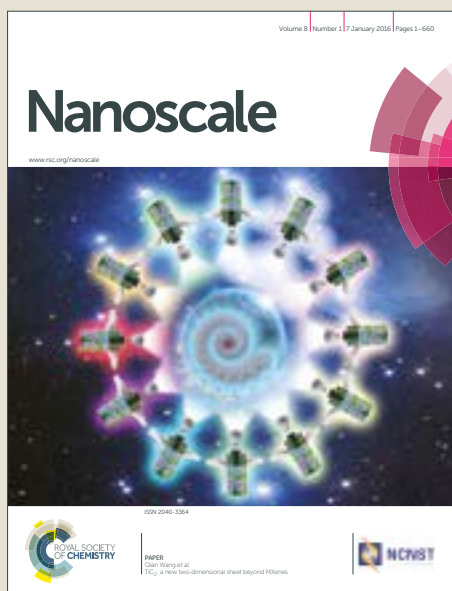


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COMMUNICATION

Unconventional two-dimensional germanium dichalcogenides

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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The recently discovered two-dimensional (2D) group IV chalcogenides attract much attention owing to their novel electronic and photonic properties. All reported materials of this class favor (distorted) octahedral coordination via *p* bonding; by contrast, in the dichalcogenides where the bonding tendency approaches *sp*³, no corresponding 2D phase has been realized so far. Here, by engineering the composition of a chalcogenide heterostructure, the hitherto elusive GeTe₂ is experimentally observed in a confined 2D environment. Density functional theory simulations predict the existence of a freestanding monolayer of octahedrally coordinated GeTe₂ under tensile strain, and the existence of GeSe₂ and GeS₂ in the same form at equilibrium conditions. These 2D germanium dichalcogenides are either metallic or narrow gap semiconducting, and may lead to new applications in nanoscale electronics.

Two-dimensional (2D) materials such as graphene^{1,2} and transition metal dichalcogenides^{3,4} provide a unique platform with extraordinary physical and chemical properties and a wide range of potential applications. Among them, the recently discovered 2D group IV chalcogenides (IV = Ge, Sn; chalcogen = S, Se, Te) have attracted significant attention owing to their earth-abundance, low cost, and environmental friendliness, as well as their tunable electronic structure. Hence, they are regarded as promising candidates for sustainable electronics and optoelectronics

applications.^{5,6} Moreover, many interesting physical phenomena were found or predicted in this material class. Regarding the monochalcogenides, giant and robust in-plane ferroelectricity with high transition temperature was predicted in monolayer GeS, GeSe, SnS and SnSe,⁷⁻⁹ and was very recently demonstrated experimentally in one unit-cell thick SnTe at room temperature.^{10,11} In addition, large ferroelasticity⁷⁻⁹ and piezoelectricity,¹² colossal optical second harmonic generation susceptibility,¹³ strong visible-light absorbance,¹⁴ high photosensitivity,^{15,16} and strong in-plane electronic anisotropy¹⁷ were theoretically predicted and partly confirmed experimentally in mono- or few-layer GeS, GeSe, SnS and SnSe, and phase change characteristics were shown in few-layer GeTe.¹⁸ Regarding the dichalcogenide compounds, monolayer and few-layer SnS₂ and SnSe₂ have been synthesized and incorporated into various devices, showing promising characteristics as field effect transistors,¹⁹⁻²¹ phototransistors,²² photodetectors,²³ and photoelectrochemical cells.²⁴

However, 2D phases of other group IV dichalcogenides remain to be explored. Regarding GeS₂ and GeSe₂, their bulk phase is a complex monoclinic structure with tetrahedral motifs (Figure 1 top right),²⁵ which differ from the local structure of most (transition-) metal chalcogenides, where (distorted) octahedral motifs are typically found. Although GeS₂/GeSe₂ nanostructures have been synthesized, it has been shown to be difficult to reach the 2D limit,^{26,27} possibly due to the presence of strong interlayer chemical bonds in addition to the weak van der Waals (vdW) forces. As far as GeTe₂ and SnTe₂ are concerned, their crystalline bulk phase is hitherto unknown.²⁸ There were some reports on crystalline GeTe₂ thin films,^{29,30} but a more recent work showed that GeTe₂ would easily decompose into Te and GeTe crystallites upon thermal annealing.³¹ This is due to the fact that the competing counterpart GeTe favors a peculiar bonding mechanism, termed as metavalent bonding.^{32,33} Very recently, we showed that the formation of this bonding mechanism in GeTe requires a critical thickness of four bilayers,¹⁸ which points towards a scenario to explore the existence of unconventional germanium ditelluride at the 2D limit. Note that if a GeTe₂ crystal were to exist, it would conceptually lie at the boundary of the chemical realms of *sp*³ bonding and *p* bonding.^{28,34}

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

The stable bulk crystal structures of the existing germanium chalcogenides^{25, 35, 36} are shown in **Figure 1**.

Layered compounds with vdW gaps are of particular interest as precursors for 2D materials.^{5, 6, 37} GeSbTe compounds along the GeTe-Sb₂Te₃ pseudobinary line are very well studied materials, which serve as the core of non-volatile phase change memory devices.³⁸⁻⁴⁰ The stable crystalline polymorphs of GeSbTe compounds, such as GeSb₂Te₄, Ge₂Sb₂Te₅ and Ge₃Sb₂Te₆, exhibit layered structures with alternating "cation" Ge/Sb, "anion" Te atomic layers and gaps arranged along the [0001] direction.⁴¹⁻⁴⁴ This leads to atomic building blocks of various size separated by gaps. For instance, GeSb₂Te₄ consists of septuple-layer blocks with the stacking sequence $-g-abcabca-g-bcabcb-g-cabcabc-$, where g represents the gap, and we use the labels " a " = (0, 0), " b " = (2/3, 1/3) and " c " = (1/3, 2/3) to indicate the in-plane positions of the atoms in each layer. The gaps between the building blocks are commonly referred to as "vdW gaps", although the gap size (the spacing along the [0001] direction) is considerably smaller (~ 2.9 Å) than in other vdW crystals, such as MoS₂ (~ 4.2 Å), implying that additional chemical interactions stronger than pure vdW forces might be present.

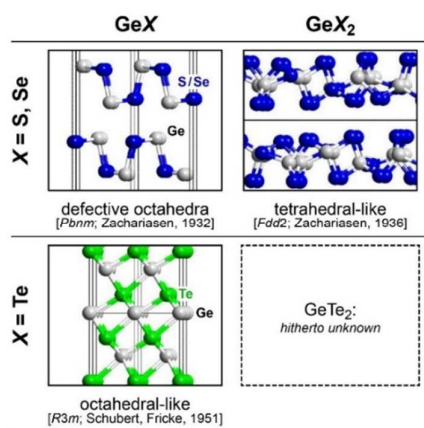


Figure 1. Crystal structures of bulk germanium chalcogenides. The orthorhombic structure types of the lighter mono- (top left) and dichalcogenides (top right) were reported in the 1930s already.^{25, 35} Germanium monotelluride, GeTe, takes a rhombohedrally distorted rocksalt-like structure with distorted octahedral coordination environments (bottom left).³⁶ Bulk germanium ditelluride, GeTe₂ (bottom right) is hitherto unknown; see text for details.

We engineered the composition of the GeSbTe heterostructure by increasing the concentration of Te, relative to the ideal stoichiometric composition GeSb₂Te₄. Tellurium here is the essential element to create gaps: it has the highest number of valence electrons, and Te layers detach from each other to avoid Te-Te bonding, which is energetically unfavourable.³⁴ If the excess Te content does not segregate, it has to be accommodated in Te-rich atomic blocks. Formally, there are two potential candidates for this: the well-known Sb₂Te₃, but also a hypothetical building block with the composition GeTe₂.

Upon magnetron sputtering, we have now produced a Te-rich GeSbTe thin film (~ 80 nm) and covered it with a ZnS-SiO₂ capping layer (~ 3 nm), which prevents environmental effects such as

oxidation. Electron energy loss spectroscopy (EELS) experiments confirm that no oxidation of the samples has taken place (**Figure S1**). The thin films were amorphous upon sputtering, and were annealed at elevated temperature (300 °C) for 1 hour to obtain the stable crystalline phase. Afterwards, a poly-crystalline state with grain sizes ranging from several tens to several hundreds of nanometers was observed, and no phase segregation was detected. Energy dispersive spectroscopy (EDS) experiments show that the average stoichiometric composition over many grains is close to Ge_{1.02}Sb₂Te_{4.66} (**Figure S2**). Although EDS is semi-quantitative, it very clearly indicates an excess of Te in the sample compared to idealized GeSb₂Te₄.

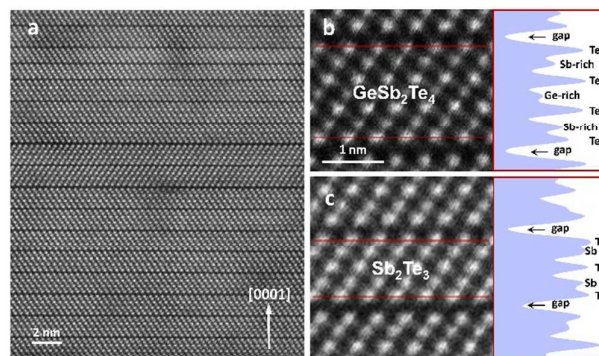


Figure 2. Experimental data of conventional atomic blocks. **a** A STEM-HAADF image in the $[11\bar{2}0]$ view; the z axis is along the [0001] direction. The scale bar is 2 nm. **b-c** Magnified HAADF images and the corresponding intensity profiles of the septuple-layer GeSb₂Te₄ block and the quintuple-layer Sb₂Te₃ block.

To investigate the atomic structure of this Te-rich compound, state-of-the-art scanning transmission electron microscopy (STEM) experiments were performed (see ESI). Such imaging method has been shown to be powerful in identifying the atomic structure and defects in highly relevant chalcogenides.⁴⁵⁻⁴⁸ A representative high-angle annular dark-field (HAADF) image is shown in **Figure 2a**. The intensity peaks (bright spots) appear at the positions of atomic columns, and the intensity value of the spots is approximately proportional to the square of the averaged atomic number of each column along the view direction.⁴⁹ Since Sb and Te have very close atomic numbers, 51 and 52 respectively, their corresponding intensities are very similar. In comparison with Sb and Te, Ge has a lower atomic number 32 and thus shows much lower image intensity. Intensity profiles of STEM image confirm the absence of Te elemental segregation, and show that septuple-layer blocks (as in ideal GeSb₂Te₄) are the major constituent of the samples. By evaluating the intensity of each atomic layer in these blocks in **Figure 2b**, a Ge-rich layer (center) can be clearly identified. According to the stoichiometry of GeSb₂Te₄, the other six layers can be considered as two Sb-rich layers and four Te layers. The parameters a_{hex} and c_{hex} of the GeSb₂Te₄ septuple-layer blocks are estimated from the HAADF images as 4.23 Å and 41.3 Å, respectively (**Figure S3**), in good agreement with the values reported in previous work.⁴⁷ Quintuple-layer blocks (**Figure 2c**) were also frequently observed in HAADF images. The image

intensity of all the atomic layers in these quintuple-layer blocks is high, suggesting the composition of Sb_2Te_3 . The presence of Sb_2Te_3 blocks can be expected, as they are constituent blocks of some GeSbTe compounds, such as GeSb_4Te_7 .⁵⁰

In addition, however, many triple-layer atomic stacks were also observed in our experiment, as shown in **Figure 3**. The thickness of these triple-layer blocks is 3.84 Å, which is comparable to the thickness of three atomic layers inside a GeSb_2Te_4 block. The triple-layer block is well separated from other blocks with a gap of 2.98 Å, similar to those found between GeSb_2Te_4 blocks (2.88 Å). The outer two atomic layers show the same image intensity as the Te layers, whereas the middle layer looks much darker, suggesting it to be either a Ge layer or a Sb layer with vacancies. EDS mapping experiments can now unambiguously distinguish the different elemental contributions at the atomic scale. As shown in **Figure S4**, EDS mapping rules out the possibility of Sb with vacancies, and therefore, the triple-layer structure must indeed be GeTe_2 . Inside the triple-layer, the two Ge-Te spacings are equivalent, giving the building block inversion symmetry. The atoms occupy the same three special sites as in other blocks with the sequence $-g\text{-abc-}g-$, and the bond angle derived is 86° . This gives a slightly distorted octahedral coordination for GeTe_2 (**Figure 3d**), similar to $\text{SnS}_2/\text{SnSe}_2$ and the 1T structure of MoS_2 .^{5,6}

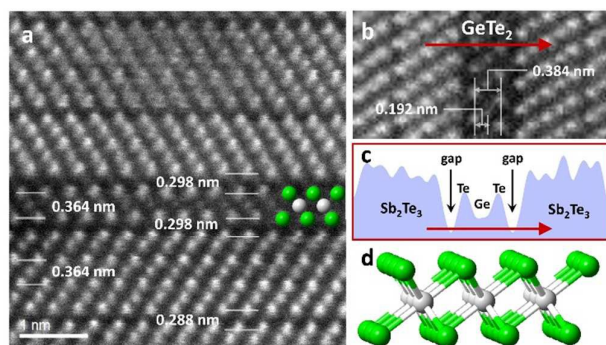


Figure 3. Experimental data and model of GeTe_2 triple-layer. **a** The HAADF image of a GeTe_2 triple-layer structure. **b-c** HAADF image and intensity distribution across the GeTe_2 triple-layers. **d** Atomic model of 2D GeTe_2 , similar to $\text{SnS}_2/\text{SnSe}_2$ or 1T- MoS_2 structure.

In summary of the above results, the formation of this unconventional GeTe_2 phase can be considered as the result of excess Te in the sample, in comparison with the stoichiometry of GeSb_2Te_4 . The extra Te leads to the formation of GeTe_2 and Sb_2Te_3 in addition to GeSb_2Te_4 , compensating the Te-rich stoichiometry $\text{GeSb}_2\text{Te}_{4+x}$. We note that the formation of GeTe_2 is not expected to occur only in GeSb_2Te_4 , but could also be obtained with other GeSbTe compositions, such as $\text{Ge}_2\text{Sb}_2\text{Te}_5$, as long as excess Te is integrated into the layered structures. In fact, a similar triple-layer structure has been observed in a slightly Te-rich composition with respect to $\text{Ge}_2\text{Sb}_2\text{Te}_5$.⁵¹ Although the chemical composition of the structural fragment was not determined, it could still be taken as the indication of GeTe_2 .

Next, we determine whether the observed GeTe_2 units can be stable in the freestanding case. Since our samples are poly-

crystalline, we cannot directly apply exfoliation methods to obtain freestanding GeTe_2 . Instead, DFT simulations are performed to shed light on this question (see ESI). Idealized monolayer GeTe_2 is modeled in a hexagonal cell with a large vacuum slab (20 Å) along the vertical direction (**Figure 4a**). Upon atomic and cell relaxation, GeTe_2 keeps the octahedral geometry with a lattice parameter of 3.86 Å, six equivalent Ge-Te bonds with length 2.81 Å, and a slightly distorted Te-Ge-Te bond angle of 86.4° . Upon relaxation, GeTe_2 displays metallic behaviour. The corresponding electronic density of states (DOS) and band structure are presented in **Figure 4b-c**. To determine whether a system is stable or not, it is important to assess both its chemical and dynamical stability, which can be done by performing the quantum chemical Crystal Orbital Hamiltonian Population (COHP) bonding analysis^{52,54} and phonon dispersion calculations,⁵⁵ respectively. The COHP dissects the electronic band structure into bonding (stabilizing) and antibonding (destabilizing) interactions between neighbouring atoms, and has been applied to GeSbTe materials with success before.⁵⁶ In monolayer GeTe_2 , a finite antibonding interaction (red arrow) is found at the Fermi level (**Figure 4b**), indicating chemical instability. In addition, small but non-negligible imaginary phonon frequencies near the Γ point are found, implying that the model is not fully dynamically stable.

It is important to note that the computationally optimized lattice parameter of freestanding GeTe_2 (3.85 Å) is much smaller than that obtained from STEM experiments (4.23 Å), suggesting that the GeTe_2 units are under in-plane tensile strain inside the GeSbTe heterostructure. Similar situation occurs in another type of GeSbTe heterostructures, where GeTe and $\text{Sb}_2\text{Te}_3/\text{Sb}_2\text{Te}$ slabs with various thickness are grown repeatedly. Tensile strain on GeTe slabs across gaps was observed and the origin was attributed to the lattice mismatch between GeTe and $\text{Sb}_2\text{Te}_3/\text{Sb}_2\text{Te}$.⁵⁷⁻⁵⁹ In our case, the mismatch is even stronger. If 2D GeTe_2 would adopt the calculated lattice parameter with the presence of GeSb_2Te_4 surrounding, a large amount of unfavorable Te-Te covalent bonds would form (**Figure S5**), resulting in very high energy penalties.³⁴ This indicates that the gap between GeTe_2 and GeSbTe is not a pure vdW gap, and there exists covalent interaction across the gap.

To mimic the experimental conditions, we applied in-plane tensile strain to monolayer GeTe_2 , and found that tensile strain indeed stabilizes the dynamical properties of the lattice. For instance, at 4% tensile strain, the imaginary phonon frequencies are all removed (see **Figure 4d** and a zoomed-in version in **Figure S6**). Our combined theoretical and experimental results, therefore, point to a potential recipe to produce monolayer or even few-layer GeTe_2 based on the application of an in-plane tensile strain of a few percent.

Since GeTe_2 might be difficult to obtain without strain, one may wonder whether its lighter homologues, GeS_2 and GeSe_2 , can be produced in a freestanding configuration. As shown in **Figure 1** (top right), the bulk isomorphous crystal structures of GeS_2 and GeSe_2 are rather complex, and it remains unclear whether such a phase can be synthesized in 2D form. Here, instead we consider 2D GeSe_2 and GeS_2 in the simpler octahedral coordination. The atomic structures and the corresponding DFT data are shown in **Figure 4e-h** and **4i-l**. Similar to their telluride analogue, 2D GeSe_2 and GeS_2 retain the octahedral coordination environments upon relaxation, but with smaller equilibrium lattice parameters (3.62 Å, 3.44 Å) and

bond lengths (2.58 Å, 2.43 Å). Both models are dynamically stable, as no imaginary frequency is present in the phonon dispersion curves, and they are chemically stable, as the antibonding interaction at the Fermi level is either marginal or completely absent (black arrow). 2D GeSe₂ displays metallic behaviour at equilibrium and undergoes a metal–semiconductor transition under in-plane tensile strain. A narrow and indirect band gap (~0.12 eV) appears at 4% tensile strain (Figure 4g and Figure S7). 2D GeS₂ is instead predicted to be a narrow gap semiconductor with an indirect gap of 0.73 eV. The band gap widens to 0.86 eV at 4%

tensile strain. In all semiconducting states, the minimum of the conduction band is located at the M point of the Brillouin zone, while the top of the valence band is found along the $\Gamma \rightarrow M$ path. Since freestanding GeSe₂ and GeS₂ are predicted to be stable from DFT simulations, it should be possible to produce them following the same strategy as for GeTe₂: first produce GeSe₂/GeS₂ triple-layers inside Se/S-rich gapped heterostructures, then apply mechanical exfoliation or other methods to obtain freestanding GeSe₂/GeS₂.

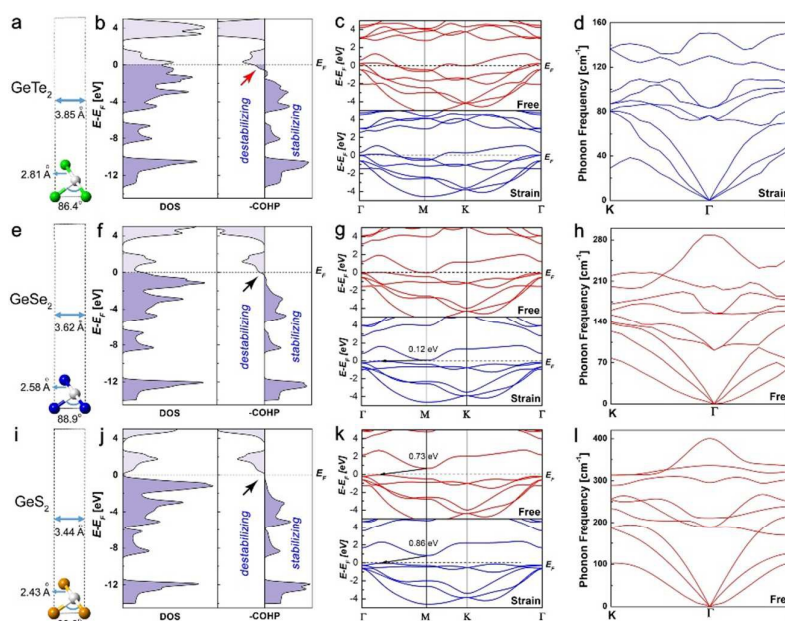


Figure 4. DFT calculations of 2D germanium dichalcogenides. The atomic model, density of states (DOS), Crystal Orbital Hamiltonian Population (COHP), band structure, and phonon dispersion of a–d GeTe₂, e–h GeSe₂ and i–l GeS₂. The DOS and COHP of the freestanding models are shown, while both freestanding and strained models are shown for the band structures, strained GeTe₂ and freestanding GeSe₂ and GeS₂ are shown for the phonon dispersions. The employed in-plane tensile strain is 4%.

In conclusion, we have explored the existence of crystalline GeTe₂, a compound unknown in the bulk that is located at the interface of *sp*³ and *p* bonded main-group chalcogenides. We started with the stable GeSb₂Te₄ compound and engineered its composition to be Te-rich. We confirmed that a moderate excess of Te does not lead to phase segregation, but instead drives the formation of Te-rich atomic blocks. Upon sputtering and subsequent thermal annealing, we successfully obtained 2D crystalline GeTe₂ confined within a gapped GeSbTe heterostructure. The central Ge atom is octahedrally coordinated, and the chemical identity was clearly established using EDS mapping, which, to our knowledge, together represent the first proof of such structural feature in the germanium dichalcogenide family. Clear gaps between the GeTe₂ triple layers and the adjacent 2D GeSb₂Te₄/Sb₂Te₃ building blocks were found, which suggests the possibility to isolate this material experimentally: first growing a single crystal of Te-rich GeSbTe heterostructure, e.g. through epitaxial methods;^{45, 47} then, applying exfoliation techniques to produce monolayer GeTe₂. In such case, in-plane tensile strain may be needed to stabilize this material. It is also known that distortions

induced by hydrogenation can stabilize 2D metal dichalcogenides,^{60, 61} which could be an alternative approach to stabilizing monolayer GeTe₂ as well. We note that the synthesis strategy proposed in this work could be used to form other unconventional 2D materials, such as octahedrally bonded 2D GeSe₂ and GeS₂, where strain engineering is no longer required. These newly proposed 2D germanium dichalcogenides show metallic or narrow-gap semiconducting band structures at equilibrium, and tunable electronic behaviour under tensile strain. Contrary to most 2D group IV chalcogenides having band gaps larger than silicon, 2D germanium dichalcogenides have narrow gaps below 1 eV, which may lead to new applications in nanoscale and flexible electronic devices. It is worth mentioning that another unconventional 2D phase of group IV monochalcogenides in the X-IV-IV-X form with interesting electronic and topological properties has been predicted through DFT calculations^{62, 63} and partially realized in experiments⁶⁴. Our work on unconventional germanium dichalcogenides further enriches the 2D IV-VI material family and shall stimulate further investigations in this exciting direction.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank Ming Xu and Chao Chen for the help on sample preparation, Danli Zhang for the EDS and EELS experiments, Peter C. Schmitz and Zhiwei Shan for useful discussions. WZ gratefully thanks the support of National Natural Science Foundation of China (61774123 and 51621063), the Youth Thousand Talents Program of China and the Young Talent Support Plan of Xi'an Jiaotong University. IR, HD, CJ, MW and RM acknowledge the funding by the DFG (German Science Foundation) within the collaborative research center SFB 917 "Nanoswitches". The authors also acknowledge the support by the HPCC platform of Xi'an Jiaotong University and JARA-HPC from RWTH Aachen University under project JARA0150, and the International Joint Laboratory for Micro/Nano Manufacturing and Measurement Technologies of Xi'an Jiaotong University. XQ acknowledges the start-up funds from Texas A&M University. Portions of this research were conducted with the advanced computing resources provided by Texas A&M High Performance Research Computing.

Author contribution

JW performed sample preparation and TEM experiments with the help of LL and analyzed the data with TL, HD, CJ, MW and WZ. DFT calculations were carried out by ID, LZ and BZ. The paper was written by WZ, VLD, QX and RM with the help and through contributions from all co-authors. The project was initiated and conceptualized by WZ.

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