Lateral heterojunctions of atomically precise graphene nanoribbons (GNRs) hold promise for applications in nanotechnology, yet their charge transport and most of the spectroscopic properties have not been investigated. Here, we synthesize a monolayer of multiple aligned heterojunctions consisting of quasi-metallic and wide-bandgap GNRs, and report characterization by scanning tunneling microscopy, angle-resolved photoemission, Raman spectroscopy, and charge transport. Comprehensive transport measurements as a function of bias and gate voltages, channel length, and temperature reveal that charge transport is dictated by tunneling through the potential barriers formed by wide-bandgap GNR segments. The current-voltage characteristics are in agreement with calculations of tunneling conductance through asymmetric barriers. We fabricate a GNR heterojunctions based sensor and demonstrate greatly improved sensitivity to adsorbates compared to graphene based sensors. This is achieved via modulation of the GNR heterojunction tunneling barriers by adsorbates.
The significance of heterojunctions is established in semiconductor physics. Vertically grown compound semiconductor heterostructures such as GaAs/AlGaAs have been developed to enable high electron mobility transistors, light-emitting diodes, laser diodes, and solar cells. Tunneling through multiple potential barriers in superlattice heterostructures has found use in quantum cascade lasers. More recently, van der Waals (vdW) heterostructures that are fabricated from monolayers of layered materials have attracted research interest. Graphene nanoribbon (GNR) heterostructures differ from compound semiconductor and vdW heterostructures in that the bottom-up synthesis allows for the formation of one-dimensional (1D) lateral interfaces with atomic precision. This synthesis approach enables electronic band structure engineering, i.e., control of parameters such as the energy bandgap, the band offset, and the effective mass of carriers that are important for charge transport. Conventional top-down fabrication methods such as lithography do not have the precision required for reproducible, atomically precise GNR heterojunctions that have well-defined, sharp band offsets. Thus, bottom-up GNR heterojunctions are promising for novel device concepts such as energy-efficient tunnel field-effect transistors (TFETs). TFETs based on GNR heterostructures might also be useful for chemical sensing devices. Yet progress is hampered by the absence of experiments that probe the electronic properties of GNR heterojunctions. There are two main obstacles for the fabrication of GNR heterojunction-based tunneling devices that are overcome in the present work. The first one is the random orientation of bottom-up synthesized GNRs that yield disconnected heterojunctions scattered over the substrate surface. The second obstacle is the presence of significant Schottky barriers at the metal–GNR interface, which can determine the device performance.

In the present work, we use the lateral fusion approach to fabricate a monolayer film consisting of aligned lateral heterojunctions of wide-bandgap armchair GNRs of $N = 7$ carbon atom width (7-AGNRs) and their quasi-metallic derivatives (mostly 14-AGNRs) on a stepped Au(788) surface. The GNR heterojunctions are comprehensively characterized by scanning tunneling microscopy (STM), angle-resolved photoemission spectroscopy (ARPES), and Raman spectroscopy and are integrated into a back-gated FET structure. This allows to perform ensemble studies of charge transport in GNR heterojunctions. We demonstrate that the current through the device has the characteristic dependencies on bias voltage, charge carrier concentration, channel length, and temperature that are associated with tunneling transport. We quantitatively describe the charge transport behavior of GNR heterojunction devices using a multi-barrier tunneling model. Performing chemical doping of GNR heterojunctions with alkali metal adatoms, we observe a highly superlinear modulation of the tunneling current in lieu of the conventional linear current modulation. The operation of our devices is based on modulation of bulk conductance through GNR heterojunctions, and not Schottky barriers. Our observations of tunneling conductance and chemical sensing using atomically precise GNR heterojunctions highlight their application potential.

Results

**GNR heterojunction concept.** Densely aligned, parallel 7-AGNRs can be grown on a stepped Au(788) crystal. Thermally activated lateral fusion leads to the formation of narrow-bandgap (quasi-metallic) 14-AGNR segments as illustrated in Fig. 1a. Wider GNRs with $N = 21$, 28, and so forth are less abundant, and similarly to 14-AGNRs are also quasi-metallic. GNR segments of different widths form an aligned array of GNR heterojunctions, where quasi-metallic GNRs are connected by wide-bandgap 7-AGNR segments, for example, 14-/7-14-AGNR or 14-/7-21-AGNR. Parallel sequences of heterojunctions may also join one another to form “Y-junctions,” e.g., a 14-AGNR may split into two 7-AGNRs that are each in turn fused with two neighboring GNRs. Charge transport can be probed by transferring such a GNR heterojunction array to an insulating substrate and depositing metallic electrodes to form source and drain contacts. The wide-bandgap 7-AGNR segments act as energy barriers. GNR heterojunctions form a variety of conducting paths, which may also intersect with one another. Charge carriers traverse a multiple barrier potential profile along their path from source to drain (Fig. 1b). There are two primary mechanisms of charge transport from one quasi-metallic segment to another: tunneling through the 7-AGNR barrier and thermionic emission over the barrier (Fig. 1b). The tunneling and thermionic currents depend on temperature (with the temperature dependence of the latter much stronger than the former), on the applied electric field, and on the barrier shape. The barrier length $d$ is the length of the 7-AGNR segment. For electron (hole) injection from the 14-AGNR segment into the 7-AGNR segment, the barrier height $\Phi_b$ is given by the conduction (valence) band offset, i.e., the difference between the first conduction (valence) sub-bands of the 7- and 14-AGNR (Fig. 1c, d). Due to the large bandgap of 7-AGNRs, the difference in $\Phi_b$ between the 7-14-AGNR and the 7-21-AGNR junctions can be neglected. GNR fusion can also produce non-lateral heterojunctions, such as heterojunctions between the lateral armchair edge and the terminal zigzag edge of an AGNR. These non-lateral heterojunctions may host localized midgap edge states, which alter the effective barrier. However, as we will see from the STM data presented below, our GNRs are aligned, and therefore the density of such junctions is minimized. Moreover, the edge state wave function falls off rapidly in the GNR bulk, therefore we do not expect a substantial change to the barrier transparency, which is determined by $d$ and $\Phi_b$. In Supplementary Note 1 (Supplementary Fig. 2), we also show scanning tunneling spectroscopy (STS) measurements of our GNR heterojunction system, which suggest the similarity of the local density of states of 7-AGNR segments regardless of the configuration of GNR heterojunctions.

**Synthesis and characterization of aligned GNR heterojunctions.** STM studies reveal that the lateral fusion (see “Methods”) of densely aligned 7-AGNRs on an Au(788) crystal leads to the formation of numerous 14-AGNRs and wider GNRs. (Fig. 2a and Supplementary Note 1). The fused GNRs have a length of the order of tens of nm, and many of them are connected by short (several nm) 7-AGNR segments. Together, these form well-aligned paths for charge transport. The linear density of 7-AGNR tunneling barriers is about one per 20 nm, and the average barrier length is about 4 nm (Fig. 2a and Supplementary Fig. 1). We characterize fused GNRs by ARPES and ultra-high vacuum (UHV) Raman spectroscopy. Upon fusion of aligned 7-AGNRs, we observe new features in the ARPES spectra (Supplementary Note 2). A linearly dispersing energy band is observed, consistent with calculations (Fig. 2b, c and “Methods”). Based on the peculiar variation of the photoemission intensity for GNRs in momentum space (Supplementary Note 2), we attribute this band to the first valence sub-band of 14-AGNRs, labeled VB$^{14-AGNR}$ hereinafter. The apex of VB$^{14-AGNR}$ is touching the Fermi level ($E_F$), which is in line with the observed Fermi level pinning in GNRs on an Au substrate. UHV Raman spectra before and after the fusion were measured in situ (Fig. 2d) and are compared to the calculations (see “Methods”) for 7-AGNRs and 14-AGNRs (Fig. 2e). The initial Raman spectrum consists primarily of 7-AGNR-derived modes. Upon fusion, we observe changes in the regions of the G-like and D-like modes (whose atomic displacements resemble the G and D
modes in graphene) and the appearance of well-separated peaks in the low-frequency region. We observe radial breathing-like modes at 399 cm\(^{-1}\) for 7-AGNRs (RBLM,) and at 204 cm\(^{-1}\) for 14-AGNRs (RBLM.). The frequencies of all peaks that appear after fusion are in excellent agreement with the calculations for 14-AGNRs. During GNR fusion, we have monitored the UHV Raman spectrum, which allowed us to optimize the process for maximum 14-AGNR peak intensities (Supplementary Note 4). STM, ARPES, and Raman spectroscopic measurements consistently show that the fused sample is a monolayer of aligned multiple heterojunctions of quasi-metallic GNRs and wide-bandgap 7-AGNR segments.

**Charge transport characterization.** For the transport measurements, a film of aligned GNR heterojunctions was transferred to a doped Si wafer with 300 nm SiO\(_2\) using electrochemical delamination\(^{25}\) to fabricate back-gated FETs. The GNR orientation and structural quality of the transferred sample were confirmed by polarized Raman measurements (Supplementary Note 4). Electrical contacts to the film were fabricated by electron-beam lithography. In the FET devices (Fig. 3a), the drain current \(I_d\) was measured as a function of the drain voltage \(V_d\) and the back-gate voltage \(V_g\). We fabricated devices with different channel lengths \(L\) and a fixed channel width \(W\) (25 \(\mu\)m). The GNR heterojunctions were aligned along the channel between the source and drain contacts. After device fabrication, each sample was mounted on a sample holder that enables charge transport measurements to be carried out in UHV.

We observe nonlinear \(I_d-V_d\) behavior and a clear \(V_g\) dependence (Fig. 3b). A strong field effect is observed for both electron (\(V_g>0\)) and hole (\(V_g<0\)) conduction, demonstrating bipolar operation (Fig. 3c). The current \(I_d\) is modulated by \(V_g\) by two orders of magnitude, with higher hole conduction than electron conduction. We extract the field-effect mobility using the direct transconductance method (DTM): \(\mu_{DTM} = 6.0 \times 10^{-5} \text{cm}^2/\text{V}s\) at \(V_d = 6 \text{V}\) and \(\mu_{DTM} = 8.3 \times 10^{-4} \text{cm}^2/\text{V}s\) at \(V_d = 9 \text{V}\) (see “Methods”). Such low values of \(\mu_{DTM}\) cannot be explained by conventional band transport and are more typically associated with hopping transport, which occurs due to charge carrier transitions between localized states\(^{27-30}\). However, the temperature dependence of \(I_d\) in our devices does not agree with a variable-range hopping model (Supplementary Note 5 and Supplementary Fig. 7). Our devices have weak temperature dependence. Increasing the temperature from 4 K to room temperature increases the current by less than one order of magnitude (Fig. 3d, Supplementary Note 5, and Supplementary Fig. 6). Therefore, we exclude hopping transport, as well as the thermionic emission over the barrier as the conduction mechanisms in our system. In Supplementary Note 6, we also compare the temperature dependence of conduction in our aligned heterojunctions to the model of nuclear tunneling of polarons, which was recently used by Richter et al. to interpret the charge transport in a network of narrow-bandgap 5-AGNRs\(^{31}\). While the fit parameters in the master equation used by Richter et al. for 5-AGNRs look very reasonable, the fit parameters needed to describe our data by the same master equation are rather unrealistic. Therefore, we cannot claim the polaron conduction between quasi-metallic AGNRs as a dominant transport mechanism in our system. Note that the structure of our system, consisting of alternating wide-bandgap and quasi-metallic GNR segments, is different from those of the 5-AGNR network, where narrow-bandgap GNRs are densely packed. Quantum mechanical tunneling through potential barriers is compatible with the dependencies observed in our GNR heterojunctions\(^{32}\). Further evidence that tunneling through 7-AGNR segments governs the transport is the channel length dependence of conduction in our FETs. We observe an exponential drop in \(I_d\) with increasing \(L\) (Fig. 3e). The exponential trend in \(I_d\) differs from the 1/\(L\) scaling of conductance of an Ohmic conductor. If Schottky barriers would dominate the charge transport, all the applied \(V_d\) would drop near the contacts. In this situation, \(I_d-V_d\) characteristics of devices with different \(L\) should be the same, up to multiplication of the current by a constant factor that reflects different numbers of conducting paths in different devices. As a consequence, the slopes of \(I_d-V_d\) curves in semilogarithmic plots (log(\(I_d\)) versus \(V_d\)) should be independent of the channel length. However, in our data this is not the case, as we will show later. In single semiconducting GNR devices with short contact separation, Schottky barriers led to nonlinear \(I_d-V_d\) characteristics\(^{19}\). Our
devices have a contact separation $L \geq 200$ nm, and several 7-AGNR barriers are traversed by charge carriers between the source and drain. Therefore, these tunneling barriers are expected to dominate device resistance. In the "Methods," we quantitatively compare the impact of heterojunction barriers and of Schottky barriers on the total device resistance and find that the contribution of the latter is negligible. Finally, we note that the statistical variation from device to device is insignificant as compared to the observed trend with length $L$. Different devices of the same $L$ show a narrow distribution of conductance (Supplementary Note 5 and Supplementary Figs. 8 and 9). Consequently, conduction is not governed by a small number of conducting paths, as is the case in molecule-based systems. Rather, the number of contributing paths is sufficiently high to be considered a true ensemble measurement of conduction through AGNRs.

**Tunneling barrier analysis of transport measurements.** We model our system as a set of parallel conducting quasi-metallic 14-AGNRs that are connected in series by 7-AGNR tunneling barriers (Fig. 4a). A voltage $V_d$ across the contacts leads to trapazoidal barrier potential profiles, corresponding to the development of electric field and potential drops across the semiconducting barrier segments. The potential drop per semiconducting segment is $V = V_d / M$ where $M$ is the number of junctions between the contacts. The tunneling of a charge carrier through the barriers is considered to be sequential. A charge carrier entering a 14-AGNR segment following a tunneling event through a 7-AGNR barrier undergoes rapid inelastic scattering through emission of optical phonons. In the related material of carbon nanotubes (CNTs), charge carriers are scattered by optical phonon emission on length scales estimated to be as short as 10 nm. To describe the $I_d-V_d$ characteristics, we use the Wentzel–Kramers–Brillouin (WKB) approximation. Equation (4) of ref. 36 expresses the tunneling current $I$ as a function of the voltage $V$ across a trapazoidal barrier as

$$I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} P(E) [f(E) - f(E + eV)] dE. \quad (1)$$
Here $e$ and $h$ are the electron charge and Planck’s constant, respectively. The Fermi distribution function is given by

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)},$$

where $E_F$ depends on $V_g$ and $V_d$ as $E_F(V_g, V_d) = E_F^0(T) + \alpha(T) (V_g + \beta V_d)$. Here $E_F^0$, $\alpha$, and $\beta$ are phenomenological fitting parameters. The parameter $\alpha$ accounts for the modulation of channel potential by $V_d$ (see “Methods”). The quantity $E_F^0(T)$ accounts for the temperature dependence of $E_F$. $P(E)$ in Eq. (1) is the tunneling probability through the barrier of length $d$ and is given by the following expression:

$$P(E) = A \exp\left(-\frac{2}{\hbar} \int_0^d \sqrt{2m\varphi(x, V) - E} \, dx\right).$$

Here $\varphi(x, V) = \Phi_b + (x/d) \cdot (-eV)$ is the barrier height as a function of the coordinate $x$, $\Phi_b$ denotes the barrier height at $x = 0$, and $m$ is the effective mass inside the barrier which we take from ARPES data. The prefactor $A$ is proportional to the number of parallel 1D channels across the source–drain contacts and it was not allowed to vary significantly for all devices and it was kept constant for the $L$-dependent measurements shown below. The barrier height $\Phi_b$ is fixed at a constant value of $\Phi_b = 1.35$ eV for all fits throughout our work (see “Methods” for determination of $\Phi_b$ for GNR heterojunctions on SiO$_2$). The real GNR heterojunction system consists of several barriers in sequence where the tunneling current is limited by the longest and most opaque barrier. For simplicity, our model ignores the distribution of $d$ within one device and assumes one effective value of $d$. Figure 4b depicts a sketch of the $I_d$–$V_d$ relations for three barriers with different $d$ indicating that the voltage drop across each barrier becomes closer to each other at high $I_d$. Thus, our model is more accurate in the high $I_d$ regime. At low $I_d$ and $V_d$, the effects of disorder including the distribution of $d$ and $M$, trap states, and inhomogeneous surface potential are expected to play a more important role.

Figure 4c depicts the temperature dependence of the experimental and modeled $I_d$–$V_d$ characteristics of a $L = 350$ nm device for $T = 4, 100, 200$, and $295$ K. The experimental data for $L = 300, 500$, and $700$ nm devices at different $V_g$ were fitted by restricting the number of tunneling barriers $M$ to be proportional to the channel length $L$ (Fig. 4d–f). To estimate the role of contacts, we plot $M$ as a function $L$ (Fig. 4f, inset). By analogy with the conventional transfer length method used for Ohmic conductors, we interpret the linear extrapolation of this dependence to $L = 0$ as the effective number of tunneling barriers at the contacts. This yields 2.6 barriers in total for two contacts, or 1.3 effective barriers per contact. Therefore, our model corroborates our conclusion about the relative insignificance of contact Schottky barriers in our experiments. In all FETs, the fit yields practically identical values of tunneling barrier length $d = 3$ nm. The semilogarithmic plots are shown in the lower panels in Fig. 4d–f. One can see that the slope of the $I_d$–$V_d$ curves in the semilogarithmic plots decreases with increasing $L$. This is because of the increase in $M$ and indicates that $V_d$ drops not only at the contacts but also inside the channel. The semilogarithmic plots reveal a generally worse
agreement of the model fit with experiment at small $I_d$ and $V_d$ as discussed in the context of Fig. 4b. Our model accounts for the experimentally observed charge transport behavior of GNR heterojunctions over a wide range of experimental conditions, including temperature, $V_g$, and length dependence of $I_d$–$V_d$ characteristics, using a set of only six fit parameters ($A$, $d$, $M$, $E_0(T)$, $a(T)$, and $\beta$).

One might question on whether the 7/14- or 7/21-AGNR heterojunctions are truly what is the most important aspect limiting charge transport, because the conduction path is rather...
complicated. It includes connections between adjacent branches, and the distribution of current and voltage across junctions varies continuously upon applied bias due to the nonlinear nature of the elementary junction conductance. However, our STM data show that our network is composed out of aligned atomically precise wide-bandgap/quasi-metallic AGNR heterojunctions of well-defined types. Thus, each charge traverses a set of well-defined elementary junctions. Although we cannot be certain about the particular structure of the conducting path, the assumption that each path always traverses a set of well-defined junctions is realistic. In our model, we assume that we have $M$ such junctions in series. Agreement between the simulation results and the experimental data cannot probably serve as unambiguous proof for this simplified model. This, however, does not exclude that the gate-tunable tunneling conductance across the 7-AGNR barrier is at the heart of the observed transport properties.

### Tunneling current modulation by adsorbates

We performed in situ doping of our devices by Li adatoms in a UHV system (Fig. 5a), observing a strong modulation of the transport properties of the GNR heterojunctions. Upon chemical doping by Li, the $E_F$ shifts deeply into the conduction band of quasi-metallic GNRS as schematically shown in Fig. 5b. ARPES spectra of fused GNRS on Au(788) reveal the shift of VB $\text{14-AGNR}$ relative to $E_F$ by $-0.7$ eV after deposition of $\approx 1 \text{Å}$ of Li, visualizing the partially occupied CB $\text{1-AGNR}$ (Fig. 5c and Supplementary Note 3).

Compared to 14-AGNRs, achieving degenerate electron doping of wide-bandgap 7-AGNRs requires a much larger Li coverage. The $I_d$–$V_d$ characteristics reveal a dramatic increase in channel current upon Li doping performed in three consecutive steps of $\approx 0.1 \text{Å}$ each (Fig. 5d and Supplementary Fig. 11). The $I_d$–$V_d$ curves of Li-doped GNR heterojunctions are accurately reproduced by our tunneling barrier model (Fig. 5d). The surface doping of GNR heterojunctions by Li adatoms shifts $E_F$ and effectively reduces the barrier height to $\Phi_h - E_F$ (Fig. 5e). In the model calculations, $M$ and $\delta$ were held constant. The fit values of $E_F$ for the sample in its pristine state and after Li doses 1–3 were 4, 25, 63, and 103 meV relative to CB $\text{1-AGNR}$, respectively. These values are in good agreement with the shifts inferred by comparison with ARPES (Supplementary Note 7). Our model is also accurately reproducing the $I_d$–$V_d$ characteristics of the Li-doped $L = 500 \text{ nm}$ device (Supplementary Note 7).

The channel current through a band conductor scales approximately linearly with charge carrier density. Surface doping of graphene by alkali metal adatoms leads to a modest increase in channel current as a result of the combined effects of increased carrier density and reduced mobility due to charged impurity scattering. In contrast, in an ideal system the tunneling current through a GNR heterojunction is exponentially dependent on the tunneling barrier height. As a consequence, upon alkali metal doping we observe an increase in the current ratios of the doped and pristine samples $(I_d/I_{d0})$ by a factor 50 for the $L = 200 \text{ nm}$ device operated at $V_d = -6 \text{ V}$ and by a factor 180 for the $L = 500 \text{ nm}$ device operated at $V_d = -14 \text{ V}$ (Fig. 5f). According to our tunneling model, the difference in current modulation for the two devices is mostly related to the voltage drops across one heterojunction ($V_d/M$) and to the slightly different values of $E_F$ (Supplementary Note 7). We also performed identical adorption experiments using a graphene FET (Supplementary Note 8). The current in graphene increases only by a factor <2 after deposition of identical amounts of Li (Fig. 5f). The adsorbate-induced current modulation in the GNR heterojunction FETs is highly nonlinear in Li dose. The operation of our devices based on modulation of the channel conductance, and therefore GNR heterojunction FETs, differ from the CNT Schottky barrier transistors, in which adsorbates modulate electron tunneling only at the contact. To confirm the potential application of GNR heterojunctions for tunneling devices, we analyze the channel referenced sub-threshold swing $S_{\text{ref}}$, which is the Fermi level change (known as the channel potential change) required to modulate the drain current by one decade: $S_{\text{ref}} = e^{-1} \partial E_F/\partial \log_{10}(I_d)$. At room temperature for the $L = 200 \text{ nm}$ GNR heterojunction FET (Fig. 3d), we obtain $S_{\text{ref}} = 34 \text{ mV/dec at } V_d = 8 \text{ V}$ (see “Methods”). This value is smaller than the fundamental thermionic limit of $\text{ln}(10)k_B T/e = 60 \text{ mV/dec}$ in metal oxide semiconductor FETs. GNR heterojunctions can thus be applied as a sensor that unites the steep slope current scaling of TFETs with an accessible surface for adsorption. We find a sensitivity to adsorbates of $s = \partial I_d/\partial q = 2.4 \times 10^{-12} \text{ A cm}^2 \cdot \text{e}$, where $q$ is the Li dose per unit area (see “Methods”). With the observed current noise of $\Delta I_d = 2 \text{ pA}$, the corresponding sensor resolution to Li dose is $r = \Delta I_d/s = 8 \times 10^8 \text{ cm}^2$, equivalent to $8 \text{ Li atoms per square micron, or 1 ppm of a monolayer of Li}$.

The adsorption of Li modifies the field effect of GNR heterostructures in a non-trivial fashion (Fig. 5g). We observe the loss of bipolar field effect, wherein electron conduction can be modulated by $V_g$ while modulation of hole conduction is strongly suppressed. As illustrated in Fig. 5h, in the pristine system, a “diamond-like” shape emerges in the plot of $I_d$ versus $V_g$ and $V_d$ corresponding to bipolar gate modulation of both electron and hole currents. The “diamond” is reminiscent of that emerging in Coulomb blockade and is thus a direct consequence of the gate modulation of tunneling conduction. Upon Li deposition, $I_d$ no longer exhibits a field effect for $V_g < 0$. For comparison, graphene exhibits a bipolar field effect with a shifted neutrality point after the first Li dose (Supplementary Fig. 12), in good agreement with previous work in the low-doping regime. At higher Li doses, only electron conduction can be modulated by gate voltage (Supplementary Fig. 12), in agreement with previous work in the high-doping regime where the mismatch in density of states within bulk and contact graphene regions imparts asymmetry to the field effect. The asymmetric field effect in heavily doped GNR heterojunction FETs may thus originate from several mechanisms. In common with graphene, a shift in density of states between bulk and contact regions is expected. Furthermore, Li adsorption may occur on the GNR surfaces, GNR edges, and on the exposed SiO$_2$ surface, contributing to a more complex environment for charge exchange than graphene. Further work to understand the microscopic mechanisms of field effect in heavily doped GNR heterojunctions is required.

We note that alkali metals are strong electron donors and hence induce a large current modulation in our devices. However, the working principle of sensing any adsorbate in this kind of sensor is charge transfer. Some gases even have a large charge transfer of one elementary charge per adsorbed molecule. We thus expect that GNR heterojunction-based sensors can also effectively detect other adsorbates, provided their charge transfer is sufficiently large. To achieve a scaled, single junction device with steep sub-threshold swing, the minimal GNR structure required for tunneling transport must be identified and successfully integrated in a transistor structure with high gate efficiency.

### Discussion

In summary, we have synthesized a monolayer film of aligned atomically precise heterojunctions of wide-bandgap and quasi-metallic GNRSs on Au(788) and comprehensively characterized them by STM, ARPES, and Raman spectroscopy. After the alignment-preserving transfer of the film onto a SiO$_2$/Si substrate, we have measured charge transport along the GNR heterojunctions.
in a back-gated FET geometry. The characteristic dependencies of the current on drain and gate voltages, temperature, and channel length indicate that charge transport proceeds by quantum mechanical tunneling through the wide-bandgap 7-AGNR segments in the GNR heterojunctions. The experimental transport data are in agreement with computations (WKB approximation) of the tunneling current through multiple tilted barriers. Our model is able to describe all observed experimental current–voltage curves.
characteristics in the high bias regime using a minimal set of fit parameters, including the effective barrier height, the junction length, and the number of junctions. In our samples, the uniformity achieved in the atomically precise GNR heterojunctions and the degree of GNR alignment is sufficient to observe tunneling transport in the GNR heterojunction network. This is one of the key experimental findings of our work. We have demonstrated that the adsorption of atoms on the GNR heterojunction surface strongly modulates the tunneling conductance by charge transfer doping. We employed the step slope response of GNR heterojunction-based tunnel FETs with their accessible surface area to realize a nanoelectronic sensor with a giant sensitivity to adsorbates. Our results are important not only for applications of bottom-up synthesized carbon nanomaterials but also for the wider nanoscience field.

**Methods**

**Growth of GNR heterojunctions.** The synthesis of aligned GNR heterojunctions for our tunneling devices consists of the following steps: (1) deposition of approximately one monolayer coverage of 10,10-dibromo-9,9 bianthracene molecules on a clean Au(788) surface (prepared by standard Ar+ sputtering and annealing cycles) in UHV; (2) dehalogenation of the precursor molecules and assembly of the aligned polymer chains by annealing at ~200 °C for 10 min; (3) cyclization and lateral fusion at ~410 °C for 180 min. The first two steps are identical to the synthesis of densely aligned 7-AGNRs on Au(788)20,25,37 while the third step is performed at higher temperature and longer annealing time. The annealing temperature and time were optimized to get a maximum amount of 14-AGNRs using in situ studies with UHV Raman spectroscopy (Supplementary Note 4).

**STM measurements.** STM imaging of an in situ prepared GNR heterojunction sample was done at room temperature and in UHV (base pressure was 4 × 10−11 mbar) in the Athen STM chamber in Cologne. The STM images were processed (background subtraction and contrast adjustment) using the WxsM software44.

**ARPES experiments.** During ARPES experiments, the base pressure was <2 × 10−10 mbar. In all experiments, the aligned GNR heterojunctions were oriented along the slit of analyzer and linearly horizontally polarized light was used. The ARPES measurements on Li doping (Fig. 5c and Supplementary Fig. 5) and the ARPES data shown in Supplementary Figs. 3f−j have been performed at HZB BESSY II (U112-PM2 beamline, 12-ARPES end-station) using a vertical analyzer slit and the polar angle of manipulator to tune θ into 10°K with the photon energy of 25 eV. The GNR synthesis and fusion were performed in situ. ARPES measurements on Li doping (Fig. 5c and Supplementary Fig. 4) and the ARPES data shown in Supplementary Figs. 3f−j have been performed at HZB BESSY II (U112-PM2 beamline, 12-ARPES end-station) using a vertical analyzer slit and the polar angle of manipulator to tune θ into 10°K with the photon energy of 45 eV. The sample was synthesized at the University of Cologne (Germany) and transferred in situ by UHV Raman spectroscopy to our lab. The sample was transferred to the ARPES end-station in a suitcase filled by Ar. Li doping was performed in situ using a SAES getter. The amount of deposited Li, estimated by a quartz crystal microbalance sensor, was about 1 Å.

**Energy band structure calculations and ARPES intensity simulations.** Density functional theory (DFT) calculations of the band structure of 7-AGNRs and 14-AGNRs were carried out using the PPLO-1400-48 code (improved version of the original PPLO code by Koepenick and Eschrich15 utilizing the generalized gradient approximation (GGA) to the exchange–correlation potential. The GNRs were assumed freestanding and hydrogen-terminated. A k-point grid of 12 × 1 × 1 was used to sample the Brillouin zone. Atomic positions were relaxed until the forces on each atom were <10−2 eV/Å. The calculated electronic bands of 7-AGNRs and 14-AGNRs that are shown in Fig. 2b were shifted in energy to match the experimental Vb1. The photoemission intensity that is shown in Supplementary Fig. 3 was calculated using the dipole approximation for the matrix element with a plane wave as a final state7,26.

**Raman spectroscopy measurements.** All Raman measurements presented in this work were performed in the back-scattering geometry using a Renishaw inVia set up with a 633-nm laser at room temperature. UHV Raman studies shown in Fig. 2 were performed in the same set-up where the GNR heterojunctions were synthesized21. In the UHV studies, the laser was polarized along the GNR alignment direction (z), and the collected Raman signal was a sum over the GNR plane (z and yz). UHV Raman data were acquired using a ×50 long-working distance objective with a numerical aperture of 0.4 and the laser power of 7 mW. This laser power does not affect the sample quality due to the UHV conditions. Polarized Raman measurements of the GNR heterojunctions transferred onto the SiO2/Si substrate, shown in Supplementary Fig. 5d, were performed in ambient conditions with a 785-nm diode laser with 5 mW power. The low laser power shown in Supplementary Fig. 5c, were acquired with the laser polarized along the alignment direction of GNR heterojunctions using a notch filter and 0.8 mW laser power.

**Calculation of Raman spectra.** Theoretical modeling of the Raman spectra has been performed in the framework of DFT. All computations were carried out using the SIESTA DFT package46,47,48. Perdew–Burke–Ernzerhof (PBE)49–51,52. Density functional theory (DFT) calculations of the band structure of 7-AGNRs and 14-AGNRs using in situ studies with UHV Raman spectroscopy (Supplementary Note 4). Electron beam lithography was used to define the source and drain electrodes. For this purpose, the samples were coated with a double layer of poly (methyl methacrylate) (PMMA). The bottom layer (molecular weight 250 kg/mol) is undercut that facilitates lift-off processing. The PMMA-coated substrates were exposed in an electron beam writer, developed, and a 10-nm layer of titanium and 30-nm layer of gold were deposited by thermal evaporation. Subsequently, the metal was removed from the unexposed regions of the sample using a lift-off process.

**Device fabrication.** The devices were prepared on highly doped single-sided polished Si substrates with 300-nm-thick thermally grown SiO2. First, 150 × 150 μm2-sized contact pads were patterned using optical lithography. For the contact pads, we used 10 nm of titanium for adhesion followed by 50 nm of gold. Subsequently, the aligned GNR heterojunction film was transferred with known orientation onto the substrate25. The GNR alignment was checked by polarized Raman measurements (Supplementary Note 4). Electron beam lithography was used to define the source and drain electrodes. For this purpose, the samples were coated with a double layer of poly (methyl methacrylate) (PMMA). The bottom layer (molecular weight 250 kg/mol) is more sensitive than the top layer (molecular weight 950 kg/mol), resulting in an undercut that facilitates lift-off processing. The PMMA-coated substrates were exposed in an electron beam writer, developed, and a 10-nm layer of titanium and 30-nm layer of gold were deposited by thermal evaporation. Subsequently, the metal was removed from the unexposed regions of the sample using a lift-off process.

**UHV transport characterization.** Prior to the UHV transport characterization, the SiO2/Si wafers with GNR heterojunction devices were glued (silver epoxy) onto sapphire plates, which were mounted onto omicron-type sample holders. The sample holders were equipped with five spring-contact pins mounted at one end (see Fig. 5a). The source and drain contact pads on the sample were each connected by 25 μm Au wire with one pin of the source contact. Similarly, the back-gate contact was attached to one pin. Upon insertion into the UHV cryostat sample receptacle, the five pins make contact with BNC-type feedthroughs that connect the device inside the UHV chamber to the electronics outside. For each device, we only used three pins (source, drain, and gate). For the application of VG and the measurement of the gate leakage current, a Keithley 2400 source measure unit (SMU) was used. Another SMU of the same type was used for the application of the gate voltage Vg. The measurement of the LB field-effect mobility was determined as: 

$$\mu_{\text{B}}(W/2, W/2, d) = \frac{g_{\text{B}}(W/2, W/2, d)}{C_{\text{SiO}}},$$

where \(C_{\text{SiO}}\) is the capacitance per unit area of the SiO2 back gate dielectric and \(g_{\text{B}}(W/2, W/2, d)\) is the conductance. 

**Schottky and tunneling barrier heights.** In our FETs, charge carriers are injected from the metal source contact to either quasi-metallic (14-AGNRs, 21-AGNRs, ...) Schottky and tunneling barrier heights. Below we compare the Schottky barrier heights of the 7-AGNR/metal and the 14-AGNR/metal contacts with the tunneling barrier height \(\Phi_{\text{B}}\). The estimation of the Schottky barriers for carrier injection from the contacts to GNRs and the tunneling barrier \(\Phi_{\text{B}}\) requires the information of the transport bandgap and the valence and conduction band offsets (VC and CB, respectively). These band parameters were estimated based on the substrate band offsets of the Coulomb interaction51,52. As a consequence, the bandgap can range from 2.3 to 2.5 eV for 7-AGNRs on Au[111] substrate to ~3.7–3.9 eV for isolated.
The bandgap of 14-AGNRs on Au is ~0.2 eV and for an isolated 14-AGNR it is around 0.7 eV. For 7-AGNRs on SiO2, theory predicts that the bandgap is ~3.3 eV, that is about 85% smaller than a barrier isolated 7-AGNR25. If we scale down the bandgap for isolated 14-AGNRs by 85%, we obtain 0.6 eV, which is valid for 14-AGNRs on SiO2. For estimation of the tunneling barrier $\Phi_b$ on SiO2, we assume electron–hole symmetry with the chemical potential of 7-AGNRs and 14-AGNRs lying symmetrically in the gap. This estimation yields $\Phi_b = 1.35$ eV as a tunneling barrier for both electrons and holes and ignores the effects of charged impurities in the SiO2 that may affect the GNR bandgap and the position of $E_F$.

The position of the Fermi level $E_F$ depends on the gate voltage. Rearranging the above equation yields $\Phi_b = E_F - E_b$. This integration was performed numerically.

The sensitivity $S$ is defined as the change in output per unit of adsorbate. For our experiments, it is appropriate to take $S = \partial I_d/\partial q$, where $q$ is adsorbate density. Due to the nonlinear nature of charge transport in GNR heterojunction arrays, $S$ is not a constant. We take a representative value for the first Li exposure of an $L = 200$ nm graphene array (Fig. 5g). A single Li dose of 0.1 Å corresponds to a 70 V shift in graphene neutrality point (Supplementary Fig. 12), corresponding to a change in carrier density $\Delta n = 3 \times 10^{12}$ cm$^{-2}$ in our experiments, we find a current noise of approximately $\Delta I = 2 \text{nA}$, yielding a resolution of $r = 8 \times 10^{5}$ cm$^{-2}$.

**Data availability**

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Received: 8 September 2020; Accepted: 23 March 2021;
Published online: 05 May 2021

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**Model for tunneling transport**

To calculate the tunneling probability $P(E)$ through a trapezoidal barrier, we used the following expression:

$$P(E) = A \exp \left( -\int_0^E \sqrt{2m} \phi(x, V) - Edx \right)$$

$$= A \exp \left( -4Ed/3eV(\Phi_b - E - E_b)^2 \right) \cdot \left( \Phi_b - E - E_b \right)$$

This equation is valid only for the case when the tunneling occurs between the edges of the barrier, i.e., the tunneling length is equal to the geometrical length of the barrier $d$. This is the case if $\Phi_b > E > E_b$, and $\Phi_b - E > E > E_b$. Depending on the sign of $V_G$, the barrier can either decrease or increase by the amount [eV] along the tunneling path. Since the situation is symmetrical with respect to the direction of the applied voltage, we can consider the following in the case of $V_G > 0$. In the case $\Phi_b > E > E_b$, the barrier has to tunnel under the triangular barrier and the transmission coefficient is described by the Fowler–Nordheim theory36. In Eq. (4), if $d$ indicates the barrier length, $m$ is the charge carrier effective mass inside the barrier, $\phi(x, V) = \Phi_0 + x/a(x)$ ($a(x)$ is the barrier height at coordinate $x$, $V$ is the applied voltage, and $\Phi_0$ denotes the barrier height at $x = 0$). In the case of a triangular barrier, the integration over $x$ in the exponent of Eq. (3) should be performed from zero to the value $x$, determined by the condition $\phi(x, V) = E = 0$. The expression for $P(E)$ then reads:

$$P(E) = A \exp \left( -4Ed/3eV(\Phi_b - E - E_b)^2 \right) \cdot \left( \Phi_b - E - E_b \right)$$

in agreement with the exponent in Eq. (4) of ref. 32. The integral over $E$ in Eq. (1) is to be calculated in the range $E = 0, E < E_b$. This integration was performed numerically.

The position of the Fermi level $E_F$ in Eq. (1) is determined by the carrier concentration in the channel, which in turn is controlled by $V_G$. The carrier concentration $n$ in the channel of the heterojunction is given by $n = n_0 + C_V(V_G)$, where $C_V$ and $n_0$ are the density of states by a constant and the former taken as the reference potential against which both gate potential $V_G$ and drain potential $V_D$ are applied.

**Sub-threshold swing and sensitivity**

The sub-threshold swing $S = \partial V_T/\partial \log(I_D) = \partial V_T/\partial \log(I_D)/\partial \log(I_L)$, where $V_T$ is the gate voltage, $I_D$ is the drain current, and $V_L$ is the surface potential. A back-gated FET structure with channel length comparable to oxide thickness leads to poor gating efficiency: $\partial \log(1)/\partial \log(1) = 1$. We report therefore an analysis of the channel referenced sub-threshold swing $S_{\text{sub}} = e^2/\partial \log(I_D)/\partial \log(I_L)$. For the $L = 200$ nm device at room temperature, charge of $V_T$ by 70 V leads to the modulation of $I_D$ from 33 to 265 nA (Fig. 3d). Such $V_T$ change in turns corresponds to the charge carrier density $\Delta n = 5 \times 10^{12}$ cm$^{-2}$ or 0.033 electrons per 14-AGNR unit cell, resulting in the Fermi level shift by $-27$ meV from the band edge. Therefore, the modulation of $I_D$ by one decade corresponds to a 34-mV shift of the Fermi level, that is $S_{\text{sub}} = 34$ meV/dec.

The sensitivity $S$ is defined as the change in output per unit of adsorbate. For our experiments, it is appropriate to take $S = \partial I_D/\partial q$, where $q$ is adsorbate density. Due to the nonlinear nature of charge transport in GNR heterojunction arrays, $S$ is not a constant. We take a representative value for the first Li exposure of an $L = 200$ nm graphene array (Fig. 5g). A single Li dose of 0.1 Å corresponds to a 70 V shift in graphene neutrality point (Supplementary Fig. 12), corresponding to a change in carrier density $\Delta n = 3 \times 10^{12}$ cm$^{-2}$ in our experiments, we find a current noise of approximately $\Delta I = 2 \text{nA}$, yielding a resolution of $r = 8 \times 10^{5}$ cm$^{-2}$.
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