene edges [42, 43], which prefer in-plane to on-top adsorption [44]. A study by Nevalaita and Koskinen [41] showed the stability of 2D patches or membranes depends on the relative intrinsic stability of the 2D metal, the commensurability and the resulting strain at the interface, the possibility of carbide formation, and the chemical bonding at the interface. These different aspects could account for the difference in the formation of ordered 2D clusters or patches (as observed in this study) and disordered planar clusters (as found for Pt) as well as the free energy of the structure [45]. Furthermore, the number of metal atoms forming in a pore will affect the free energy, mainly the entropy term, and the resulting clusters would become more disordered as the number of atoms increase, a result supported by this study. To verify the experimentally observed 2D planar Sn clusters, possible cluster configurations and their energetics were further investigated using first-principles density functional theory (DFT) calculations. Figure S6 in the ESM shows the optimized atomic structures for freestanding Sn clusters in the absence of a graphene matrix and the corresponding relative formation energies. Here, initial trial structures were built using experimental observations with two competing configurations for each cluster. The morefrequently observed configurations (comprising up to five atoms) have lower formation energies than the corresponding competing structures, by 0.09, 1.18, and 1.21 eV for 3, 4, and 5 atom clusters, respectively. However, the calculated energy differences for larger clusters indicated that the first configurations should be ~10¹² times more frequently observed than the second one based on the Boltzmann factor exp(– $\Delta E/(k_BT)$). These results are inconsistent with the frequencies those attained through experimental observation. Moreover, for six atoms, a 3D configuration had the lowest formation energy, implying that graphene edge-metal atom interfacial interactions (edge effects) play an important role in individual formation stability.

To better explore the role of interfacial effects, the adsorption energetics of a Sn atom adsorbed on graphene or within a C vacancy were calculated. As shown in Fig. 7, the adsorption energy for vacancies (-1.60 eV and -0.19 eV for a monovacancy and divacancy, respectively) is much lower than that on graphene (3.19 eV), confirming the stabilization effect of these graphene pores. Moreover, the adsorption energies for the armchair and zigzag edges are -0.43 eV and -2.65 eV, respectively, indicating that the reaction can be exothermic within larger pores. Overall, these results confirmed that pores can stabilize Sn atoms through interactions with the graphene pore edges.



Figure 7 Sn adsorption on C vacancies in graphene: (a) VC1, (b) VC2, (c) armchair edge and (d) zigzag edge.

3 Conclusions

This work explored congregating Sn atoms in graphene pores to form stanene or novel 2D single-atom thick membranes. No structures resembling stanene were observed, though 2D planar membranes were formed. Clusters of three or more atoms adopted either a star-like or close-packed structural configuration. Planar Sn patches comprising more than eight atoms were not observed. DFT studies looking at the cluster configurations and energetics (without the graphene matrix) deviated from experimental observations for membranes larger than five atoms. This is attributed to interfacial forces between the graphene pore edges and Sn atoms. This study provides a framework for understanding single-atom thick Sn planar membranes embedded in graphene as well as the dynamic behaviour of anchored 2D planar Sn clusters over graphene under electron irradiation, advances the use of graphene pores as a means to suspend single-atom thick 2D metals, and further enhances our understanding of 2D metals.

4 Methods

4.1 Sample preparation

The base graphene was prepared through thermal CVD over Cu foil, as described in previous studies [46, 47]. The graphene was then transferred onto standard Lacey carbon Mo TEM grids through spin-coating with PMMA before etching the Cu foil away with APS. To deposit the Sn on the graphene, a TEM grid with transferred graphene was placed in a quartz vial with a nominal amount of Sn acetyle acetonate (acac). The vial was then evacuated to ca. 10⁻⁶ mbar, sealed, and heated to 300 °C for 12 h to sublime and decompose the Sn acac and leave nominal amounts of Sn atoms on the graphene surface. After deposition, the specimen was loaded into the TEM and exposed to beam shower for 5-30 minutes (ca. 9 nA). Energy-dispersive spectroscopy was performed to confirm the presence of Sn. Prior to the TEM in-situ experiments, the specimen was annealed under vacuum (< 10⁻⁶ mbar) overnight at 250 °C [48].

4.2 TEM studies

The experiments were conducted on a Titan³ TEM equipped with a monochromator and a Cs corrector for the primary objective lens. The electron acceleration voltage was 80 kV. The current density was typically 3.8 nA/nm².

4.3 Image simulation

The multi-slice high-resolution image simulations were conducted using JEMS software. All the simulation parameters were equivalent to those used in the TEM experiments. The acceleration voltage was 80 kV. The energy spread was set at 0.2 eV. The chromatic (Cc) and spherical (Cs) aberrations were set as 1 mm and 1 μ m, respectively. The focuses were typically 2 and 3 nm, with a defocus spread of 2 nm.

4.4 DFT calculations

The first-principles DFT calculations were performed using the projector-augmented wave (PAW) method and the Perdew–Burke–Emzerhof exchange correlation functional [49, 50], as implemented in the Vienna *ab initio* simulation package [51, 52]. The graphene was modelled by an $8 \times 8 \times 1$ supercell with slabs separated by a vacuum space of 20 Å to avoid spurious interactions between the images. A plane-wave basis was employed with a kinetic energy cut-off of 450 eV. The Γ point was used for K-point sampling. The optB88 functional was employed to include the effects of the van der Waals forces [53].

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Electronic Supplementary Material: Supplementary material (TEM, EDX, EELS analysis, DFT calculation and movies ESM1–ESM4 which provide an in-depth demonstration of the dynamic character of the star clusters anchored to graphene) is available in the online version of this article at https://doi.org/10.1007/s12274-020-3108-y.

References

- Kochat, V.; Samanta, A.; Zhang, Y.; Bhowmick, S.; Manimunda, P.; Asif, S. A. S.; Stender, A. S.; Vajtai, R.; Singh, A. K.; Tiwary, C. S. et al. Atomically thin gallium layers from solid-melt exfoliation. *Sci. Adv.* 2018, 4, e1701373.
- [2] Jin, C. H.; Lin, F.; Suenaga, K.; Iijima, S. Fabrication of a freestanding boron nitride single layer and its defect assignments. *Phys. Rev. Lett.* 2009, 102, 195505.
- [3] Corso, M.; Auwärter, W.; Muntwiler, M.; Tamai, A.; Greber, T.; Osterwalder, J. Boron nitride nanomesh. *Science* 2004, 303, 217–220.
- [4] Dean, C. R.; Young, A. F.; Meric, I.; Lee, C.; Wang, L.; Sorgenfrei, S.; Watanabe, K.; Taniguchi, T.; Kim, P.; Shepard, K. L. et al. Boron nitride substrates for high-quality graphene electronics. *Nat. Nanotechnol.* 2010, *5*, 722–726.
- [5] Britnell, L.; Gorbachev, R. V.; Jalil, R.; Belle, B. D.; Schedin, F.; Mishchenko, A.; Georgiou, T.; Katsnelson, M. I.; Eaves, L.; Morozov, S. V. et al. Field-effect tunneling transistor based on vertical graphene heterostructures. *Science* **2012**, *335*, 947–950.
- [6] Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. Two-dimensional atomic crystals. *Proc. Natl. Acad. Sci. USA* 2005, *102*, 10451–10453.
- [7] Coleman, J. N.; Lotya, M.; O'Neill, A.; Bergin, S. D.; King, P. J.; Khan, U.; Young, K.; Gaucher, A.; De, S.; Smith, R. J. et al. Twodimensional nanosheets produced by liquid exfoliation of layered materials. *Science* **2011**, *331*, 568–571.
- [8] Liu, K. K.; Zhang, W. J.; Lee, Y. H.; Lin, Y. C.; Chang, M. T.; Su, C. Y.; Chang, C. S.; Li, H.; Shi, Y. M.; Zhang, H. et al. Growth of large-area and highly crystalline MoS₂ thin layers on insulating substrates. *Nano Lett.* **2012**, *12*, 1538–1544.
- [9] Komsa, H. P.; Krasheninnikov, A. V. Two-dimensional transition metal dichalcogenide alloys: Stability and electronic properties. J. Phys. Chem. Lett. 2012, 3, 3652–3656.
- [10] Gong, Y. J.; Lin, Z.; Ye, G. L.; Shi, G.; Feng, S. M.; Lei, Y.; Elías, A. L.; Perea-Lopez, N.; Vajtai, R.; Terrones, H. et al. Tellurium-assisted low-temperature synthesis of MoS₂ and WS₂ monolayers. ACS Nano 2015, 9, 11658–11666.
- [11] Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L. J.; Loh, K. P.; Zhang, H. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nat. Chem.* **2013**, *5*, 263–275.
- [12] Yang, L. M.; Frauenheim, T.; Ganz, E. The new dimension of silver. *Phys. Chem. Chem. Phys.* 2015, 17, 19695–19699.
- [13] Yang, L. M.; Frauenheim, T.; Ganz, E. Properties of the free-standing two-dimensional copper monolayer. J. Nanomater. 2016, 2016, 8429510.
- [14] Saxena, S.; Chaudhary, R. P.; Shukla, S. Stanene: Atomically thick free-standing layer of 2D hexagonal tin. *Sci. Rep.* 2016, *6*, 31073.

- [15] Zhu, F. F.; Chen, W. J.; Xu, Y.; Gao, C. L.; Guan, D. D.; Liu, C. H.; Qian, D.; Zhang, S. C.; Jia, J. F. Epitaxial growth of two-dimensional stanene. *Nat. Mater.* **2015**, *14*, 1020–1025.
- [16] Deng, J. J.; Xia, B. Y.; Ma, X. C.; Chen, H. Q.; Shan, H.; Zhai, X. F.; Li, B.; Zhao, A. D.; Xu, Y.; Duan, W. H. et al. Epitaxial growth of ultraflat stanene with topological band inversion. *Nat. Mater.* 2018, *17*, 1081–1086.
- [17] Lalmi, B.; Oughaddou, H.; Enriquez, H.; Kara, A.; Vizzini, S.; Ealet, B.; Aufray, B. Epitaxial growth of a silicene sheet. *Appl. Phys. Lett.* 2010, 97, 223109.
- [18] Houssa, M.; Dimoulas, A.; Molle, A. Silicene: A review of recent experimental and theoretical investigations. *J. Phys. Condens. Matter* 2015, 27, 253002.
- [19] Bianco, E.; Butler, S.; Jiang, S. S.; Restrepo, O. D.; Windl, W.; Goldberger, J. E. Stability and exfoliation of germanane: A germanium graphane analogue. *ACS Nano* **2013**, *7*, 4414–4421.
- [20] Jiang, S. S.; Butler, S.; Bianco, E.; Restrepo, O. D.; Windl, W.; Goldberger, J. E. Improving the stability and optical properties of germanane via one-step covalent methyl-termination. *Nat. Commun.* 2014, 5, 3389.
- [21] Yuhara, J.; Shimazu, H.; Ito, K.; Ohta, A.; Araidai, M.; Kurosawa, M.; Nakatake, M.; Le Lay, G. Germanene epitaxial growth by segregation through Ag(111) thin films on Ge(111). ACS Nano 2018, 12, 11632–11637.
- [22] Fortin-Deschênes, M.; Waller, O.; Menteş, T. O.; Locatelli, A.; Mukherjee, S.; Genuzio, F.; Levesque, P. L.; Hébert, A.; Martel, R.; Moutanabbir, O. Synthesis of antimonene on germanium. *Nano Lett.* 2017, *17*, 4970–4975.
- [23] Yuhara, J.; He, B. J.; Matsunami, N.; Nakatake, M.; Le Lay, G. Graphene's latest cousin: Plumbene epitaxial growth on a "nano watercube". Adv. Mater. 2019, 31, 1901017.
- [24] Zhao, J.; Deng, Q. M.; Bachmatiuk, A.; Sandeep, G.; Popov, A.; Eckert, J.; Rümmeli, M. H. Free-standing single-atom-thick iron membranes suspended in graphene pores. *Science* **2014**, *343*, 1228–1232.
- [25] Quang, H. T.; Bachmatiuk, A.; Dianat, A.; Ortmann, F.; Zhao, J.; Warner, J. H.; Eckert, J.; Cunniberti, G; Rümmeli, M. H. *In situ* observations of free-standing graphene-like mono- and bilayer ZnO membranes. *ACS Nano* **2015**, *9*, 11408–11413.
- [26] Yin, K. B.; Zhang, Y. Y.; Zhou, Y. L.; Sun, L. T.; Chisholm, M. F.; Pantelides, S. T.; Zhou, W. Unsupported single-atom-thick copper oxide monolayers. 2D Mater. 2016, 4, 011001.
- [27] Wang, X. L.; Wang, C. Y.; Chen, C. J.; Duan, H. C.; Du, K. Freestanding monatomic thick two-dimensional gold. *Nano Lett.* 2019, 19, 4560–4566.
- [28] Zhao, X. X.; Dan, J. D.; Chen, J. Y.; Ding, Z. J.; Zhou, W.; Loh, K. P.; Pennycook, S. J. Atom-by-atom fabrication of monolayer molybdenum membranes. *Adv. Mater.* 2018, *30*, 1707281.
- [29] Liu, Y. N.; Gao, N.; Zhuang, J. C.; Liu, C.; Wang, J. O.; Hao, W. C.; Dou, S. X.; Zhao, J. J.; Du, Y. Realization of strained stanene by interface engineering. J. Phys. Chem. Lett. 2019, 10, 1558–1565.
- [30] Xu, C. Z.; Chan, Y. H.; Chen, P.; Wang, X. X.; Flötotto, D.; Hlevyack, J. A.; Bian, G.; Mo, S. K.; Chou, M. Y.; Chiang, T. C. Gapped electronic structure of epitaxial stanene on InSb(111). *Phys. Rev. B* 2018, *97*, 035122.
- [31] Liao, M. H.; Zang, Y. Y.; Guan, Z. Y.; Li, H. W.; Gong, Y.; Zhu, K. J.; Hu, X. P.; Zhang, D.; Xu, Y.; Wang, Y. Y. et al. Superconductivity in few-layer stanene. *Nat. Phys.* **2018**, *14*, 344–348.
- [32] Xu, Y.; Yan, B. H.; Zhang, H. J.; Wang, J.; Xu, G.; Tang, P. Z.; Duan, W. H.; Zhang, S. C. Large-gap quantum spin hall insulators in tin films. *Phys. Rev. Lett.* **2013**, *111*, 136804.
- [33] Liu, C. C.; Jiang, H.; Yao, Y. G. Low-energy effective Hamiltonian involving spin-orbit coupling in silicene and two-dimensional germanium and tin. *Phys. Rev. B* 2011, 84, 195430.

- [34] Ta, H. Q.; Zhao, L.; Yin, W. J.; Pohl, D.; Rellinghaus, B.; Gemming, T.; Trzebicka, B.; Palisaitis, J.; Jing, G; Persson, P. O. Å. et al. Single Cr atom catalytic growth of graphene. *Nano Res.* 2018, *11*, 2405–2411.
- [35] Robertson, A. W.; Montanari, B.; He, K.; Kim, J.; Allen, C. S.; Wu, Y. A.; Olivier, J.; Neethling, J.; Harrison, N.; Kirkland, A. I. et al. Dynamics of single Fe atoms in graphene vacancies. *Nano Lett.* 2013, 13, 1468–1475.
- [36] Moreno, M. S.; Egerton, R. F.; Midgley, P. A. Differentiation of tin oxides using electron energy-loss spectroscopy. *Phys. Rev. B* 2004, 69, 233304.
- [37] Wei, D. C.; Liu, Y. Q.; Wang, Y.; Zhang, H. L.; Huang, L. P.; Yu, G. Synthesis of N-doped graphene by chemical vapor deposition and its electrical properties. *Nano Lett.* **2009**, *9*, 1752–1758.
- [38] Rodríguez-Manzo, J. A.; Cretu, O.; Banhart, F. Trapping of metal atoms in vacancies of carbon nanotubes and graphene. ACS Nano 2010, 4, 3422–3428.
- [39] Zhao, J.; Deng, Q. M.; Avdoshenko, S. M.; Fu, L.; Eckert, J.; Rümmeli, M. H. Direct *in situ* observations of single Fe atom catalytic processes and anomalous diffusion at graphene edges. *Proc. Natl. Acad. Sci. USA* 2014, *111*, 15641–15646.
- [40] Maniraj, M.; Stadtmüller, B.; Jungkenn, D.; Düvel, M.; Emmerich, S.; Shi, W.; Stöckl, J.; Lyu, L.; Kollamana, J.; Wei, Z. et al. A case study for the formation of stanene on a metal surface. *Commun. Phys.* **2019**, *2*, 12.
- [41] Nevalaita, J.; Koskinen, P. Stability limits of elemental 2D metals in graphene pores. *Nanoscale* 2019, 11, 22019–22024.
- [42] Antikainen, S.; Koskinen, P. Growth of two-dimensional Au patches in graphene pores: A density-functional study. *Comput. Mater. Sci.* 2017, 131, 120–125.
- [43] Malola, S.; Häkkinen, H.; Koskinen, P. Gold in graphene: In-plane adsorption and diffusion. *Appl. Phys. Lett.* 2009, 94, 043106.
- [44] Pastewka, L.; Malola, S.; Moseler, M.; Koskinen, P. Li⁺ adsorption at prismatic graphite surfaces enhances interlayer cohesion. J. Power Sources 2013, 239, 321–325.
- [45] Dong, C. Z.; Zhu, W. P.; Zhao, S. Y.; Wang, P.; Wang, H. T.; Yang, W. Evolution of Pt clusters on graphene induced by electron irradiation. J. Appl. Mech. 2013, 80, 040904.
- [46] Ta, H. Q.; Perello, D. J.; Duong, D. L.; Han, G. H.; Gorantla, S.; Nguyen, V. L.; Bachmatiuk, A.; Rotkin, S. V.; Lee, Y. H.; Rümmeli, M. H. Stranski–Krastanov and Volmer–Weber CVD growth regimes to control the stacking order in bilayer graphene. *Nano Lett.* 2016, *16*, 6403–6410.
- [47] Rümmeli, M. H.; Gorantla, S.; Bachmatiuk, A.; Phieler, J.; Geißler, N.; Ibrahim, I.; Pang, J. B.; Eckert, J. On the role of vapor trapping for chemical vapor deposition (CVD) grown graphene over copper. *Chem. Mater.* 2013, 25, 4861–4866.
- [48] Zhao, L.; Ta, H. Q.; Dianat, A.; Soni, A.; Fediai, A.; Yin, W. J.; Gemming, T.; Trzebicka, B.; Cuniberti, G.; Liu, Z. F. et al. *In situ* electron driven carbon nanopillar-fullerene transformation through Cr atom mediation. *Nano Lett.* **2017**, *17*, 4725–4732.
- [49] Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* 1994, 50, 17953–17979.
- [50] Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- [51] Kresse, G.; Furthmüller, J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 1996, 54, 11169–11186.
- [52] Kresse, G; Furthmüller, J. Efficiency of *ab-initio* total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, *6*, 15–50.
- [53] Klimeš, J.; Bowler, D. R.; Michaelides, A. Chemical accuracy for the van der Waals density functional. J. Phys. Condens. Matter 2009, 22, 022201.