Investigation of edge states in artificial graphene nano-flakes

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Abstract
Graphene nano-flakes (GNFs) are predicted to host spin-polarized metallic edge states, which are envisioned for exploration of spintronics at the nanometer scale. To date, experimental realization of GNFs is only in its infancy because of the limitation of precise cutting or synthesizing methods at the nanometer scale. Here, we use low temperature scanning tunneling microscope to manipulate coronene molecules on a Cu(111) surface to build artificial triangular and hexagonal GNFs with either zigzag or armchair type of edges. We observe that an electronic state at the Dirac point emerges only in the GNFs with zigzag edges and localizes at the outmost lattice sites. The experimental results agree well with the tight-binding calculations. Our work renders an experimental confirmation of the predicted edge states of the GNFs.

Keywords: artificial graphene nano-flakes, scanning tunneling microscopy, molecular designer, single molecule manipulation, metallic edge states, two-dimensional electron gas, massless Dirac fermions
(Some figures may appear in colour only in the online journal)

1. Introduction
The low-energy quasi-particles of graphene can be described as massless Dirac fermions with the two pseudospin components contributed by the two different types of sublattices [1–8]. Following the successful experimental fabrication, rich electronic and chemical properties of graphene-based materials were uncovered [9–13]. When cutting a graphene sheet into nanometer size, interesting new properties may emerge [14–17]. Particularly, the so-called graphene nanoribbons (GNRs) and graphene nano-flakes (GNFs) are predicted to feature remarkable electronic properties such as spin-polarized metallic edge states and band gap [14, 18–31]. GNFs are anticipated to exhibit a richer variety of electronic properties than GNRs due to the unique features in their shape, size, and edge morphology. For instance, the quantum dots mimicked by GNFs are featured with extremely long spin relaxation and decoherence time due to small spin–orbit and hyperfine coupling in carbon atom [32–36]. Additionally, as a result of the specific boundary conditions involved in the Dirac equations, the energy spectrum of the GNFs can be tuned by edge type [14–17, 37, 38]. Generally speaking, there are two fundamental types of edges in GNFs, the zigzag and arm-chair ones. The GNFs with zigzag edges exhibit a half-filled flat band at the Fermi level, which renders a zero-energy state locating at the edges of GNFs. Based on theoretical works [33, 34, 39–44], the electronic properties, such as the density of states (DOS) and the metallic edge states, differ in GNFs with distinctive shapes, sizes and types of edges [37, 38, 45–47].
Figure 1. (a) Schematic of STM manipulation of coronene molecules on a Cu(111) surface. (b) STM images presenting the construction process of a triangular AGNF with zigzag edges (set-point: $-1 \, V$, $0.3 \, nA$, $46 \times 46 \, \text{nm}^2$). A schematic graphene model in which the sublattice A (B) colored in blue (red) is illustrated in the rightmost panel in (b). (c) The 3D STM image of the last panel in (b).

Compared with numerous theoretical works, the experimental progresses in fabricating and characterizing GNFs are relatively slow. Although some GNFs samples have been successfully manufactured by the soft-landing mass spectrometry [48], it is still very challenging to accurately control the shape, size or edge type with reasonable repetition rate [49, 50]. The main obstacle is to cut out or synthesize GNFs with precise edge morphology at the nanometer scale. An alternative approach to examine the physics of GNFs is to fabricate artificial graphene systems that are made out of ultra-cold atom [51, 52], nanopatterned quantum wells [53, 54] or artificial molecular system [55–57]. The later one, artificial molecular system was firstly proposed by C-H Park and S G Louie in 2009 [58]. By scanning tunneling microscope (STM) tip manipulating, a feasible method widely used in on-surface molecular study [59–61], CO [62–68] or coronene molecules [55, 56] are patterned on a Cu(111) surface to create potential lattice, the two-dimensional electron gases (2DEGs) of metal surface are confined and scattered. A triangular nano-potential lattice results in the 2D massless Dirac system which is considered to behave equivalently to those of the low-energy charge carriers in real graphene layer [58, 64, 69–71]. In this work, we used this method to build artificial GNFs (AGNFs) with different geometries aiming to study the metallic edge states in the GNFs. Specifically, we construct triangular and hexagonal AGNFs with either zigzag or armchair edges. We confirm that the edge state can only be observed in the AGNFs with the zigzag edges and the edge states are localized at the outmost sublattice sites.

2. Results and discussion

We first deposit coronene molecules on a Cu(111) substrate. The molecules are randomly distributed on the surface (see methods section for details). Figure 1(a) demonstrates the STM manipulation process which is carried out at 4.8 K: the STM tip is moved down from the normal scanning height to approach an adsorbed coronene molecule to reach a distance of $\sim 2 \, \text{Å}$ between the tip and coronene. A bias voltage of $-2 \, \text{V}$ is applied between the STM tip and the Cu(111) substrate to lift up the coronene molecule to the tip. Then, the lifted molecule is laterally dragged to a desired location. The tip is set back to the normal scanning height and the molecule is dropped off from the tip onto the destination substrate by reducing the magnitude of bias voltage. According to our previous works [55, 56] and STM images (figure 1(b)), the coronene molecule is believed to be intact, with all the hydrogen atoms remained, after the manipulation process. By repeating this manipulation process, we can move the randomly distributed coronene molecules one by one into a designed shape. Figure 1(b) presents the step-by-step construction of a triangular AGNF with zigzag edges. In the rightmost panel of Figure 1(b), a schematic graphene model is plotted. The repulsive potential provided by the coronene molecules confines the 2DEGs of the Cu(111) surface state electrons in the hexagonal channels between the coronene molecules, resulting in an artificial graphene system [58] (see the model shown in figure 1(b)). Although there may be a weak charge transfer between coronene molecules and STM tip during the manipulation process, the charges transferred will be immediately neutralized once the coronene molecules are dropped and contact with the Cu(111) substrate. Therefore, it will not influence the repulsive potential of coronene molecules or the scattering process. Finally, a molecular potential wall consisting of many molecules is built surrounding the AGNF to confine the 2DEGs and insulate the AGNF from external Cu(111).
Figure 2. (a) STM image (46 × 46 nm²) of a triangular AGNF with armchair edges (set-point: −1 V, 0.3 nA). Inset: blue (red) circles denote sublattice-A (B) atoms, and the hexagonal frame represents a six-member ring of the artificial graphene. (b) $dI/dV$ spectrum averaged over the whole AGNF area excluding the coronene molecule sites and subtracting substrate background. The red line indicates the Dirac point energy. (c) STS map (46 × 46 nm²) acquired at the Dirac point (−0.29 V). The black dots show the positions of the coronene molecules. Amplitude of the Cu(111) surface state is indicated in the color bar. (d) Atomic structure of the equivalent GNF. The sublattice A (B) atoms are colored in blue (red). (e) and (f) Tight-binding (TB) calculation results of the structure shown in (d): total DOS (e) and spatial distribution of DOS at the Dirac point ($E = 0$ eV) (f). The size of the dots is proportional to the DOS intensity in (f).

Figure 2(a) shows an equal-lateral triangular AGNF with armchair edges. The lattice constant is $\sim 3.0$ nm, and the length of each side of the triangular flake is $\sim 40$ nm. The color circles overlaid in figure 2(a) highlight the artificial ‘carbon atoms’, in which blue (red) circles denote sublattice-A (B) atoms, and the hexagonal frame represents a six-member ring of the artificial graphene. The atomic model of an equivalent GNF is presented in figure 2(d), in which the two sublattices, A and B, are colored in blue and red, respectively. As we can see in figure 2(a), few coronene molecules have a slight shift (2–3 Å) from the lattice sites in the AGNF, which only slightly influence the electronic states locally without resulting in any significant effect on the overall electronic features of the AGNF [55]. Figure 2(b) shows a $dI/dV$ spectrum averaged over the whole area of this AGNF, excluding the coronene molecules and subtracting the substrate background. The spectrum displays a V shape sided by two peaks, which signifies the DOS of the massless Dirac fermions. The valley of the V-shape, which corresponds to the Dirac point [58, 69, 70], locates at −0.29 V [55]. The theoretical works [58, 64, 69–71] reveal that the V shape is almost linear at the energy level close to the Dirac point and becomes non-linear when the energy level is away from the Dirac point due to the presence of other electronic states. The spatial distribution of the DOS at the Dirac point (−0.29 V) is plotted in figure 2(c). The boundary regions overlapped with black color in figure 2(c) (and the blue regions at the boundaries of the AGNFs in figures 3(e), 4(c) and 5(c)) are the locations occupied by the coronene molecules to form the walls due to the relatively low electronic states of the coronene molecules at the Dirac energy. The density spreads over the whole AGNF homogeneously without any edge-state feature. It is worthwhile to note that the ‘red dots’ shown inside the AGNFs are in the similar amplitude to the surface states on the clean substrate outside the AGNF, indicating that the DOS at the Dirac point in this armchair AGNF is in the similar amplitude to the Cu(111) surface state. We use a TB model to calculate the electronic properties of the structure shown in figure 2(d). Due to the electron-hole symmetry, the energy level of the Dirac point is at 0 eV. The calculated DOS plotted in figure 2(e) shows a symmetric V shape with two peaks located $\sim 60$ meV below and above the Dirac point. The calculated DOS nicely reproduces the feature of the $dI/dV$ spectrum in figure 2(b). Figure 2(f) displays the spatial distribution of DOS at the Dirac point, showing that the DOS spreads over the whole GNF, similar as the experimental result shown in figure 2(c).

Figure 3(a) shows a triangular AGNF with zigzag edges. The lattice constant and flake size are same as those of the AGNF shown in figure 2(a). The atomic model of an equivalent GNF is presented in figure 3(b). The two sublattices are inequivalent in a zigzag edge triangular GNF. This is illustrated in figure 3(c), where the atoms of the sublattices A and B sit on the solid and dashed triangles, respectively. We define the
Figure 3. (a) STM image (40 × 40 nm²) of a triangular AGNF with zigzag edges (set-point: −1 V, 0.3 nA). Inset: blue (red) circles denote sublattice-A (B) atoms, and the hexagonal frame represents a six-member ring of the artificial graphene. (b) Atomic structure of the equivalent GNF. The sublattice A (B) atoms are colored in blue (red). (c) Schematic shows four layers of equilateral triangles in this GNF from edges to center. The solid (dash) lines mark the atoms of sublattices A (B). (d) Site-specific dI/dV acquired at the different triangle layers in the AGNF. The color code follows the definition given in (c). (e) STS map (40 × 40 nm²) acquired at the Dirac point (−0.29 V). Amplitude of the clean Cu(111) surface state is indicated in the color bar. (f) and (g) TB calculation results of the structure shown in (b): (f) site-specific local DOS of the different triangle layers in the GNF. The color code follows the definition given in (c). (g) Spatial distribution of DOS at the Dirac point (E = 0 eV). The size of the dots is proportional to the DOS intensity.

The equivalent site averaged dI/dV spectra of the different triangle, ranging from large to small, are plotted in figure 3(d). The colors follow the same definition as in figure 3(c): the black, red, blue and green curves in the right (left) panel are the spectra of the A (B) sublattice atoms sitting at the triangles of the same color in figure 3(c). Figure 3(d) shows that the sublattice-A sites at the outmost triangle feature a peak at the Dirac point of −0.29 V, and all other sites, including the inner triangles of the sublattice-A sites and all the sublattice-B sites, feature a V-shape valley at the Dirac point. Figure 3(e) explicitly shows the state at −0.29 V is localized at the three zigzag edges of the AGNF. We then perform TB calculation on a triangular zigzag-edge GNF of the same size. Figure 3(f) shows the site-specific local DOS, revealing that the sublattice A atoms feature a sharp peak at the Dirac point and the peak intensity decays from the edges to the interior rapidly. In contrast, this peak is absent in the sublattice B atoms. Figure 3(g) displays the spatial distribution of the DOS at the Dirac point, showing that only sublattice-A atoms exhibit appreciable DOS, and the edges feature highest DOS intensity. Overall, the TB calculation captures the major characteristics of the edge state observed in the experiments.

Figure 4(a) shows a hexagonal armchair-edge AGNF. Similar to the triangular armchair-edge AGNF, the averaged dI/dV spectrum is a V shape, as shown in figure 4(b), where the Dirac point is located at −0.3 V. To note, the Dirac point of this AGNF is 10 meV down-shifted compared with those of the other AGNFs. This is because the triangular lattice of the coronene molecules in this structure is about 1 Å larger than the other cases. Figure 4(c) displays spatial distribution of DOS at the Dirac point, showing the density spreads over the entire...
AGNF without any edge-state feature. These results corroborate the TB calculation of the model shown in figure 4(d). The calculated total DOS presented in figure 4(e) nicely reproduces the V shape feature exhibited in the dI/dV, whereas the spatial distribution of DOS at $E = 0$ eV plotted in figure 4(f) reveals a uniformly distributed DOS.

Last, we present the results of a hexagonal zigzag-edge AGNF as shown in figure 5(a). The atomic model of an equivalent GNF is presented in figure 5(d), illustrating three edges are A sublattice while the other three edges are equivalently B sublattice. The colored hexagons define the equivalent site atoms of the two sublattices. Figure 5(b) shows the dI/dV spectra acquired at the sites sitting at different hexagons while the colors follow the same definition as in figure 5(d): the black, red, blue and green curves in the right (left) panel are the spectra of the A (B) sublattice atoms sitting at the hexagons of the same colors in figure 5(d). The sites at the outmost hexagon of both sublattices feature a peak at the Dirac point and the sites at all the inner hexagons feature a V-shape valley at the Dirac point. Figure 5(c) shows the DOS at $-0.29$ V is localized at the six zigzag edges of the AGNF. We perform TB calculation on the structure shown in figure 5(d). Both sublattices exhibit same site-specific local DOS as shown in figure 5(e): a peak at the Dirac point is presented only at the outmost hexagon. Figure 5(f) reveals that the DOS at the Dirac point ($E = 0$ eV) are mainly confined at the six edges, identical for the two sublattices. This symmetric behavior is given by the symmetric geometry of the two sublattices in the hexagonal GNFs.

Finally, we will discuss the comparison between the theoretical and experimental results. Firstly, in figures 2(c) and (f), 4(c) and (f), we can observe the spatial distributions of some weak electronic states at the Dirac point. The TB calculation shows that there does not exist any edge states at the Dirac point of an armchair graphene nanoflake. In our calculation, a Gaussian broadening of 2.3 meV has been employed to simulate the energy resolution of STS mapping in our experiments. With this energy broadening, the electronic states at the Dirac point become non-zero. Secondly, figure 3(f) shows that all the A-sublattice equilateral-triangular layers (green to black), from the edges to center, have a peak at the Dirac point in the theoretical results. In contrast, only the edges (black) of the AGNF have a peak in the experimental data shown in figure 3(d). This discrepancy is caused by the following reasons: (1) the TB calculation only considers the nearest neighbor hopping. This might not be able to perfectly describe the artificial graphene systems, in which the second-nearest neighbors or even larger distance effects may play a role. (2) Broadening effects due to the limited energy and spatial resolutions smear out the peak features in the TB calculation. Considering these effects, however, the TB model can qualitatively capture the major features of the AGNFs, that is, the presence of the metallic edge states in the zigzag AGNFs.

Next, we will discuss the effects of the position and thickness of the external molecular wall on the edge states. We intend to insulate the area of the AGNFs from the surrounding Cu surface states using thick external walls. However, it turns
out that the thickness of the wall does not affect the results significantly. As shown in figure 3(a), there are several locations where the wall is much thinner than the other parts. The STS mapping shown in figure 3(e) does not reveal that the thinner wall leads to weaker edge state signal. Furthermore, the position of the wall is not very sensitive to the edge states as described below. For example, in figure 3(b), the distance between the outmost sublattice sites of the AGNF (the locations where the edge states happen) and the outmost coronene lattice sites is $d/\sqrt{3} (\sim 1.73 \text{ nm})$, where $d = 3.0 \text{ nm}$ is the space between adjacent coronene sites. Therefore, the molecular wall is positioned at a distance larger than $d/\sqrt{3} (1.73 \text{ nm})$ away from the outmost coronene lattice sites to avoid destroying any of the edge states. Besides, the distance between the wall and the outmost sites of the triangular coronene lattice should be less than $d (3.0 \text{ nm})$ so that the boundaries of the AGNF can thus be defined.

### 3. Conclusions

In conclusion, we present an experimental study to evidence the edge states in the AGNFs. The comparisons between the zigzag-edge and armchair-edge AGNFs of triangular and hexagonal shapes confirm that the edge states at the Dirac point only exist at the outmost sublattice atoms of the zigzag edges.

### 4. Experimental and theoretical methods

**Sample preparation:** the experiments were performed in an ultrahigh vacuum STM integrated with scanning tunneling spectroscopy (STS) systems (Scienta Omicron) with a base pressure of $8 \times 10^{-10} \text{ mbar}$. Liquid helium is used to keep the operation temperature constantly at 4.8 K. The Cu(111) single-crystalline substrate was cleaned by several cycles of Ar$^+$ sputtering and annealing. Coronene molecules (Sigma Aldrich) were thermally evaporated onto the Cu(111) substrate at the room temperature by using an organic molecular evaporator. STS mapping was performed to acquire spatially resolved DOS of the whole AGNFs. The STS spectra were measured using a lock-in amplifier with a sine modulation of 1.5 kHz and a modulation of 4 mV. Each $dI/dV$ spectrum was normalized by $(I/V)$ data to obtain the DOS or site-specific local DOS plot. All STM and STS data were acquired in a constant current mode. Before and after acquiring the $dI/dV$ mapping data, we obtained the $dI/dV$ spectra of the clean Cu(111) substrate using the same STM tip. We acquired 10000 $dI/dV$ spectra in the AGNF regions in a $100 \times 100$ grid. Then we subtracted every spectrum by the average spectrum of the clean Cu(111) substrate. Next, we excluded the data taken at the sites of the coronene molecules, so only the data taken at the hexagonal channels in the AGNF are selected. A bias voltage of $-2 \text{ V}$ is applied between the STM tip and Cu(111) substrate, which enables the tip to lift up a single coronene molecule. Additional coronene molecules were packed closely to form walls surrounding the lattice to construct AGNFs. The orientation of the walls with respect to the lattice defines the edge morphology of the AGNFs, i.e. zigzag or arm-chair edges.

**TB calculation:** we also carried out the TB calculations with a nearest-neighboring hopping parameter of 65 meV
using the Python package (pybinding). The hopping parameter ($t$) is obtained with the formula: $t = v_F \frac{2d}{\sqrt{3}h}$, where $d$ is the lattice constant (3 nm), $h$ is the reduced Planck constant, and $v_F$ is the Fermi velocity ($2.6 \times 10^5$ m s$^{-1}$), the Fermi velocity of AGNFs system is calculated by the formula: $v_F = \frac{2d}{\sqrt{3}m}$, where $m$ is the effective mass of the Cu surface-state band is 0.4$m_e$ [55]). The site-specific local DOS is obtained through the Green function, which is derived from the Kernel polynomial method with a Gaussian broadening of 2.3 meV. The DOS is calculated from the eigenvalues with the same Gaussian broadening.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Author contributions

QZ, GK and NL designed the experiments, and QZ and GK set up the experiments. QZ and GK performed the experiment. QZ, TW and AX designed the simulations and TW, AX performed the simulations. QZ and NL wrote the manuscript, TW, GK, and AX revised it.

Competing interests

The authors declare no conflict of interest.

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References

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Electric field effect in atomically thin carbon films Science 306 666–9
[2] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubonos S V and Firsov A A 2005 Two-dimensional gas of massless Dirac fermions in graphene Nature 438 197–200
[3] Zhang Y, Tan Y-W, Stormer H L and Kim P 2005 Experimental observation of the quantum Hall effect and Berry’s phase in graphene Nature 438 201–4
[4] Berger C et al 2006 Electronic confinement and coherence in patterned epitaxial graphene Science 312 1191–6
[5] Wallace P R 1947 The band theory of graphite Phys. Rev. 71 622–34
[6] McClure J W 1956 Diamagnetism of graphite Phys. Rev. 104 666–71
[7] Ando T and Nakanishi T 1998 Impurity scattering in carbon nanotubes - absence of back scattering J. Phys. Soc. Japan 67 1704–13
[8] Ando T, Nakanishi T and Saito R 1998 Berry’s phase and absence of back scattering in carbon nanotubes J. Phys. Soc. Japan 67 2857–62
[9] Levy N, Burke S A, Meaker K L, Panulisgui M, Zettl A, Guinea F, Neto A H C and Crommie M F 2010 Strain-induced pseudo-magnetic fields greater than 300 tesla in graphene nanobubbles Science 329 544–7
[10] Abanin D A, Novoselov K S, Zeitler U, Lee P A, Geim A K and Levitov L S 2007 Dissipative quantum Hall effect in graphene near the Dirac point Phys. Rev. Lett. 98 196806
[11] Kane C L and Mele E J 2005 Quantum spin Hall effect in graphene Phys. Rev. Lett. 95 226801
[12] Bolotin K I, Ghahari F, Shulman M D, Stormer H L and Kim P 2009 Observation of the fractional quantum Hall effect in graphene Nature 462 196–9
[13] Banhart F, Kotakoski J and Krasheninnikov A V 2011 Structural defects in graphene ACS Nano 5 26–41
[14] Son Y-W, Cohen M L and Louie S G 2006 Half-metallic graphene nanoribbons Nature 444 347–9
[15] Nakada K, Fujita M, Dresselhaus G and Dresselhaus M S 1996 Edge state in graphene ribbons: nanometer size effect and edge shape dependence Phys. Rev. B 54 17954–61
[16] Ezawa M 2006 Peculiar width dependence of the electronic properties of carbon nanoribbons Phys. Rev. B 73 045432
[17] Fujita M, Wakabayashi K, Nakada K and Kusakabe K 1996 Peculiar localized state at zigzag graphite edge J. Phys. Soc. Japan 65 1920–3
[18] Son Y-W, Cohen M L and Louie S G 2006 Energy gaps in graphene nanoribbons Phys. Rev. Lett. 97 216803
[19] Dutta S and Pati S K 2010 Novel properties of graphene nanoribbons: a review J. Mater. Chem. 20 8207–23
[20] Abergel D S L, Apalkov V, Berashevich J, Ziegler K and Chakraborty T 2010 Adv. Phys. 59 261–482
[21] Berger C et al 2004 Ultrathin epitaxial graphite: 2D electron gas properties and a route toward graphene-based nanoelectronics J. Phys. Chem. B 108 19912–6
[22] Novoselov K S et al 2007 Room-temperature quantum Hall effect in graphene Science 315 1379
[23] Geim A K and Novoselov K S 2007 The rise of graphene Nat. Mater. 6 183–91
[24] Li G and Andrei E Y 2007 Observation of Landau levels of Dirac fermions in graphite Nat. Phys. 3 623–7
[25] Hu Y et al 2018 Bandgap engineering of graphene nanoribbons by control over structural distortion J. Am. Chem. Soc. 140 7803–9
[26] Garnica M, Schwarz M, Dukce J, He Y, Bischoff F, Barth J V, Auwärter W and Stradi D 2019 Comparative study of the interfaces of graphene and hexagonal boron nitride with silver Phys. Rev. B 94 155431
Garnica M, Schwarz M, Dukce J, He Y, Bischoff F, Barth J V, Auwärter W and Stradi D 2016 Phys. Rev. B 99 089901 (erratum)
Merino-Diez N et al 2018 Switching from reactant to substrate engineering in the selective synthesis of graphene nanoribbons J. Phys. Chem. Lett. 9 2510–7
El-Sayed A et al 2020 Synthesis of graphene nanoribbons on a kinked Au surface: revealing the frontier valence band at the brillonizion center J. Phys. Chem. C 124 15474–80
Rahim J-W, Bardarson J H and Slager R J 2018 Unified bulk-boundary correspondence for band insulators Phys. Rev. B 97 115143
Li Y et al 2013 Absence of edge states in covalently bonded zigzag edges of graphene on Ir(111) Adv. Mater. 25 1967–72
[31] Li Y, Zhang W, Morgenshtern M and Mazzarello R 2013 Electronic and magnetic properties of zigzag graphene nanoribbons on (111) surface of Cu, Ag, and Au Phys. Rev. Lett. 110 216804

[32] Ritter K A and Lyding J W 2009 The influence of edge structure on the electronic properties of graphene quantum dots and nanoribbons Nat. Mater. 8 235–42

[33] Zarenia M, Chaves A, Farias G A and Peeters F M 2011 Energy levels of trianular and hexagonal graphene quantum dots: a comparative study between the tight-binding and Dirac equation approach Phys. Rev. B 84 245403

[34] Heiskanen H P, Manninen M and Akola J 2008 Electronic structure of triangular, hexagonal and round graphene flakes near the Fermi level New J. Phys. 10 103015

[35] Trauzettel B, Bulaev D V, Loss D and Burkard G 2007 Spin qubits in graphene quantum dots Nat. Phys. 3 192–6

[36] Fernández-Rossier J and Palacios J J 2007 Magnetism in graphene nanoislands Phys. Rev. Lett. 99 177204

[37] Zhou A and Sheng W 2012 Van Hove singularities in graphene Nano Lett. 12 904313

[38] Akola J, Heiskanen H P and Manninen M 2008 Edge-dependent selection rules in magic triangular graphene flakes Phys. Rev. B 77 193410

[39] Ezawa M 2007 Metallic graphene nanodisks: electronic and magnetic properties Phys. Rev. B 76 245415

[40] Szalowski K 2013 Indirect coupling between localized magnetic moments in triangular graphene nanoflakes Phys. E 52 46–53

[41] Fthenakis Z G 2013 Energetics of graphene flakes Mol. Phys. 111 3289–96

[42] Potasz P, Güçlü A D, Wójs A and Hawrylak P 2012 Electronic properties of gated triangular graphene quantum dots: magnetism, correlations, and geometrical effects Phys. Rev. B 85 075431

[43] Hämäläinen S K, Sun Z, Boneschanscher M P, Uppstu A, Ijäs M, Harju A, Vannakelbergh D and Liljeroth P 2011 Quantum-confinement effects in atomic and well-defined graphene nanostructures Phys. Rev. Lett. 107 236803

[44] Park S-h, Borne J, Vanegas A L, Corbetta M, Sander D and Kirschner J 2011 Direct observation of electron confinement in epitaxial graphene nanoislands ACS Nano 5 8162–6

[45] Romanovsky I, Yannouleas C and Landman U 2011 Unique nature of the lowest Landau level in finite graphene samples with zigzag edges: Dirac electrons with mixed bulk-edge character Phys. Rev. B 83 045421

[46] Kabir M and Saha-Dasgupta T 2014 Manipulation of edge magnetism in hexagonal graphene nanoflakes Phys. Rev. B 90 035403

[47] Barnard A S and Snook I K 2011 Modelling the role of size, edge structure and terminations on the electronic properties of graphene nano-flakes Modelling Simul. Mater. Sci. Eng. 19 0154001

[48] Rieder H J, Rouhaniapur A, Talarico A M, Palermo V, Samori P and Müllen K 2006 Processing of giant graphene molecules by soft-landing mass spectrometry Nat. Mater. 5 276–80

[49] Keerthi A, Sánchez-Sánchez C, Deniz O, Ruffieux P, Scholmeyer D, Feng X, Narita A, Fasel R and Müllen K 2020 On-surface synthesis of a chiral graphene nanoribbon with mixed edge structure Chem. Asian J. 15 3807–11

[50] Sun Q, Yao X, Gröning O, Eimre K, Pignedoli C A, Müllen K, Narita A, Fasel R and Ruffieux P 2020 Coupled spin states in armchair graphene nanoribbons with asymmetric zigzag edge extensions Nano Lett. 20 6429–36

[51] Bloch I 2005 Ultracold quantum gases in optical lattices Nat. Phys. 1 23–30

[52] Zhu S-L, Wang B and Duan L-M 2007 Simulation and detection of Dirac fermions with cold atoms in an optical lattice Phys. Rev. Lett. 98 260402

[53] Wang S et al 2018 Observation of Dirac bands in artificial graphene in small-period nanopatterned GaAs quantum wells Nat. Nanotechnol. 13 29–33

[54] Du L et al 2018 Emerging many-body effects in semiconducting artificial graphene with low disorder Nat. Commun. 9 3299

[55] Wang S, Tan L Z, Wang W, Louie S G and Lin N 2014 Manipulation and characterization of aperiodical graphene structures created in a two-dimensional electron gas Phys. Rev. Lett. 113 196803

[56] Yan L, Hua M, Zhang Q, Ngu T U, Guo Z, Wu T C, Wang T and Lin N 2019 Symmetry breaking in molecular artificial graphene New J. Phys. 21 083005

[57] Montambaux G 2018 Artificial graphenes: Dirac matter beyond condensed matter C. R. Phys. 19 285–305

[58] Park C-H and Louie S G 2009 Making massless Dirac fermions from a patterned two-dimensional electron gas Nano Lett. 9 1793–7

[59] Zhang Q, Kuang G, Pang R, Shi X and Lin N 2015 Switching molecular kondo effect via supramolecular interaction ACS Nano 9 12521–8

[60] Kuang G, Zhang Q, Lin T, Pang R, Shi X, Xu H and Lin N 2017 Mechanically-controlled reversible spin crossover of single Fe-phyrin molecules ACS Nano 11 6295–300

[61] Yan L, Xia B, Zhang Q, Kuang G, Xu H, Liu J, Liu P N and Lin N 2018 Stabilizing and organizing Bi$_{12}$Cu$_4$ and Bi$_{12}$Cu$_{14}$ nanoclusters in two-dimensional metal–organic networks Angew. Chem. 130 4707–11

[62] Gomes K K, Mar W, Ko W, Guinea F and Manoharan H C 2012 Designer Dirac fermions and topological phases in molecular graphene Nature 483 306–10

[63] Ropo M, Paavilainen S, Akola J and Räsänen E 2014 Density-functional investigation of molecular graphene: CO on Cu(111) Phys. Rev. B 90 241401

[64] Polini M, Guinea F, Lewenstein M, Manoharan H C and Pellegrini V 2013 Artificial honeycomb lattices for electrons, atoms and photons Nat. Nanotechnol. 8 625–33

[65] Paavilainen S, Ropo M, Nieminen J, Akola J and Räsänen E 2016 Coexisting honeycomb and kagome characteristics in the electronic band structure of molecular graphene Nano Lett. 16 3519–23

[66] Gardener T S, van den Broeke J J, Moes J R, Swart I, Delerue C, Slot M R, Smith C M and Vannakelbergh D 2020 p orbital flat band and Dirac cone in the electronic honeycomb lattice ACS Nano 14 13638–44

[67] Freaney S E, van den Broeke J J, Harsveld van der Veen A J J, Gardenier T S, van den Broeke J J, Moes J R, Swart I, Delerue C, Slot M R, Smith C M, Vannakelbergh D 2020 p orbital flat band and Dirac cone in the electronic honeycomb lattice ACS Nano 14 13638–44

[68] Feilhauer J, Apel W and Schweitzer L 2015 Merging of the Fermi level in Kekulé-like artificial graphene ins small-period nanopatterned GaAs quantum wells Nano Lett. 14 2980–3

[69] Tarruell L, Greif D, Uehlinger T, Jotzu G and Esslinger T 2012 Ultra-cold fermions in a tunable honeycomb lattice New J. Phys. 14 053015

[70] Nádvorník L et al 2012 From laterally modulated two-dimensional electron gas towards artificial graphene New J. Phys. 14 053002