Twisted bilayer zigzag-graphene nanoribbons with stacking offset-tunable edge states

Dongfei Wang,1, 4, * De-Liang Bao,1, * Chang-Tian Wang,1 Shiyong Wang,3 Peng Fan,1 Shantanu Mishra,2 Lei Tao,1 Xingliang Feng,5, 6 Klaus Müllen,7 Yu-Yang Zhang,1 Roman Fasel,2 Pascal Ruffieux,2, † Shixuan Du,1, ‡ and Hong-Jun Gao1, §

1Institute of Physics & University of Chinese Academy of Sciences, Beijing 100190, China.
2Nanotech@surfaces Laboratory, Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland.
3Key Laboratory of Artificial Structures and Quantum Control, School of Physics and Astronomy, Shanghai Jiao Tong University, Shanghai, China.
4CIC Nanogune BRTA, 20018, Donostia-San Sebastián, Spain.
5Center for Advancing Electronics Dresden (cfaed) and Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany.
6Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany.
7Max Planck Institute for Polymer Research, 55128, Mainz, Germany.

Abstract

Stacking two-dimensional layered materials such as graphene and transitional metal dichalcogenides with nonzero interlayer twist angles has recently become attractive because of the emergence of novel physical properties. Stacking of one-dimensional nanomaterials offers the lateral stacking offset as an additional parameter for modulating the resulting material properties. Here, we report that the edge states of twisted bilayer zigzag-graphene nanoribbons (TBZGNRs) can be tuned with both the twist angle and the stacking offset. Strong edge state variations in the stacking region are first revealed by density functional theory (DFT) calculations. We construct and characterize twisted bilayer zigzag graphene nanoribbon (TBZGNR) systems on a Au(111) surface using scanning tunneling microscopy. A detailed analysis of three prototypical orthogonal TBZGNR junctions exhibiting different stacking offsets by means of scanning tunneling spectroscopy reveals emergent near-zero-energy states. From a comparison with DFT calculations, we conclude that the emergent edge states originate from the formation of flat bands whose energy and spin degeneracy are highly tunable with the stacking offset. Our work highlights fundamental differences between 2D and 1D twistronics and spurs further investigation of twisted one-dimensional systems.

Keywords: edge state, zigzag graphene nanoribbon, twisted bilayer, STM/STS, von-Hove singularity.
Monolayer graphene is a zero-energy gap semimetal hosting effective massless Dirac fermions\textsuperscript{1}. Recently, bilayer graphene with a twist angle near 1° has drawn much research attention because novel electronic ground states appear, i.e., a Mott insulating phase and superconductivity\textsuperscript{2-8}. Electrons cannot move as freely as those in monolayer graphene due to the moiré potential and become strongly correlated. As a result, flat bands are formed near the Fermi energy. In tunneling experiments, the flat bands reveal themselves as differential conductance peaks with near-zero energy\textsuperscript{9-12}. However, this is not the first time that researchers have observed flat bands in graphene systems. For example, the electrons at the edge of zigzag graphene nanoribbons (ZGNRs) become strongly correlated when the width of the ribbon decreases\textsuperscript{13-16}. As a result, energy bands with little dispersion emerge in the range \(2\pi/3 \leq |k| \leq \pi\) in reciprocal space (the wavenumber \(k\) is normalized by the primitive translation vector of the ZGNR)\textsuperscript{17-20}, corresponding to the edge states of the ZGNR. Manipulation of such edge states with tailored properties is a long-lasting interesting topic with potential applications in nanodevices. One of the methods used to tune the edge states involves stacking of one ZGNR on top of another in a parallel way. There, the energy gaps between the flat bands can be modulated with different sublattices matching up\textsuperscript{21-25}. Recently, specially cut-off edges of twist bilayer graphene have been revealed to host inhomogeneous edge states\textsuperscript{26-28}. Moreover, crossed GNRs are theoretically predicted to be beam splitters and electron mirrors when integrated into nanodevices\textsuperscript{29-31}. All of the above results suggest new possibilities for tuning the ZGNR edge states in a bilayer case. However, pioneering experimental and theoretical research demonstrating the tunability of the edge state with both the twist angle and stacking offset is still missing.

In this paper, we demonstrate that the edge states of twisted bilayer zigzag-graphene nanoribbons (TBZGNRs) are highly tunable from both theoretical and experimental perspectives. First, modelling TBZGNR junctions with two 6-ZGNRs (the width of the ZGNR is 6 carbon atom chains) and density-functional-theory (DFT) calculations reveal that the edge states can be tuned over a wide range by changing not only the twist angles but also the in-plane stacking offset. Second, TBZGNR junctions were constructed with twist angle \(\theta\) well controlled by STM tip
lateral manipulation (with accuracy less than 5°). Spatially resolved scanning tunneling spectroscopy (STS) on several edges of the orthogonal TBZGNR junctions revealed two main features: 1) a reduction in the energy gap compared to that of monolayer ZGNR, and 2) emergent near-zero-energy peaks at the edges. Additional detailed DFT calculations were performed on several TBZGNR models with θ=90°. The results showed that the emergent peaks are attributable to the formation of near-zero-energy flat bands located at the edge of the stacking area due to the interlayer interaction. Moreover, the spin degeneracy of these flat bands is highly tunable with the in-plane stacking offset, which dominates the stacking symmetry. Additional calculations suggested that the out-of-plane stacking offset (interlayer distance), whose change affects the interlayer electrostatic potential and edge spin distribution, is another parameter with which to manipulate the overlapping edge states.

### Tunability of edge states in TBZGNRs revealed by first principles calculations

The edge states of monolayer ZGNRs manifest themselves as dispersionless bands and present as von-Hove singularities (VHS) in the calculated density of states (DOS) (peaks of the grey shadow in Fig. 1b-e). A band gap close to the Fermi energy develops due to enhanced electron-electron interactions in finite one-dimensional (1D) geometries. By placing one ribbon on top of the other, as illustrated in Fig. 1a and f, the edge states are affected largely by different twist angles and in-plane stacking offsets. When the twist angle θ=0° (parallel), two layers of ZGNRs typically exhibit AA or AB stacking. For AA stacking, hybridization between edge states of the top and bottom ribbons is maximized, leading to a strong edge electron hopping between the ribbons. A DFT-calculated projected density of states (PDOS) on the edges of AA-stacking bilayer ZGNRs showed that the rearranged flat bands were also revealed as VHS but with a relatively larger energy gap than the monolayer case (dashed curve in Fig. 1b). In contrast, when the two ribbons achieved AB stacking, the edge states of the top and bottom ZGNRs fell in a hybridization-avoiding geometry. The flat bands barely changed, while the gap between them was reduced slightly (solid curve in Fig. 1b). In addition to parallel AA and AB stacking, one can
also stack ZGNRs with an arbitrary twist angle $\theta$ and form a TBZGNR junction, as illustrated in Fig. 1a. Figure 1b-e clearly shows that the edge states (solid curve, shown as VHS in PDOS) of TBZGNR junctions vary significantly with the twist angle $\theta$.

It is noteworthy that for a given single twist angle, there remains a rich diversity
of twist symmetries tuned by the in-plane stacking offset. This is in marked contrast to two-dimensional (2D) materials in which the twist angle alone entirely defines the moiré unit cell and hence the full stacking geometry. In relation to this, the additional in-plane stacking offset used to define the geometry of the TBZGNR can be regarded as an offset vector defining the portion of the 2D moiré unit cell describing the finite overlap area and edge segments of twisted 1D structures. As an illustrative example, a TBZGNR junction with $\theta=90^\circ$ (Fig. 1f) can adopt either high (left) or low (right) stacking symmetry, whereby the edge states of junctions with different symmetries show significant changes (Fig. 1g-i). Furthermore, a reduction in the stacking symmetry directly reduces the symmetry of the interlayer electrostatic potential, as shown in Fig. 1j-l. Since a lateral external electric field was predicted to alter the spin-polarized edge states of ZGNRs\textsuperscript{20}, the stacking offset-dependent electrostatic potential could be the factor altering the edge states in those $\theta=90^\circ$ junctions. Following the theoretical predictions described above, we built experimental TBZGNR junctions and took corresponding measurements as discussed in the following sections.

**Experimental realization of TBZGNRs and detection of the edge state**

High-quality monolayer 6-ZGNRs were synthesized on Au (111) via a bottom-up method\textsuperscript{32} (Fig. 2a, also see the Methods section and Fig. S1). It is challenging to build a TBZGNR junction directly with vertical STM tip manipulation. However, we noticed that the ribbon could easily be moved or even bent\textsuperscript{33} on the Au surface with the STM tip (Fig. S2). Thus, we built the junction by pushing one ribbon on top of another, which was near the step edge on the lower terrace. This idea is illustrated in Fig. 2b-c, in which a TBZGNR junction is formed with a twist angle $\theta$. The twist angle can be controlled during manipulation. We succeeded in building TBZGNR junctions with different twist angles $\theta$, as shown in Fig. 2d-f and Fig. S3. The decoupling effect of the bottom ZGNR makes the edge states of the top ZGNR visible only in the overlap region. From Fig. 2h, one can see that the STS at the edge of the monolayer ZGNR still mimics the line shape of Au (111), but the DOS at the edge of the bilayer junction changes considerably and exhibits a pronounced peak near zero energy. The corresponding $dI/dV$ mapping image shown in Fig. 2g clearly revealed
that this near-zero-energy peak was only localized at the TBZGNR junction edge. In this sense, the TBZGNR junction cannot be treated as a quantum dot that is more similar to a single atom or molecule. The manipulation process is reversible, as demonstrated in Fig. 2i-l.

**Fig. 2.** | **TBZGNR junctions obtained by STM lateral tip manipulation.** **a,** Bond resolved STM topography image of the as-grown monolayer ZGNR. **b-c,** Schematic diagrams of ZGNRs near a step edge before and after STM tip manipulation, respectively. **d,** A histogram showing experimentally achieved twist angles θ between the top and bottom ZGNRs. **e-f,** STM topography images of two as-fabricated TBZGNR junctions with the edge states of the top ribbon clearly visualized. The twist angles of these two junctions are 53° and 87° respectively. **g,** dl/dV mapping image at -40 mV of the TBZGNR junction shown in **f.** **h,** Three typical STS measured on the junction edge (Blue), on the edge of monolayer ZGNR (pink) and on the Au (111) surface (grey). **i-k,** Three STM topography images demonstrating reversible manipulation of the top ZGNR on the surface of the bottom ZGNR. **l,** Corresponding dl/dV spectra taken at points 1-3 before manipulation (red), after manipulation (blue) and manipulating the ribbon back to the initial position (pink). The blue curve and pink curve have offsets of 0.7 and 1.4 compared to the red curve for better data visualization. Scale bar: (a) 0.6 nm, (e-g, i-k), 2 nm. Tunneling parameters: (a) V=-0.4 V, I=620 pA; (e, i-k) V=-0.3 V, I=1.0 nA; (f) V=-93.7 mV, I=165 pA; (g, h) V_{stab}=-0.32 V, I_{stab}=1.0 nA. V_{osc}=0.5 mV; (l) V_{stab}=-0.3 V, I_{stab}=1.0 nA. V_{osc}=0.7 mV.

To obtain more information regarding the edge states of the top layer ZGNR
within the junction, we took the spatially resolved STS at the edges. Three typical spectra recorded at the edges of TBZGNR junctions named A, B and C, and with similar \( \theta \approx 90^\circ \), are shown in Fig. 3a-c, respectively (see STS data for the other twist angles in Fig. S6). From Fig. 3a, we determined that the lower edge gave energy gap values of \( \Delta^0 = 0.90 \text{ eV} \) and \( \Delta^1 = 1.15 \text{ eV} \), while the upper edge gave similar gap values of \( \Delta^0 = 1.07 \text{ eV} \) and \( \Delta^1 = 1.34 \text{ eV} \). Compared to the gap values\(^3\) for the same type of ZGNR decoupled by a NaCl layer, \( \Delta^0 = 1.5 \text{ eV} \) and \( \Delta^1 = 1.9 \text{ eV} \), the band gap in our case has diminished considerably. We attribute this band gap reduction to the interlayer electron hopping-induced charge
redistribution between the two ZGNR layers, which did not occur when the ribbon was decoupled by a NaCl layer. DFT calculations showed that in the overlapped region of TBZGNR, electrons tended to accumulate at the interface (Fig. S4). As a result, the electron charge density at the ribbon edges was reduced, as was the...
corresponding effective Coulomb repulsion. The band gap reduction was proven by DFT calculations for structure Model A, as shown in Fig. 3d (see the upper panel of Fig. 4c for the atomic configuration). Compared to the PDOS on the edges of monolayer pristine ZGNR (grey shade), the band gaps of Model A were reduced (red and blue curves). It is worth noting that DFT calculations underestimated the band gaps, so the absolute values of the band gaps are not comparable to the experimental values. However, the relative values from the calculations are meaningful.

Novel emergent near-zero-energy STS peaks were discovered at the edges of the other TNBZGNR junctions B and C (Fig. 3b and c). For junction B, the near-zero-energy peak existed along the whole edge, as indicated by the red dashed line in Fig. 3b (see also Fig. 2g). However, for junction C, this near-zero-energy peak was only found to lie near one corner of the junction (point 1) and decayed very fast to the other corner (Fig. 3c). In addition to the near-zero-energy peak, we also identified other peaks at positive energies, as indicated by the black dashed lines in Fig. 3b and c. Interestingly, our DFT calculations for the other structural Models B and C, as shown in Fig. 3e and f correspondingly (see the upper panels of Fig. 4d and e for detailed configurations), showed results similar to those of the experiments. The PDOS shown in Fig. 3e clearly shows that in Model B, the near-zero-energy peak (indicated by the red dashed line) extended along the edge from point 1 to point 5 with a slight intensity reduction at the corner. Moreover, this peak in Model C decayed rapidly from one corner to the other (Fig. 3f). Additionally, the other calculated peaks indicated with black dashed lines in Fig. 3e and f also matched the experimental data nicely in terms of shape and decay behaviour along the edge for both junctions B and C. It is noteworthy that the Au (111) step edges did not show any DOS anomaly near zero energy, as shown in Fig. S7, and thus did not cause additional difficulty in the corresponding analysis.
Manipulating the edge state by tuning stacking offsets

The primary difference among Models A, B and C is that their in-plane stacking symmetries, which are tuned by the in-plane stacking offset, reduced gradually (upper panels of Fig. 4c-e). Model A has inversion, mirror, C2, and C6 symmetry within the overlapped region, while C6 symmetry is absent for Model B. Finally, there is no lattice symmetry for Model C. To obtain a deeper understanding of the edge states in Models A, B and C, we calculated the full band structures of the three models first, as shown in the lower panels of Fig. 4c-e (solid lines). For comparison, we also calculated the band structure of a monolayer ZGNR, as shown in Fig. 4b (a
justification for the calculated supercell size is presented in the Supplementary Information, Fig. S8 and Fig. S9). In the energy window we plotted, we identified 4 spin-degenerated bands below the Fermi energy for the monolayer ZGNR (Fig. 4b) as a result of band folding (see the Methods section). These bands were doubled to 8 but were still spin-degenerate for Models A and B because of symmetry protection (Fig. 4c and 4d). However, the bands below zero energy for Model C showed clear spin splitting (Fig. 4e), which was a direct result of the broken sublattice symmetry.

The band structures with projections on the upper and lower edges of the top ZGNR are superimposed on the full band structures (circles in Fig. 4b and lower panels of Fig. 4c-e). Compared to the pristine monolayer ZGNR (Fig. 4b), we can see that the edge states (focusing on bands between -0.15 eV and 0 eV) in Model A were still spin degenerate but became more dispersive (Fig. 4c). With lower symmetry in Model B, the edge states kept the spin degenerate but became isolated and closer to the Fermi energy (Fig. 4d), which explained the strong near-zero-energy peak in the calculated PDOS. For Model C without any symmetry, spin splitting of the edge states became evident immediately. New spin-polarized flat bands were developed close to the Fermi energy (Fig. 4e). As the time reversal symmetry was still reserved in Model C, spin-orbital coupling\textsuperscript{34} and pseudomagnetic field effects\textsuperscript{35-37} did not lead to spin splitting at the Γ point. Other effects, such as out-of-plane bending and lattice distortion, were also excluded (see the corresponding discussion and Fig. S10 in the Supplementary Information).

It has been indicated that an in-plane external electric field can lift the spin degeneracies of the ZGNR edge states\textsuperscript{20}. Considering the asymmetric stacking configuration in Model C, where the moiré site is located on the corner of the junction, the effective electron charge density showed an inhomogeneous distribution within the overlap region. Thus, an inhomogeneous electrostatic potential was introduced between the edges of the top ribbon (as shown in Fig. 1l) and played the same role as an external electric field. In fact, a similar asymmetric interlayer electrostatic potential was reported for crossing armchair GNRs\textsuperscript{29}. The symmetry-reduction-induced spin splitting in edge states was double-checked by
DFT calculations based on another asymmetric TBZGNR structure, Model D (Fig. S5). It showed results consistent with those of Model C, i.e., the spin degeneracy was lifted. It is noteworthy that the interlayer electrostatic potential was sensitive to the distance between the two layers of TBZGNRs. As shown in Fig. 5a, when the interlayer distance was increased to 3.5 Å and beyond, the potential was weakened rapidly. The edge states of TBZGNR junctions with non-90° twist angles still need further exploration, and two of them are shown in Fig. S6. Due to the rich array of possible stacking configurations, it will probably be very difficult to obtain systematic conclusions without knowing the atomic structure of the overlapped region.

**Fig. 5 | Calculated electrostatic potential distribution and spin density distribution.** *a*, Electrostatic potential distribution in the middle plane between TBZGNRs as a function of interlayer distance (based on Model C). Blue and red colours correspond to positive and negative values, respectively. *b*-d, Spin density distribution in the middle plane between bilayer twist ZGNR as a function of interlayer distance. Blue and red represent majority spin and minority spin, respectively.

Considering the possible application of the TBZGNR network to spintronics, it is always worth knowing how the spin arrangements on the overlapping edges evolve when the interlayer distance changes (out-of-plane stacking offset). Starting from an
initial antiferromagnetic order for each ZGNR, when the interlayer distances were larger than the optimal distance (~3.0 Å), none of the spin arrangements in any model changed, but the intensity weakened gradually (Fig. 5b-d). When the interlayer distance decreased, the spin arrangement in Model A maintained antiferromagnetic order at 2.75 Å but showed spin confinement at 2.5 Å, i.e., two antiferromagnetic corners in the overlap region (Fig. 5b). In Model B, antiferromagnetic order of only one ZGNR was demonstrated at shorter distances (Fig. 5c). In Model C, the spin arrangement became rather asymmetric at 2.75 Å and was not localized on the edges but extended into the inside of the overlapped region at 3 Å, as displayed in Fig. 5d. The above results again emphasize the significance of stacking offset and suggest that spin frustration may exist between the two layers of TBZGNRs with short interlayer distances. Therefore, the out-of-plane stacking offset can serve as a selectable parameter for tuning the edge states of the overlapped region beyond the twist angle and in-plane stacking offset when designing a spintronic device using TBZGNRs.

**Conclusions**

We have demonstrated the presence of highly tunable edge states in the TBZGNR junction from both first-principles calculations and experiments. The featured edge states of the as-fabricated TBZGNRs combined with the reproduced theoretical results enabled us to elucidate the dominant role of stacking offsets on the edge states of TBZGNRs. Our results revealed that in twisted bilayer 1D systems, in addition to the twist angle, which is the prime factor in the 2D case, the stacking offset is another important parameter influencing the edge states as well as the charge and spin distributions of the junctions. The as-investigated 1D twisted junctions are foreseen to be construction units for nano devices, such as spin filters31,38,39. Our discovery also offers exciting opportunities for explorations on 1D twisted junctions based on materials with more abundant electronic, optical, and topological properties.
Methods

Density functional theory calculations. DFT calculations were performed using the Vienna ab initio simulation package (VASP)\textsuperscript{40,41} code with the projector augmented wave (PAW)\textsuperscript{42} method. The local spin density approximation (LSDA)\textsuperscript{43} of Perdew-Zunger was adopted for the exchange-correlation functional. The energy cut-off of the plane-wave basis sets was 400 eV. The computational models comprised a 2.69 nm × 2.69 nm × 2 nm unit cell containing two overlapping ZGNRs with twist angles of 90°. The calculations of monolayer ZGNR used a unit cell of the same size but with only one layer of ZGNR. The numbers of carbon rings in widths/lengths of all ZGNRs were 6/11. The thickness of the vacuum layer was ~1.7 nm. The Brillouin zone was sampled with only the Γ-point. During structural relaxation, all atoms were relaxed until the force on each atom was less than 0.01 eV/Å. For the PDOS calculations, we used a 40×1×1 k mesh, where 40 was along the direction of the ZGNR that was projected on.

STM/STS manipulation and characterization. All STM/STS measurements were performed in ultrahigh vacuum at a temperature of 4.4 K. Before switching off the feedback loop to record the differential tunneling conductance (dI/dV) spectra, the tip was stabilized at a current (I\textsubscript{stab}) and a sample bias voltage (V\textsubscript{bias}). The dI/dV signal was then recorded using a lock-in technique with a bias modulation frequency of 987 Hz. Lateral STM tip manipulation of the nanoribbon was achieved via three steps. Step 1: the target GNR was located on the upper terrace of Au(111) with another GNR close to the step edge with STM topography images. The manipulation path and direction and position the tip were selected near the target GNR edge, which was on the opposite of the manipulation direction. Step 2: the tip was moved closer to the Au (111) surface by adjusting the current setpoint and sample bias and typical parameters such as V=10 mV and I=1 nA. The feedback loop was opened and the tip was moved slowly along the designed path with slow speed. Step 3: the nanoribbon was checked after manipulation by scanning the target area again. If the twist angle was not what the experiment required, Steps 1 and 2 were repeated until the TBZGNR junction was fabricated.
Sample preparation. Graphene nanoribbons were synthesised by following the growth protocol presented in a previous report. After precursor deposition at room temperature with the Au(111) surface held at room temperature (Fig. S1(a)), polymerization of these precursors was achieved by direct filament heating with a 2.2 A current for 10 min, and a temperature of approximately 140 °C was measured with a thermometer. These polymers were further planarized by heating again at approximately 180 °C for 10 minutes, as shown in Fig. S1(b). Most of the ribbons were synthesized on the Au terrace, with some others formed near step edges, as shown in the inset of Fig. S1(b). The width of the ribbon was approximately 1.2 nm, and the length of the ribbon was usually between 10 and 40 nm, as shown in Fig. S1(c). An atomically resolved STM topography image revealed that the monolayer ZGNR was composed of 6 zigzag carbon chains, as displayed in Fig. 2(a). Due to the itinerant d electron on the Au (111) surface, the intrinsic density of states of the nanoribbon was usually immersed in the Au surface state. As shown in Fig. S1(d), the dI/dV spectra taken at the upper and lower edges of the monolayer ZGNR (red and blue curves, respectively) showed line shapes similar to those taken on the Au (111) substrate (dashed grey curve). The reduction in the density of states near -0.5 V was due to partial screening of the Au surface state by the nanoribbon. To measure the intrinsic band structure of the nanoribbon, a less conducting layer should be intercalated between the Au surface and the nanoribbon. A previous report observed the intrinsic density of states of the zigzag edge after intercalation of a NaCl layer at the ZGNR/Au interface. However, using a STM tip to achieve vertical manipulation of the ribbon and move it onto a NaCl island is rather difficult.

Data availability

The data supporting the findings of this study are available within the article and in the Supplementary Information. All relevant data are available from the authors upon reasonable request.
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Author contributions

H.-J.G. supervised the overall research. S. D., P. R., R. F. and H.-J. G. designed the experiments. D. W., P. F., S. M. and S. W. performed the scanning tunneling microscopy experiments. D.-L. B., C.-T. W., L. T., Y.-Y. Z. and S. D. performed the theoretical calculations. X. F. and K. M. provided the molecular precursors. D. W., D.-L. B., S. D., P. R. and H.-J. G. wrote the manuscript. All authors analysed the data and contributed to the preparation of the manuscript.

* Contributed equally to this work.
† pascal.ruffieux@empa.ch
‡ sxdu@iphy.ac.cn
§ hjgao@iphy.ac.cn
SUPPORTING INFORMATION

Supporting information is available online and includes the following:

• Reversible STM Tip Manipulation of ZGNRs
• STM images of more TBZGNR Junctions
• Charge Redistribution within the TBZGNR junction
• DFT results for another TBZGNR structural model, Model D
• Influence of the Au (111) surface state and step edge on the spectra of monolayer ZGNR
• Exclusion of out-of-plane bending and lattice distortion effects
• Exclusion of supercell size and a possible intersupercell interaction effect
• References
• Figures S1-S10