Tunable angle-dependent electrochemistry at twisted bilayer graphene with moiré flat bands

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Tailoring electron transfer dynamics across solid–liquid interfaces is fundamental to the interconversion of electrical and chemical energy. Stacking atomically thin layers with a small azimuthal misorientation to produce moiré superlattices enables the controlled engineering of electronic band structures and the formation of extremely flat electronic bands. Here, we report a strong twist-angle dependence of heterogeneous charge transfer kinetics at twisted bilayer graphene electrodes with the greatest enhancement observed near the ‘magic angle’ (~1.1°). This effect is driven by the angle-dependent tuning of moiré-derived flat bands that modulate electron transfer processes with the solution-phase redox couple. Combined experimental and computational analysis reveals that the variation in electrochemical activity with moiré angle is controlled by a structural relaxation of the moiré superlattice at twist angles of <2°, and ‘topological defect’ AA stacking regions, where flat bands are localized, produce a large anomalous local electrochemical enhancement that cannot be accounted for by the elevated local density of states alone.

In electrochemical reactions, the flow of charge from electrode to electrolyte drives chemical transformations at the interface, and such interfacial electron transfer reactions underpin key technologies that interconvert electrical and chemical energy. Advances in the development of atomically thin, so-called two-dimensional (2D) materials have provided distinctive avenues for controlling interfacial charge transfer and surface reactivity due to their electronic properties that are exceptionally manipulable by subtle structural modifications and other external electrostatic perturbations. Specifically, defects and edge sites present at 2D surfaces are recognized as reactive hot spots in interfacial charge transfer processes owing to their modified electronic properties. However, the small areal fraction of edge sites constrains the maximized utilization of the whole surface. In addition, it is generally challenging to achieve rational control of atomic defects and an optimized selectivity of the defect-induced enhancement.

Atomic layers that are 2D are also the building blocks for the design of artificial van der Waals (vdW) materials through the deterministic assembly of multiple layers. These vdW heterostructures possess weak interlayer interactions that allow arbitrary azimuthal orientations (‘twist angles’) between the 2D lattices to be independently controlled, introducing a unique degree of freedom for modulating the electronic properties of 2D materials. Apart from hosting low-temperature correlated-electron physics, these topological defects are conceptually analogous to structural atomic defects that generate localized states that can impact interfacial charge transfer chemistry. While a handful of studies interrogating the effects of interlayer twist on chemical reactivity have been reported, these experiments have been restricted to large twist angles well outside the flat band and ‘magic angle’ regime. The possibility of exploiting this concept of moiré flat bands and topological defects to modulate interfacial charge transfer rates has therefore remained unexplored.

Here, we probe the kinetics of a heterogeneous electron transfer reaction at well-defined twisted bilayer graphene (TBG) surfaces and show that the kinetics can be strongly tailored by the interlayer moiré twist angle, $\theta_m$, at small angles (0.22° $\leq \theta_m \leq 5°$). In TBG, the azimuthal misorientation between two homologous layers creates an in-plane quasiperiodic modulation in the crystallographic registry, revealed as a moiré superlattice pattern that displays alternating regions of AA, AB/BA and saddle-point (SP) stacking configurations. The periodicity of the moiré supercells, also known as the moiré wavelength, $\lambda_m$, and the size of the mini-Brillouin zone of the moiré superlattice are both highly dependent on $\theta_m$. Hybridization between adjacent Dirac cones results in an electronic band structure that is strongly modified by the twist angle as shown in Fig. 1c for ‘magic angle’ TBG ($\theta_m = 1.1°$). At this $\theta_m$, the bands around 0 eV become remarkably flat, creating a massively

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enhanced electronic density of states (DOS) concentrated within a narrow energy range of ~20 meV (Fig. 1d). At larger \( \theta_m \), the bands become more dispersive, with increasing bandwidths and higher energies associated with the locations of the van Hove singularities (Extended Data Fig. 1). As we now show, these moiré flat-band-originated DOS enhancements at van Hove singularities play a critical role in governing the heterogeneous electron transfer rate at a graphene–electrolyte interface, making \( \theta_m \) a descriptor of the interfacial reaction kinetics. We also demonstrate that spatially localized moiré flat bands allow the reaction kinetics to be precisely tuned by the topological defect (AA stacking) density, which is modulated as a function of \( \theta_m \).

**Results and discussion**

**Interfacial electrochemistry at magic angle graphene.** We fabricated hexagonal boron nitride (hBN)-supported TBG samples with controlled interlayer twist angles in the range of 0.22–5.1° (Methods for details). Figure 1c shows an optical micrograph of a TBG/hBN sample in contact with a graphite flake as the electrical contact. Figure 1f shows a typical constant-current scanning tunnelling microscopy (STM) image of an exemplary TBG/hBN sample displaying a clear moiré superlattice pattern as observed previously. For ultraclean TBG surfaces such as these, the strong electronic localization of flat bands in real space makes it possible to visualize the AA sites as elevated spots, while AB/BA and SP sites appear lower in STM topography.

For ultraclean TBG surfaces such as these, the strong electronic localization of flat bands in real space makes it possible to visualize the AA sites as elevated spots, while AB/BA and SP sites appear lower in STM topography. The twist angle and uniaxial heterostrain are measured by geometric analysis (Methods) of the local moiré superlattice patterns obtained from STM maps that are collected from multiple arbitrary locations in each sample (Supplementary Figs. 2–4). This random sampling approach is used to ensure reasonably uniform local twists throughout a TBG sample (Supplementary Fig. 5) prior to electrochemical measurements.

Scanning electrochemical cell microscopy (SECCM) with ~100 nm spatial resolution allows us to obtain electrochemical measurements exclusively at the basal plane of TBG (Fig. 1g). A quartz nanopipette (Supplementary Fig. 6) filled with 2 mM hexaaaminemeruthenium(III) chloride and 100 mM aqueous potassium chloride is used to make meniscus contact with the sample surface, creating a confined electrochemical cell in which localized voltammetry is performed at a series of locations. Typical
Quantum capacitance and interfacial charge transfer model. Applying an electric potential ($V_{app}$) across a solid–solution interface results in the formation of an electrical double layer adjacent to the solid surface, which serves to screen the excess charge\(^{17,38}\). At low-dimensional materials like graphene, the charged ions of the double layer also act cumulatively as an effective electrostatic ‘gate’ that shifts the Fermi level, $\epsilon_F$, relative to the band edges of the material via dynamic electron/hole doping. Consequently, a considerable fraction of $V_{app}$ is consumed as a change of the chemical potential ($V_q$), while the remainder is confined in the electric double layer ($V_{dl}$). The contribution from $V_q$ is modelled by introducing an additional capacitance, the so-called quantum capacitance ($C_q$)\(^{19,40}\), in series with the double-layer capacitance ($C_{dl}$) as shown in Fig. 2a.

To evaluate $C_q$ in TBG, we computed electronic band structures for TBG over a range of $\theta_t$ (Methods) and determined theoretical $C_q$ values as a function of $V_q$ in each case. Figure 2b shows that higher values of $C_q$ near the charge neutrality point are observed in TBG for $1^\circ < \theta_t < 2^\circ$, suggesting that a lower fraction of $V_{app}$ would be spent on $C_q$ in TBG around these values of $\theta_t$ due to an enhanced DOS near $\epsilon_F$. Figure 2c shows how $V_q/V_{app}$ evolves as a function of $\theta_t$ is tuned. Higher values of $V_q/V_{app}$ are also observed near charge neutrality for $1^\circ < \theta_t < 2^\circ$, consistent with the angle dependence of $C_q$ in Fig. 2b. These results show how moiré-derived thin bands can promote bulk metal-like behaviour (increased $C_q$ and higher $V_q/V_{app}$) in low-dimensional electrodes.

To consider the impact of partitioning $V_{app}$ into $V_q$ and $V_{dl}$ in the electrochemistry of TBG, we turn to the Gerischer–Marcus\(^{37,38}\) or Marcus–Hush–Chidsey formalism with the consideration of electrode DOS\(^{45,41}\). In this framework, the outer-sphere electron transfer rate constant, $k_{red}$ (for an electroreduction reaction) is the integral of the overlap between the electronic states of the electrode and those of the solution-phase molecule at all energies ($\epsilon$). When we include considerations brought about by a finite $C_q$, $k_{red}$ can be modelled as

$$k_{red} = \nu \int_{-\infty}^{+\infty} \epsilon_{red}(\epsilon) D(\epsilon - eV_{dl}) f(\epsilon - eV_{app}) W_{Ox}(\epsilon) d\epsilon$$  \hspace{1cm} (1)

$$W_{Ox} = \left( 4 \pi \lambda k_B T \right)^{-1/2} e^{-\frac{(-\lambda \theta_t)}{4 \pi k_B T}}$$  \hspace{1cm} (2)

where $\nu$ is the integral prefactor that considers the strength of the electronic interactions between the reactant and electrode, $\epsilon_{red}(\epsilon)$...
is the proportionality function, $D(e)$ is the DOS of the electrode, $e$ is the elementary charge, $f(e)$ is the Fermi–Dirac function, $W_{0}(e)$ is the normalized probability distribution representing the electronic states of the reactant, $\delta$ is the reorganization energy, $k_{B}$ is the Boltzmann constant, $T$ is the temperature and $e^{d}$ is the energy corresponding to the standard potential, $E^{*}$. In Fig. 2d, we consider the result of applying a potential bias $V_{app}$ across the solid–electrolyte interface. In this case, $e_{d}$ is shifted by $eV_{app}$ relative to the band edge, while $eV_{d}$ shifts the entire band relative to the energy of the redox molecule. This means that ultimately, the energetic alignment of electron donor–acceptor states is affected by the relative contributions from $V_{app}$ and $V_{d}$ and $k_{red}$ is governed by $D(e)$ near $e_{d}$. Since $D(e)$ is controlled by $\theta_{m}$, this analysis predicts that $k_{red}$ should display a dependence on $\theta_{m}$.

**Angle-dependent electrochemical kinetics.** Figure 3 and Supplementary Fig. 7 examine the aforementioned expectation of a dependence of $k_{red}$ on $\theta_{m}$. TBG samples with a range of $\theta_{m}$ (representative STM images are shown in Fig. 3a) are used to measure steady-state voltammograms of Ru(NH$_3$)$_6^{2+}$ reduction. Based on the established model for voltammetric SECCM experiments$^{14,43,44}$, we performed finite-element simulations of the characteristic voltammetric responses (Supplementary Section 1) to extract the standard rate constant, $k^{0}$, from the experimental cyclic voltammetry data.

This kinetic parameter $k^{0}$ denotes the intrinsic electron transfer rate defined in the Butler–Volmer (BV) formulation$^{15}$:

$$k_{red}^{BV} = k_{red}^{0}\ e^{-a \int (V_{app} - E^{*})}$$

where $k_{red}^{BV}$ is the rate constant for the reduction reaction derived from the BV model, $a$ is the transfer coefficient (Supplementary Section 1), $R$ is the molar gas constant and $F$ is the Faraday constant. In our analysis, we consider two key effects that arise from the effects of variable $C_{0}(V_{app})$ with $\theta_{m}$ that were discussed in Fig. 2.

We first explicitly account for diffuse double-layer effects involving the migration of charged species in the diffuse layer, which would in turn affect the voltammetric response$^{14,43,44}$ (Supplementary Section 1). Second, we introduce a potential-dependent prefactor $A(V_{app})$ to the BV equations to account for the possibility of changing DOS with $V_{app}$. We determine $A(V_{app})$ by integrating the convolution of $D(e), f(e)$ and $W_{0}(e)$ over all energies to obtain theoretical $k_{red}$ values as a function of $V_{app}$ for each $\theta_{m}$ (Fig. 3c, top). Then we compare these $k_{red}$ values to those derived from the BV model with a constant prefactor, such that $A(V_{app}) = k_{red}/k_{red}^{BV}$ (Fig. 3c, bottom). Figure 3c shows the trend of the $k_{red}$ values that are derived from the Gerischer–Marcus model can be reasonably fit by the BV model with a constant prefactor for small overpotentials ($V_{app} - E^{*} < 0.2$ V). Nevertheless, we still apply this small correction for the potential
dependence of the apparent rate constant in BV equations (also Supplementary Fig. 8).

Figure 3d shows the resultant dependence of $k^c$ on $\theta_m$ extracted from the experimental voltamograms (red markers; also Supplementary Fig. 9e and Supplementary Table 1). As implied by the voltamograms in Fig. 1h, we find the $k^c$ extracted from TBG for $0.8^\circ < \theta_m < 2^\circ$ is strongly enhanced over that of Bernal (AB)-stacked bilayer graphene ($\theta_m=0^\circ$). In comparison to Bernal bilayer graphene, there is minimal enhancement of $k^c$ for $\theta_m > 4^\circ$, and for $\theta_m < 1^\circ$, $k^c$ decreases monotonically with $\theta_m$. We attribute the enhancement of $k^c$ between $\theta_m = 0.8^\circ$ and $\theta_m = 2^\circ$ to the elevated DOS arising from the flattened bands that are energetically matched with the formal potential of Ru(NH$_3$)$_6^{3+}/2+$ (Extended Data Fig. 2c). Our assertion on the criticality of energy matching with the flat bands in dictating the enhanced electron transfer kinetics in TBG was tested by electrochemical measurements with ferrocenemethanol (FeMeOH) and tris(1,10-phenanthroline)cobalt(II), Co(Phen)$_3^{2+}$, which possess formal potentials that are poorly aligned with the charge neutrality point of graphene and, for that matter, the flat bands of small angle ($\theta_m < 2^\circ$) TBG (Extended Data Fig. 2c). For FeMeOH$^{19}$, inherently facile kinetics lead to nearly reversible voltammetric responses of FeMeOH (refs. [4,26]) at all $\theta_m$ values (Supplementary Fig. 10). However, the intrinsically slow kinetics of Co(Phen)$_3^{2+}$ (Extended Data Fig. 11), revealing a considerably weaker dependence of $k^c$ on $\theta_m$ compared with that of Ru(NH$_3$)$_6^{3+}/2+$ (Extended Data Fig. 3). These results are consistent with our expectation for energetically misaligned donor–acceptor electronic states involving the flat bands; the electrochemical kinetics are not substantially dependent on the electronic flat band.

Figure 3d also shows the theoretical dependence of $k^c$ for Ru(NH$_3$)$_6^{3+}/2+$ on $\theta_m$ (blue markers) calculated from the Gerischer–Marcus model (equations (1) and (2)), manifesting a qualitatively consistent trend. The maximum enhancement is predicted between $\theta_m = 1.2^\circ$ and $\theta_m = 1.6^\circ$, where the optimal combination of large DOS and energy match is achieved after incorporating the effects of quantum capacitance. For $\theta_m > 2^\circ$, the positions of van Hove singularities become further apart from $E^0$, the magnitude of DOS gradually decays and $k^c$ diminishes as a result. While qualitatively descriptive of the experimental data, interestingly, these calculations greatly underestimate the enhancement due to flattened bands in the range $0^\circ < \theta_m < 3^\circ$. To explain the anomalous enhancement of $k^c$ at low twist angles as well as the observed monotonic decrease in $k^c$ with decreasing $\theta_m$, for $\theta_m < 1^\circ$, we evaluated the experimental and theoretical real-space variations in $k^c$ throughout the moiré superlattice.

**Spatial variation in electrokinetics at graphene moiré superlattices.** The electronic flat band formed in TBG moiré superlattices is strongly localized in real space. The local DOS (LDOS) versus energy at the three stacking regions (AA, AB/BA and SP) in ‘magic angle’ TBG ($\theta_m = 1.1^\circ$) is shown in Fig. 4a. These calculations show how the prominent enhancement of DOS near charge neutrality is strongly localized at AA sites with much lower DOS found at AB/BA or SP stacking sites, in agreement with previous studies. By contrast, Fig. 4b shows a very weak real-space partitioning of the overall DOS in TBG with $\theta_m = 3^\circ$, where flat bands are largely absent. These localization effects can also be visualized in the real-space LDOS maps shown in Fig. 4c. Importantly, because of DOS localization, the interfacial properties of moiré superlattice electrodes are also strongly modulated in real space. Specifically, Fig. 4c also shows that the potential drop across the double layer ($V_{dl}$) should be nearly uniform in real space over the moiré structure for $\theta_m = 3^\circ$, whereas $V_{dl}$ would be concentrated at AA sites for $\theta_m = 1.1^\circ$ due to higher LDOS and $C_{dl}$. Similarly, these calculations predict an enhancement of the electroreduction rate constant, $k_{red}$, for Ru(NH$_3$)$_6^{3+}/2+$ at AA sites near zero overpotential ($V_{app} = E^0$). As the overpotential increases, $\epsilon_{dl}$ shifts over the flat band due to the charging of $C_{dl}$. The enhancement effects from the flat band are diminished at high overpotentials.
Fig. 5 | Lattice relaxation and anomalous enhancement of electron transfer kinetics at AA regions of TBG. a. Experimental local $k_0$ at AA sites as a function of $\theta_m$ extracted from Fig. 3d compared to the theoretically predicted (GM) values of $k_0$ at AA, AB/BA and SP stacking regions. The horizontal and vertical error bars represent the standard deviations of $\theta_m$ and $k_{0,AA}$, respectively. The inset shows the local $k_0$ at AA sites as a function of $\theta_m$.

b. Schematic illustration of the lattice relaxation process. 

Conclusions

The intriguing interfacial electron transfer behaviour of TBG demonstrated here suggests that in addition to low-temperature correlated electronic phases, moiré-derived flat bands in vdW architectures present a distinctively tunable material platform to systematically manipulate and fundamentally probe interfacial charge transfer and (electro)chemical transformations at well-defined surfaces. In lieu of introducing foreign dopants or structural defects that can be difficult to control, we have demonstrated the feasibility of activating the pristine graphene basal plane surface with topological defects that originate from the structural symmetry breaking in twisted bilayers. We show that by the precise control of the interlayer twist angle, flat bands that are intrinsically localized to nanoscale domains in real space may be exploited to tailor the rate constant for an outer-sphere charge transfer reaction. We anticipate that flat-band engineering with moiré architectures will become a general strategy to tune the chemical reactivity of a variety of 2D surfaces beyond graphene.
Online content
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Methods

Chemicals and materials. Natural Kish graphite flakes were purchased from Graphene Supermarket. SiO2/Si wafers (0.5 mm thick with 285 nm SiO2) and polydimethylsiloxane stamps were purchased from NOVA Electronic Materials and MTI Corporation, respectively. Sn/In alloy was purchased from Custom Thermoelastic. Poly(bisphenol-A carbonate), hexaamminerruthenium(III) chloride (98%), ferrocenemethanol (97%), cobalt(II) chloride hexahydrate (98%), 1,10-phenanthroline (>99%), potassium chloride (>99%) and 4-nitrobenzenediazonium tetrafluoroborate (97%) were purchased from Sigma-Aldrich and used as received. Sulfuric acid (ACS grade, 95–98%) was used as received from Lab Chem (Fisher Scientific). All aqueous electrolyte solutions were prepared with type I water (EMD Millipore, 18.2 MΩ cm resistivity). The 2 mM solutions of tris(1,10-phenanthroline)cobalt(II) and 1,10-phenanthroline in water. In Ru(NH3)63+ and Co(phen)32+ solutions, solid KCl was added as a supporting electrolyte for a concentration of 100 mM.

Sample fabrication. Graphene and boron nitride (hBN) flakes were mechanically exfoliated onto SiO2 (285 nm)/Si substrates from their bulk crystals using the well-established ‘scotch tape’ method. Individual graphene flakes at SiO2/Si chips were located by optical microscopy (Supplementary Fig. 15a,b). The number of layers was identified by the optical contrast and further verified by Raman spectroscopy (HORIBA LabRAM EVO). Supplementary Fig. 15c,d shows optical contrast (green channel) of ~7% and ~14% at the graphene flake region, indicating a graphene monolayer and bilayer, respectively. Raman measurements were performed using a 532 nm excitation and a x100 objective lens for a minimized laser spot. The shape of the 2D band (2,600–2,750 cm−1) was used to determine the number of graphene layers. Supplementary Fig. 1e shows the 2D band presented as a sharp Lorentzian peak with a full-width at half-maximum of ~25 cm−1 (monolayer) and a broad peak (with four components) with a full-width at half-maximum of ~55 cm−1 (bilayer).

TBG samples were prepared using the ‘tear and stack’ technique on a temperature-controlled heating stage (Instec) equipped with an optical microscope (HORIBA LabRAM Evo). Supplementary Fig. 15c,d shows optical contrast (green channel) of ~7% and ~14% at the graphene flake region, indicating a graphene monolayer and bilayer, respectively. Raman measurements were performed using a 532 nm excitation and a x100 objective lens for a minimized laser spot. The shape of the 2D band (2,600–2,750 cm−1) was used to determine the number of graphene layers. Supplementary Fig. 1e shows the 2D band presented as a sharp Lorentzian peak with a full-width at half-maximum of ~25 cm−1 (monolayer) and a broad peak (with four components) with a full-width at half-maximum of ~55 cm−1 (bilayer).

STM and electron microscopy measurements. STM measurements were carried out with a Park NX10 STM module (Park System) operated in ambient conditions (that is, room temperature, 1 atm pressure). Pt–Ir tips used for imaging were fabricated via chemical etching of 0.25 mm Pt–Ir wires in saturated CaCl2 solution. Constant-current images were taken with a 0.1 V tip–sample bias and a 100 pA set point. The transmission electron microscopy images of the nanodiamonds (Supplementary Figs. 6 and 21) were obtained with a JEOL JEM 1200EX transmission electron microscope operated at 100 keV. The ~1 nm portion of the pipette was attached to the grid (PELCO Hole Grids) such that the pipette tip is positioned in the centre hole, and the rest of the pipette was cut off. Selected area electron diffraction patterns were collected on an FEI Tecnai T20 S-TWIN transmission electron microscope with a LaB6 filament operated at 200 kV. Selected area electron diffraction was used to resolve the twist angles for samples with θ ≥ 5°. To obtain the diffraction patterns, the fabricated TBG/hBN samples were transferred onto a holey silicon nitride membrane after chemical treatments.

SECCM measurements. The SECCM probes were single-channel nanopipettes pulled from quartz capillaries (inner diameter, 0.7 mm; outer diameter, 1 mm) using a laser puller (P-2000, Sutter Instrument), yielding orifices with sizes of 50–500 nm. The dimensions and geometries of the probes were determined by transmission electron microscopy, as presented in Supplementary Figs. 6 and 21. The nanodiamonds were filled with the electrolyte solution containing the redox species. Silver wire was coated with colloidal Au and inserted into the tips of the pipettes and used as quasi-counter/reference electrodes. The SECCM experiments were performed using a Park NX10 SCM Module (Park Systems). The nanopipette was positioned over the area of interest aided by an optical microscope, and then it slowly approached the sample (at 100 nm s−1) until a current >2 pA was detected due to the contact between the meniscus and the sample surface. A bias was held at a potential where the reaction takes place in a diffusion-limited rate (~0.5 V versus Ag/AgCl for Ru(NH3)63+ and 0.5 V versus Ag/AgCl for Co(phen)32+) during the approach. The local cyclic voltammograms were subsequently recorded at various locations on the sample surface. In steady-state voltammograms, the half-wave potential, Ep, is defined as the potential at i = i0/2, where i0 is the diffusion-limited current plateau. For diazonium deposition on graphite (Supplementary Fig. 22), which was used to confirm that nanodiamonds were measured by transmission electron microscopy were representative of the meniscus contact area (as demonstrated previously162), deposition was performed using a nanopipette filled with 0.1 mM 4-nitrobenzenediazonium tetrafluoroborate in 50 mM H2SO4 solution and with a constant bias of ~0.2 V versus Ag/AgCl for 20 seconds.

Calculation of DOS. The DOS for TBG was calculated as a function of θ0 using the ab initio perturbation continuum model developed previously116. This model incorporates in-plane and out-of-plane relaxation effects as correction terms to intra-layer Dirac Hamiltonians and interlayer coupling terms, respectively116. The low-energy electronic structure is based on a momentum expansion about the valley K point of the supercell Brillouin zone, allowing a smooth dependence of bands on the twist angle, for 0° ≤ θ0 ≤ 90°116. Figure 2c shows that the perturbation continuum model exactly reproduces results of the more expensive ab initio tight-binding model25, and both are in good agreement with full density functional theory (DFT) calculations115. The energy range for integration for the DOS was fixed at ±0.7 eV around the CNP. For calculation of the LDOS, the normalized moiré supercell was divided into a 90 × 90 grid in real space and sampled over 36 k points in the Brillouin zone. We kept the sublattice symmetry intact and assumed no extra screening of the interlayer coupling constants. The Fermi velocity, however, was increased by 20%, since DFT calculations of graphene without GW screening corrections are known to overestimate the experimental Fermi velocity by roughly 20% (ref. 116). The DOS of θ0 = 0° was obtained from calculations of a single bilayer unit cell with Bernal stacking, employing the same DFT-based tight-binding model as the twisted structures.

Determination of moiré angles and uniaxial heterostrain. The real-space moiré wavelengths, λs, and corresponding moiré twist angles, θ0, were obtained from the STM images by fitting the tunnelling intensities to a linear combination of bivariate Gaussians. The mesh was constructed by performing Delaunay triangulation on the Gaussian centres (Supplementary Fig. 2), enabling us to measure the three sides of each moiré triangle, λ1, λ2, or λ3. The local twist angles and uniaxial heterostrain are measured through their effects on the moiré patterns using a methodology described previously116, as summarized below.

We consider, without loss of generality, the case where one of the two moiré patterns has been twisted by θ0 ≤ 90°. This is the case for uniaxial heterostrain along the direction θ, from the x axis. The reciprocal lattice vectors of the twisted layer are related to the original reciprocal lattice vectors [kx, ky, kz] by a rotation matrix:

\[
k_{	ext{rotated}} = \begin{bmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix} k
\]

Likewise, the reciprocal lattice vectors of the strained layer are related to the original by a strain matrix, which is given below in terms of the percent strain ε and the Poisson ratio of graphene δ (for which we use δ = 0.16), and a series of rotation matrices to account for angle of strain application θ:

\[
k_{\text{rotated}} = \begin{bmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix} k
\]

In the case where one layer has been twisted and the other has been strained so, the moiré reciprocal wavelengths are

\[
\lambda_i = 4\varepsilon / \sqrt{3}\lambda_i
\]

The resultant set of equations are solved numerically using nonlinear least squares to determine θ, ε, and the Poisson ratio of graphene δ (for which we use δ = 0.16), and a series of rotation matrices to account for angle of strain application θ.

The histograms of the extracted local twist angles (θ0, θ1, and θ2) and uniaxial heterostrain (ε) are shown in Supplementary Figs. 3 and 4, respectively, and Supplementary Table 1 tabulates these values for all samples. In a few cases (samples 6, 11 and 12), Delaunay triangulation could not triangulate the moiré superlattice patterns. For samples 6 and 11, manually drawn line profiles were used to determine the periodicity of the AA stacking sites from which θ0 could
be determined (but not \( \epsilon \)). For sample 12, selected area electron diffraction (Supplementary Fig. 18) was used to determine \( \theta_{\text{app}} \).

The effects of \( \theta \) on the band structure are generally less pronounced than the effects of \( \theta_{\text{app}} \) (refs. 12,58). Accordingly, while even small changes in \( \theta \) may introduce notable changes to the correlated electronic phases that emerge at low temperatures, we infer that the effects of small variations in \( \epsilon \) on interfacial charge transfer are undetectable in our experiments for the range of heterostain observed in our samples (\( \epsilon \leq 1.1\% \)). However, it is conceivable that much higher values of heterostain may perturb charge transfer kinetics appreciably11.

Calculation of quantum capacitance. The quantum capacitance describes the variation of the electrical charge with respect to the change of chemical potential, and it has a strong dependence on the electronic structure of the material. \( C_q \) is related to the chemical potential \( (\nu_e) \) of the electron. Theoretical \( C_q \) values as a function of \( \nu_e \) for TBG are calculated using the equations below: \(^{11}\)

\[
C_q = e^2 \int_{-\infty}^{\infty} \frac{D(e) F_V(e - e_{\nu_e})}{1 + \exp\left(\frac{e - \nu_0}{k_BT}\right)} \, de
\]

\[F_V(e) = (4k_BT)^{-1} \text{sech}^2\left(\frac{e}{2k_BT}\right)
\]

where \( D(e) \) is the density of states, we centre at the CNP, and \( F_V(e) \) is the thermal broadening function; \( k_B \) is Boltzmann’s constant, and we take \( T \) to be 300 K.

The compact layer capacitance in aqueous solution is 10–20\( \mu \)F cm\(^{-2}\), independent of the ionic strength. In the diffuse-layer capacitance is \( >100 \mu F \cm^{-2} \) in 0.1 M KCl solution. \(^{38}\) The total electric double-layer capacitance is governed by the effects of the graphene surface is electrochemically gated, a micropipette (20–30 \( \mu \)m in diameter) filled with electrolyte was used to selectively wet the sample surface (Extended Data Fig. 2b). Two similar electrochemical potentials \( (\nu_1 - \nu_2) \) of the electron. The theoretical function of \( \nu_0 \) is the energy level of the formal potential, \( k_B \) is the Boltzmann constant and \( D(e) \) is the DOS. We assume that the DOS is aligned with the molecular energy levels such that \( \epsilon_0 = 0 \), and the alignement is shifted by \( \epsilon_1 \) due to the effects of quantum capacitance. The charge neutrality point of bilayer graphene relative to \( E^0 \) is determined from in situ conductance measurements described in Extended Data Fig. 2.

Finite-element simulations. The finite-element simulations were performed using COMSOL Multiphysics v.5.4 (COMSOL) to model the voltammetric responses. Simulation details and procedures of determining kinetic parameters are provided in Supplementary Section 1.

Data availability

The data supporting the findings of this study are available within the Article and its Supplementary Information files. Source data are provided with this paper. Any additional data are available from the corresponding author.

Code availability

The computer codes used for Delaunay triangulation and quantum capacitance calculations are publicly available at https://github.com/bediakolab/bediakolab_scripts. The computer code used for tight-binding band structure calculations of TBG is publicly available at https://github.com/stcarr/kp_tblg. The computer code used for calculation of theoretical electrochemical rate constants is available in the Github package for calculating Marcus–Hush–Chidsey reaction kinetics incorporating DOS: https://github.com/aced-differentiate/MHC_DOS.

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Author contributions
Y.Y. and D.K.B. conceived the study. Y.Y., K.Z. and A.L. performed the experiments. Y.Y. performed the COMSOL simulations. H.P., M.B., S.C. and V.V. carried out the theoretical calculations. I.M.C. performed the quantum capacitance calculations and STM image analysis. M.V.W. carried out the electron diffraction measurements. T.T. and K.W. provided the hBN crystals. Y.Y., K.Z., I.M.C. and D.K.B. analysed the data. Y.Y. and D.K.B. wrote the manuscript.

Competing interests
The authors declare no competing interests.

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Extended Data Fig. 1 | DOS of twisted bilayer graphene. Calculated DOS of twisted bilayer graphene with various moiré twist angles, \( \theta_m \). \( \theta_m = 0^\circ \) corresponds to Bernal (AB) stacked bilayer graphene.
Extended Data Fig. 2 | In situ conductance measurements of bilayer graphene as a function of the electrochemical bias. a, Optical micrograph of representative device for in situ conductance measurements. b, Schematic of conductance measurement. The micropipettes are filled with 2 mM Ru(NH₃)₆²⁺ in 0.1 M KCl aqueous solution. c, Flake resistance as a function of the electrochemical bias obtained from 3 different AB-stacked bilayer graphene samples, showing the position of the charge neutrality point (maximum resistance) relative to the $E^0$ values of the three redox couples interrogated in this study.
Extended Data Fig. 3 | Moiré angle dependent electron transfer rate of Ru(NH$_3$)$_6^{3+/2+}$ and Co(Phen)$_3^{3+/2+}$. a, $k^\circ$ extracted from the experimental voltammograms as a function of twist angle for the Co(Phen)$_3^{3+/2+}$ (blue squares) and Ru(NH$_3$)$_6^{3+/2+}$ (red circles) redox couples. b, $k^\circ$ for Co(Phen)$_3^{3+/2+}$ extracted from the experimental voltammograms (blue filled circles) as a function of twist angle compared to the values calculated with GM framework (black open circles). The horizontal and vertical error bars represent the standard deviations of $\theta_m$ and $k^\circ$, respectively.