particles. This type of excited-state intermolecular aggregation adds a degree of freedom for designing colloidal metal nanostructures with electronic properties that are controllable at the supramolecular level, a property, which up until now, was exclusive to organic-based architectures. Bio imaging experiments performed on living cells highlight the biocompatibility of our structures and their ability to scavenge cytotoxic agents. The approach that we have demonstrated with Au clusters is not size- or composition-specific and could be applied to different metals or alloys, allowing the realization of permanent excimer superstructures with pre-designed optical and electronic properties.

REFERENCES AND NOTES

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GRAPHENE

Tuning the valley and chiral quantum state of Dirac electrons in van der Waals heterostructures

J. R. Wallbank1,*, D. Ghazaryan1,*, A. Misra2, Y. Cao2, J. S. Tu3, B. A. Piot4, M. Potemski5, S. Pezzini5, S. Wiedmann5, U. Zeitler3, T. L. M. Lane1,*, S. V. Morozov6,7, M. T. Greenaway8, L. Eaves8, Y. A. K. Geim3, V. I. Fal’ko1,*, K. S. Novoselov1,*, A. Mishchenko1,*,

Chirality is a fundamental property of electrons with the relativistic spectrum found in graphene and topological insulators. It plays a crucial role in relativistic phenomena, such as Klein tunneling, but it is difficult to visualize directly. Here, we report the direct observation and manipulation of chirality and pseudospin polarization in the tunneling of electrons between two almost perfectly aligned graphene crystals. We use a strong in-plane magnetic field as a tool to resolve the contributions of the chiral electronic states that have a phase difference between the two components of their vector wave function. Our experiments not only shed light on chirality, but also demonstrate a technique for preparing graphene’s Dirac electrons in a particular quantum chiral state in a selected valley.

The chiral properties of Dirac electrons in monolayer graphene (1–3) and the Berry phase π associated with them have been used to explain Klein tunneling, the absence of backscattering in graphene p-n junctions (4–6), specific features in weak localization (7, 8), a peculiar Landau-level spectrum (in which one level is pinned exactly at the Dirac point, leading to the “half–integer” quantum Hall effect) (9, 10), and valley selection of the interband transitions excited by polarized light (9). Chirality is determined by the relative phase in the two-component wave function of the Dirac quasi-particles, which arises from the sublattice composition in graphene (3) and from spin states in topological insulators (10). Such a two-component wave function is typically described in terms of a specific vector—the pseudospin—which, for chiral particles, is locked to their direction of motion. However, it has proved difficult to image directly the chirality and the pseudospin polarization in electrical or optical measurements. To date, the phase shift in the sublattice composition of the electron states in graphene has been detectable only by angle-resolved photoemission spectroscopy (11–13).

Here, we report an alternative technique for pseudospin and chirality detection that is based on tunneling of electrons in van der Waals (vdW) heterostructures (14, 15) in which graphene (Gr) and hexagonal boron nitride (hBN) are stacked in a multilayer structure (Fig. 1A). In these devices, it has been shown that the exceptionally high quality of graphene, provided by its encapsulation, allows the electrons to tunnel between graphene electrodes with conservation of in-plane momentum (16, 17), making one graphene electrode a bias voltage (Vbias)–tunable spectrometer for electrons emitted by the other. However, the usual tunneling formalism, which does not take into account the interference between the two components of the wave function of the tunneling electrons, fails in the case of chiral quasi-particles. Here, we show that the tunneling current–voltage characteristics I(Vbias,B) in the presence of an in-plane magnetic field B (18), essentially depend on the pseudospin orientation and enable detection of the valley sublattice structure determined by the relative phase between the two sublattice components of the Dirac spinor vector wave function of electrons in graphene.

A small misalignment angle between the crystalline lattices of the two graphene flakes (Fig. 1E) causes specific parts of I(Vbias,B) to arise from the tunneling of electrons in specific regions of momentum space. Furthermore, for the case of chiral electrons, different states in momentum space (and thus with specific pseudospin orientation) have different tunneling probability—depending on whether the interference between the two components of electron wave function is constructive (Fig. 1, B to D) or destructive (Fig. 1, F to H) as electrons tunnel out of the emitting graphene layer (19). A particular state can be chosen...
Fig. 1. Device schematics, band structure, and chiral composition of the wave function. (A) Schematic diagram of the Si/SiO₂/Gr/hBN/Gr device (dark blue hexagonal layers are graphene electrodes; light blue, hBN; purple, Si/SiO₂ back gate). The gate voltage \( V_g \) is applied between the bottom graphene and Si substrate. (B) Two corners of the BZ [the full BZ is shown in (E)] schematically demonstrating the Fermi surfaces for emitter (blue circles) and collector (red circles). Yellow arrows mark the states in the emitter when the components of the wave function on the two sublattices are in phase [shown in (C)]. (C) Real-space distribution of the real part of the wave function on the A and B sublattices. The two components of the wave function are in phase. (D) Schematic representation of the interference of the two-component wave function of graphene electron at the given distance above the graphene layer when the electron is taken away from graphene. The original electron state at \( z = 0 \) is as in (C). (E) Small-angle rotational misalignment between the two graphene crystals leads to a small momentum mismatch between the two band structures in the reciprocal space. (F) Same as (B). Yellow arrows mark the states in the emitter when the components of the wave function on the two sublattices are out of phase [shown in (G)]. (G) Real-space distribution of the real part of the wave function on the A and B sublattices. The two components of the wave function are out of phase. (H) Same as in (D), but when the original electron state at \( z = 0 \) is as in (G). Color scales for (C), (D), (G), and (H) are the same.

Fig. 2. Tunneling characteristics of our devices. (A and B) Relative position of the bands and the Fermi levels in the two graphene electrodes rotated by a small angle with respect to each other for conditions highlighted by yellow (A) and red (B) dashed lines in (D). Red dashed lines in (D) are also marked by red arrows for clarity. (C and D) Experimental (C) and simulated (D) tunneling characteristics for a Gr/3hBN/Gr device with the graphene electrodes misaligned by 1.8°. The red cross in (C) marks the \( V_b \) and \( V_g \) used for the calculations of chirality polarization in Fig. 4, C to I. The blue dashed lines in (D) mark the conditions when the Fermi level in one of the electrodes passes through the Dirac point where the DOS is zero, which leads to the suppression of tunneling conductance. (E and F) Relative position of the bands and the Fermi levels in the Gr and BGr electrodes rotated by a small angle with respect to each other for the resonant conditions highlighted by red (E) and black (F) dashed lines in (H). In (E), the low-energy subband in the valence band in bilayer graphene touches the graphene cone. In (F), the higher-energy subband in the valence band in bilayer graphene touches the graphene cone. (G and H) Experimental (G) and simulated (H) tunneling characteristics for a Gr/5hBN/BGr device with the graphene electrodes misaligned by 0.5° (a small part of the sample is misaligned by 3°, which explains some of the weaker features). The yellow dashed lines mark the resonance when the Fermi level in monolayer graphene touches the bottom (top) of the conduction (valence) band in the bilayer graphene. The red cross in (G) marks the \( V_b \) and \( V_g \) used for the calculations of chirality polarization in Fig. 4, M to R.
with the help of a magnetic field, applied perpendicular to the current. This provides the electrons with a tunable momentum boost as they traverse the barrier (as shown previously in studies of vertical transport in III-V semiconductor heterostructures (20, 21)). For graphene, by rotating the magnetic field in the plane of the Gr/hBN/Gr device, we can resolve the contributions to the measured differential conductance, $G = dI / dV_b$, arising from electrons with clearly identifiable momenta in a given valley of graphene’s band structure, and hence detect the features related to the sublattice composition of the electronic wave functions.

In the series of vdW heterostructures studied here, a tunnel barrier of hBN separates a graphene monolayer from either a monolayer or a bilayer of graphene. During preparation, we ensure that the crystallographic orientations of the two graphene electrodes are closely aligned (Fig. 1A), by aligning the edges of the flakes in the transfer procedure (for details, see (19, 22)). The devices are placed on the oxidized surface of a doped silicon substrate, which forms an insulating back gate electrode, as in previously reported graphene tunneling transistors (16, 17, 23). The two types of multilayer stack are thus of the form Si/SiO$_2$/hBN/Gr/N-hBN/Gr/hBN, where (Gr) denotes (bilayer) graphene and N-hBN denotes $N$ layers of hBN. The typical active areas of our devices are between 10 and 100 $\mu$m$^2$.

Typical plots of $G$ versus $V_g$, and back gate voltage, $V_g$, for the Gr/3hBN/Gr and Gr/5hBN/BGr devices are presented in Fig. 2 (see examples of other aligned devices in (19)). In these aligned devices, a number of resonant features in the tunneling $R(V_g)$ characteristics are observed, such as when the Fermi level in one layer coincides with the lowest energy at which the band dispersion curves of the two layers intersect (Fig. 2A). Schematic representations of some of these resonant alignment conditions are shown in Fig. 2, with more details given in (19). These resonances are absent in the devices in which the graphene electrodes are strongly misaligned; for these devices, momentum conservation is satisfied by elastic scattering and/or phonon emission (19, 24–26).

There are qualitative differences in the tunneling conductance plots of the Gr/hBN/Gr and Gr/hBN/BGr devices mainly due to (i) the difference in the density of states (DOS) between graphene (DOS is linear with energy) and bilayer graphene (DOS is independent of energy) and (ii) the presence of the second subband in bilayer graphene. Thus, the difference in DOS leads to most features in the conductivity plot for Gr/hBN/Gr having a square-root dependence in the $V_i$ plane, whereas some of these features are linear for the Gr/hBN/BGr devices (compare blue dashed lines in Fig. 2, D and H). Also, the presence of the second subband in the bilayer roughly doubles the number of the observed resonances.

To gain further insight, we computed the tunnel conductance using a previously developed model of the device electrostatics (16, 23) and a chiral tunneling formalism (27). The only free parameters in the model are the relative angle between the crystallographic directions of the graphene flakes and the energy broadening of their plane wave states. By comparing the experimental and calculated results in Fig. 2, we can extract the relative orientation angle between the two graphene flakes, which we find to cover the range 0.5° to 3° for the group of devices that we studied.

A strong magnetic field, ~30 T, applied parallel to the graphene layers gives rise to additional

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**Fig. 3. Magnetotunneling characteristics of studied devices.** (A) Schematic representation of the BZ for the emitter (blue) and collector (red) graphene electrodes rotated by a small angle with respect to each other. Circles represent the Fermi surfaces in the two graphene layers. (B) As in (A) but with increased Fermi level in the emitter, which induces resonant condition of the type presented in Fig. 2A for all six corners of the BZ simultaneously. (C) Resonance in $dI / dV_b$ corresponding to (B). (D) As in (A) but with $B$ applied parallel to graphene layers. The Lorentz force leads to an additional momentum acquired by electrons when tunneling from the emitter to the collector, which can be represented by a relative shift of the two BZs by the vector $\Delta \vec{p}$ (gray, the BZ in $B = 0$; blue, in finite $B$). This can bring different corners of the BZ into resonance, depending on $\alpha$. (E) As in (D) but at different doping (increased Fermi level in the emitter), which brings a different corner of the BZ into resonance. (F) The resonant peak in $dI / dV_b$ splits into six peaks in finite magnetic field (red curve), each corresponding to a resonance that occurs in each corner of the BZ (green and blue curves for K and K' valleys, respectively). Examples for particular resonant conditions for two corners of the BZ are shown in (D) and (E). (G) Conductance of the Gr/5hBN/BGr device at $V_g = -45$ V for $B = 0$ T (blue) and 30 T for $\alpha$ increasing from 0° in 5° steps (black to red). Note that some minima (marked by short blue arrows) are split by the magnetic field (black arrows); see enlarged inset. (H and I) $dG / dV_b$ versus $V_g$ and $\alpha$ for the Gr/3hBN/Gr device with $V_g = 20$ V. (K and L) $dG / dV_b$ versus $V_g$ and $\alpha$ for Gr/5hBN/BGr device with $V_g = 60$ V. (H) and (K), experimental data; (I) and (L), theory. The six black, gray, and white lines in (H) and (K) are guides to the eye and mark the position of the resonances for the six corners of the BZ. (J and M) Calculated valley polarization of tunneling current for Gr/3hBN/Gr (J) and Gr/5hBN/BGr (M) devices. Note different color scales for $V_g < 0.5$ V and $V_g > 0.5$ V in (J).
fine structure in G (Fig. 3G), which is strongly dependent on the angle between $B$ and the principal axes of the graphene crystals. This is best revealed in the $G' = \partial G/\partial V_B$ plots (Fig. 3, H and K), with further examples presented in (I9). The angular dependence of these features corresponds to six intertwined sinusoids.

The origin of this fine structure is explained in Fig. 3, A to F. In zero magnetic field, all six corners of the Brillouin zone (BZ) experience resonance conditions simultaneously, leading to a single resonance peak (Fig. 3, A to C, where an example is given for the resonant alignment, similar to the “touch” depicted in Fig. 2A). In a finite magnetic field, the tunneling electrons experience a Lorentz force and gain an in-plane momentum boost, given by

$$\Delta \vec{p} = e \vec{z} \times \vec{B}$$

Here, $\vec{z}$ is a unit vector in the tunneling direction, $e$ is the electron charge, and $d$ is the thickness of the hBN tunneling barrier. In Fig. 3, D and E, this is represented as a relative shift of the two BZs, additional to the rotation arising from the small angular misalignment of the two graphene layers. Hence, depending on the orientation of magnetic field, the resonant conditions for the six corners of the BZ are fulfilled at six slightly different voltages, leading to the splitting of the resonance peak into six individual peaks. The $V_B$ value required for resonance at each particular corner is a sinusoidal function of the angle $\alpha$ between $B$ and the “armchair” direction of the graphene lattice: $V_B(\alpha, j) = V_B(0) + \Delta V(B\alpha) \sin(\alpha + j \pi/3)$, where $j = 0, 1, 2, 3, 4$ is the index of a particular BZ corner (as shown by grayscale-colored lines in Fig. 3, H and K). Our theoretical model provides a very good fit to our experimental results (Fig. 3, I and L).

The intensities of these resonances also depend on $\alpha$, so only half of the period of the sinusoid is visible (Fig. 3, H, I, K, and L). This is particularly obvious in Fig. 3, K and L, for the resonance between $V_B = 0$ and 0.25 V. This asymmetry arises from the electronic chirality of graphene. The electron wave function is a vector with two components, $\psi_A$ and $\psi_B$, representing the probability of finding the electron on the two sublattices, $A$ and $B$, of the honeycomb lattice. Chirality is the specific property of the relative phase $\phi$ between the wave-function components, which is locked to the direction of the electron’s momentum, $\vec{p} = p \cos \theta \hat{\alpha} + p \sin \theta \hat{\beta}$, counted from the nearest BZ corner. For a monolayer $\phi = 0$; for gapless bilayer graphene, it would be $\phi = 2\pi$ for AB sublattices supporting low-energy bands.

Electron tunneling from one graphene layer to another requires a correlation between the two components of the wave function in both layers. In effect, this projects the wave function in (K): For the lower intersection of the two Fermi lines, the interference between wave function components is destructive (green).
The projected states are composed of two sublattice components in the emitter and collector. As a result, momentum-dependent constructive ($\varphi_{\text{GC}} = 0$) or destructive ($\varphi_{\text{GC}} = \pi$) interference between sublattice components is governed by $|\varphi_A + \varphi_B + \frac{1}{2}\varphi_{\text{GC}}| - \cos \varphi_{\text{GC}}$ for the states both in emitter ($\varphi_A$) and collector ($\varphi_B$) and manifests itself in the tunneling characteristics ($I(V)$). Because the magnetic field selects the pairs of particular plane wave states probed by tunneling at a particular gate or bias voltage (Fig. 4, A and B), the measured asymmetry provides a direct visualization of the pseudospin polarization of the Dirac fermions. In the presence of the magnetic field, each resonance peak represents tunneling from a particular corner of the BZ. This allows one to inject electrons with a particular valley polarization, and from a selected corner of the BZ. We use the experimental parameters to calculate the amount of polarization achieved in our experiment (Fig. 3, J and M), and estimate that the valley polarization, $P = (I_X - I_Y)/(I_X + I_Y)$ (where $I_X$ ($I_Y$) is the current injected into the K(K’)-valley) can be as high as 30% (40%) for the particular Gr/3hBN/Gr (Gr/5hBN/Gr) devices. The main limit to the degree of polarization is the energy broadening of states at the Fermi levels caused by inelastic tunneling processes. However, even for the current level of disorder, with the resonances at around $V_n = 0\, \text{V}$ (e.g., resonances marked by yellow dashed lines on Fig. 2D at $V_n > 50\, \text{V}$), which maximizes the number of states participating in tunneling and sensitive to magnetic field, a polarization close to 75% could be achieved (19). By using devices with smaller misalignment between the graphene electrodes (on the order of 0.2°, now within the reach of the current technology (19)), valley polarization close to 100% is possible (19).

The same mechanism can also be used to select electrons with a particular pseudospin polarization. In Fig. 4, C to R, we present results of a calculation of the contribution of different electronic states in $k$-space to the tunnel current for the Gr/3hBN/Gr (Fig. 4, C to I) and Gr/5hBN/Gr (Fig. 4, J to R) devices. We choose the position of the Fermi levels in the emitter and collector to be very close to a resonance at $B = 0\, \text{T}$. Then, for certain directions of $B$, the resonant conditions are achieved only in one valley and for only a very narrow distribution in $k$-space (Fig. 4, G to I). Tunneling of the electrons from other parts of $k$-space is prohibited either because there are off-resonance or because of the pseudospin selection rule. Alternatively, for the Gr/3hBN/Gr device and exploiting the difference in curvature of monolayer and bilayer electronic bands, we can choose the overlap between the bands in such a way that the magnetic field reduces the overlap in one valley and increases it for the other (Fig. 4, M to R). In this case, momentum conservation at $B = 0\, \text{T}$ is fulfilled for the states marked by white dashed lines (Fig. 4O). However, only one of those lines contributes to tunneling, owing to pseudospin interference (Fig. 4, M and N).

Our technique, which enables tunneling of valley-polarized electrons in monolayer and bilayer graphene, also allows one to selectively inject carriers propagating in the same direction and to probe pseudospin-polarized quasi-particles. In principle, the technique can be extended to tunneling devices in which surface states of topological insulators are used as electrodes; then, all-electrical injection of spin-polarized current (28) with noninvasive tunneling contacts could reveal a number of exciting phenomena (29–33).

REFERENCES AND NOTES
19. Supplementary materials are available on Science Online.

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ARCHAEOLOGY
Outburst flood at 1920 BCE supports historicity of China’s Great Flood and the Xia dynasty
Qinglong Wu,1,2,3† Zhijun Zhao,2,3 Li Liu,4 Darryl E. Granger,5 Hui Wang,6 David J. Cohen,7 Xiaohong Wu,1 Maolin Ye,6 Ofer Bar-Yosef,8 Bin Lu,9 Jin Zhang,10 Peilzen Zhang,1,12 Daoyang Yuan,11 Wuyun Qi,6 Linhai Cai,12 Shibiao Bai2,13 Zhijun Zhao,2,13 Li Liu,4

China’s earliest historiographies tell of the successful control of a Great Flood leading to the establishment of the Xia dynasty and the beginning of civilization. However, the historicity of the flood and the Xia remain controversial. Here, we reconstruct an earthquake-induced landslide dam outburst flood on the Yellow River about 1920 BCE that ranks as one of the largest freshwater floods of the Holocene and could account for the Great Flood. This would place the beginning of Xia at ~1900 BCE, well before later than traditionally thought. This date coincides with the major transition from the Neolithic to Bronze Age in the Yellow River valley and supports hypotheses that the primary state-level society of the Erlitou culture is an archaeological manifestation of the Xia dynasty.

C
Teasing out chirality in graphene

A chiral elementary particle has its spin pointing in either the same or the opposite direction as its momentum. In graphene, electrons have an analogous chirality, but observing it in electrical transport experiments is tricky. To do this, Wallbank et al. studied how electrons tunnel between two slightly misaligned graphene sheets separated by a layer of insulating hexagonal boron nitride. The chiral nature of the electrons imposed restrictions on the tunneling, which made it possible to discern the signatures of chirality in the data. Science, this issue p. 575