Electron Tunneling through Boron Nitride Confirms Marcus–Hush Theory Predictions for Ultramicroelectrodes

Matej Velicky,*†§ Sheng Hu,* Colin R. Woods,‡ Piter S. Toth,* Viktor Zolyomi,* Andre K. Geim,* Héctor D. Abreuña,§ Kostya S. Novoselov,*# and Robert A. W. Dryfe*†

1Department of Chemistry and 2Department of Physics and Astronomy, University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom
3Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, United States
4MTA Premium Post Doctorate Research Program, Department of Physical Chemistry and Materials Science, University of Szeged, Rerrich Square 1, Szeged H-6720, Hungary
5Centre for Advanced 2D Materials, National University of Singapore, 117546, Singapore
#Chongqing 2D Materials Institute, Liangjiang New Area, Chongqing, 400714, China

Supporting Information

Abstract: Marcus–Hush theory of electron transfer is one of the pillars of modern electrochemistry with a large body of supporting experimental evidence presented to date. However, some predictions, such as the electrochemical behavior at disk ultramicroelectrodes, remain unverified. Herein, we present a study of electron tunneling across a hexagonal boron nitride acting as a barrier between a graphite electrode and redox mediators in a liquid solution. This was achieved by the fabrication of disk ultramicroelectrodes with a typical diameter of 5 μm. Analysis of voltammetric measurements, using two common outer-sphere redox mediators, yielded several electrochemical parameters, including the electron transfer rate constant, limiting current, and transfer coefficient. They depart significantly from the Butler–Volmer kinetics and instead show behavior previously predicted by the Marcus–Hush theory of electron transfer. In addition, our system provides a noteworthy experimental platform, which could be applied to address a number of scientific problems such as identification of reaction mechanisms, surface modification, or long-range electron transfer.

Keywords: hBN, electron tunneling, electron transfer, Marcus–Hush theory, microelectrodes

Marcus–Hush theory has long been recognized as the most successful attempt at developing a comprehensive model of electron transfer kinetics. It describes the electron transfer between reactants and products as a temperature-activated process governed by nuclear vibrations, energy reorganization, and electronic coupling. Several experimental confirmations of this theory have emerged since its inception in the 1950s, notably the observation of the so-called inverted region for intramolecular electron transfer and flattening of the exponential dependence of the rate constant on potential for electrode reactions. However, some intriguing predictions from the Marcus–Hush theory exist, which have not yet been verified experimentally. This includes the theoretical work put forth by Feldberg, who revealed peculiar implications of the Marcus–Hush theory for the steady-state voltammograms at inlaid microdisk electrodes. Specifically, he predicted a decreasing limiting current at conditions for which the electron transfer became the rate-limiting step, leading to significant deviations from the commonly employed Butler–Volmer model of electrochemical kinetics.

In this work, we achieve such reduction in electron transfer rate by placing layers of hexagonal boron nitride (hBN) of well-defined thickness on a graphite electrode. hBN consists of two-dimensional (2D) layers, in which boron and nitrogen atoms are covalently bound in an alternating hexagonal pattern, similar to graphene. These layers are held together by van der Waals (vdW) forces in bulk hBN. The lattice mismatch between hBN and graphene is only 1.5%, their bulk interlayer spacing is nearly identical (3.3–3.4 Å), and...

Received: October 22, 2019
Accepted: December 9, 2019
Published: December 9, 2019
its polar nature renders hBN insulating, with a wide band gap of ~6 eV.5,10 These characteristics lead to an increased carrier mobility in graphene, supported or encapsulated by hBN, owing to the atomic flatness, lack of dangling bonds, and suppression of charge doping at the graphene/hBN interface.11–13 It transpires from the present work that hBN is a suitable medium to study long-range electron tunneling, which leads to the manifestation of the Marcus–Hush behavior.

The quantum tunneling effect is a direct consequence of the Heisenberg uncertainty principle and is most pronounced for light particles, such as electrons, whose de Broglie wavelength is comparable to the tunneling distance.14 Initially discovered for trapped electrons,15 long-range electron tunneling gradually defined many diverse research fields including scanning tunneling microscopy, molecular electronics, and DNA sequencing.16,17 A significant body of the electrochemical tunneling studies have involved the following two approaches of modifying conducting electrodes: self-assembled monolayers of redox species tethered to an insulating alkyl chain or insulating films blocking a redox mediator in solution.18 The most successful efforts of the latter approach, a strategy chosen in the current work, include electrochemical tunneling through a thermally grown SiO2 layer on PtSi19,20 and an ω-hydroxy thiol layer on Au21,22 both of which have been applied to determine the density of electronic states (DOS) of various redox mediators.

hBN provides an inorganic alternative with a precise control of the tunneling distance, especially within the subnanometer regime, unattainable even for the state-of-the-art tunneling layers of Al2O3 grown by atomic layer deposition at thicknesses of ~1 nm.23 Additionally, the high crystallinity of hBN and narrow barrier width ensure scattering-free ballistic electron tunneling and therefore no ohmic heating within the dielectric.24 It is therefore not surprising that hBN has been utilized as a tunneling barrier in solid-state devices. This includes hBN being sandwiched between two metals, two graphene/graphite layers, and a metal and graphene.24–28 Most of these studies found that the tunneling current increased exponentially with the applied voltage and decayed exponentially with the hBN thickness to negligible levels for ~6-layer hBN. Both experiments and theory suggest that hBN is not simply a passive insulating barrier but rather that it affects the tunneling through carrier interactions with phonons, defects, and dopants.27–29

Herein, we employ atomically flat hBN as a tunneling barrier to an electrochemical reaction between a redox mediator in a liquid solution and a graphite electrode (Figure 1). We make use of the electron-beam (e-beam) lithography and poly-(methyl methacrylate) (PMMA) mask to fabricate inlaid disk ultramicroelectrodes (Supporting Figure S1) and employ a modified microdroplet electrochemical cell technique described elsewhere.30 The use of a high-quality, crystalline 2D insulator has some advantages over the two traditional tunneling approaches described above, owing to the chemical inertness of hBN, the lack of dangling bonds on its basal plane surface, and a microscopic size of the tunneling area. These characteristics lead to an atomically flat electrode surface, well-defined control of the tunneling distance via the number of hBN layers (N), and significant reduction in the occurrence of pinholes and defects. Additionally, hBN provides a “simple” inorganic tunneling barrier, contrasting with complex organic barriers, which possess discrete molecular energy levels and specific chemical interactions leading to multiple possible configurations. Both redox mediators used here, [IrCl6]3− and [Ru(NH3)6]3+ oxidation and [Ru(NH3)6]3− reduction in this system exhibit the expected exponential dependence of the tunneling current (and therefore electron transfer rate) on the tunneling distance for monolayer (1L) and bilayer (2L) hBN. However, significant deviations in the measured electrochemical parameters are observed for thicker hBN, which we interpret as a previously predicted, but not yet verified manifestation of the Marcus–Hush theory.3 We further rationalize these results based on the density functional theory (DFT) calculations of the energy levels in the graphite/hBN/liquid heterostructure.

**RESULTS AND DISCUSSION**

**Anatomy of the Tunneling Device.** The electron tunneling from (to) the redox mediator in the liquid phase, through hBN of varied thickness, to (from) the graphite electrode was realized using devices depicted in Figure 1a,b. The basal planes of both graphite and hBN have planar sp2 hybridization, are chemically inert, and lack dangling bonds. Crucially, their surfaces, which face each other in the resulting heterostructure shown in the optical image of Figure 1c,d, are chemically inert, lack of dangling bonds, and that the tunneling distance is controlled by the number of hBN layers. In reality, we do observe some contaminants trapped between the hBN and graphite, which favorably agglomerate in micro/nanosopic pockets visible in atomic force microscopy (AFM) (Figure 1f).
due to the self-cleaning process occurring at the vdW interfaces.\(^{15}\) Importantly, the average height of these pockets is at least 5 nm, leading to a negligible overlap between the electrode surface and the graphite.\(^{17}\) which therefore results in a mere reduction of the apparent tunneling area. The outer-sphere nature of the two redox mediators also ensures that the tunneling process only depends on the DOS and is not sensitive to the chemical groups present at the electrode surface.

**Voltammetry of the Electron Tunneling through hBN.** The electron tunneling through hBN in the graphite/hBN/liquid heterostructure was measured using a micro-droplet electrochemical cell shown in Figure 1a and e. The results of the voltammetric (i.e., current–voltage) measurements are summarized in Figure 2. The tunneling process is driven by the difference between the energy (formal potential) of the [IrCl\(_6\)]\(^{3−}\)/[IrCl\(_6\)]\(^{2+}\) oxidation and [Ru(NH\(_3\))\(_6\)]\(^{3+}/2+\) reduction levels (\(E_{\text{0,ff}}\)) or \(E_{\text{F}}\) in the liquid and the Fermi level (\(E_F\)) of graphite, to which positive or negative potentials are applied (\(E\)), respectively. As a result, [IrCl\(_6\)]\(^{3−}\)/[IrCl\(_6\)]\(^{2+}\) are oxidized or reduced to [IrCl\(_6\)]\(^{2−}\) or [Ru(NH\(_3\))\(_6\)]\(^{3+}\) and positive or negative currents are recorded, respectively. Voltammograms on the bare graphite, labeled as 0L in Figure 2, were also recorded as a control.

The voltammograms of [IrCl\(_6\)]\(^{3−}\) oxidation in Figure 2a exhibit the steady-state sigmoidal shape expected for disk ultramicroelectrodes, for both the bare graphite (black curve) and hBN layers (green curves). Rather than maintaining the limiting value of the potential-independent plateau, however, the current density (\(j\)) rises further at large positive potentials, owing to the graphite oxidation side-reaction delimiting the potential window. Importantly, all hBN voltammograms maintain a similar shape to that of the bare graphite, but are offset to increasingly more positive potentials upon increasing \(N\). The red curves, fitted to the voltammograms using an empirical function based on the Butler-Volmer formalism, as described in Methods, allowed us to extract the standard heterogeneous electron transfer rate constant (\(k_b\)), limiting current density (\(j_{\text{lim}}\)), and transfer coefficient (\(a\)). The \(k_b\) of [IrCl\(_6\)]\(^{3−}\) oxidation on bare graphite averaged over all the devices (\(k_b\)) was \((1.4 \pm 0.2) \times 10^{-3} \text{ cm s}^{-1}\), about 1 order of magnitude lower than reported previously,\(^{34}\) not entirely unexpected considering the exposure of the topmost surface to PMMA during device fabrication.

Interestingly, the partial oxidation of graphite, observed at large positive potentials in voltammograms of Figure 2a, left the consecutive [IrCl\(_6\)]\(^{3−}\) voltammograms unaffected, but had notable implications for the subsequent [Ru(NH\(_3\))\(_6\)]\(^{3+}\) voltammetry. The [Ru(NH\(_3\))\(_6\)]\(^{3+}\) reduction voltammograms shown in Figure 2b are qualitatively similar to those of [IrCl\(_6\)]\(^{3−}\) in that they exhibit the sigmoidal steady-state behavior and the hBN curves occur at increasingly more negative potentials as the hBN thickness increases. However, the \(k_b\) values are much higher than expected. Specifically, the \(k_b\) of [Ru(NH\(_3\))\(_6\)]\(^{3+}\) reduction was \((9.5 \pm 2.0) \times 10^{-2} \text{ cm s}^{-1}\), which is 3–4 orders of magnitude higher than reported previously\(^{15}\) and close to value observed for laser-activated graphite.\(^{16}\) This indicates that mild oxidation introduces sp\(^3\) disorder in the graphitic lattice and leads to an increase in the DOS near the Fermi level (\(E_F\)), which lies within 0.05 eV of \(E_{\text{F}}\).\(^{36}\) We recognize that these effects render our analysis semiquantitative, and as such, our main aim is to expose qualitative trends, rather than to obtain absolute values of electrochemical quantities. The evolution of the voltammetric background with \(N\) in the pure supporting electrolyte is detailed in Supporting Figure S2.

**Dependence of the Electron Transfer Rate on Tunneling Distance.** Figure 3a shows that the measured rate constants (\(k_{\text{ET,hBN}}\)) of [IrCl\(_6\)]\(^{3−}\) and [Ru(NH\(_3\))\(_6\)]\(^{3+}\), albeit different in absolute value, both decay with the hBN thickness. This is in qualitative agreement with both experiments and predictions for coherent quantum tunneling.\(^{16,21,37}\) The exponential dependence of the electron transfer rate constant between an electrode and redox species (\(k_{\text{ET}}\)) on the tunneling distance between the two (\(x\)) is described as\(^{18}\)

\[
k_{\text{ET}}(x) = k_{\text{ET}}(0)e^{-\beta x}
\]

(1)

where \(k_{\text{ET}}(0)\) and \(k_{\text{ET}}(x)\) are the \(k_{\text{ET}}\) values at the electrode surface (\(x = 0\)) and at the distance \(x\) from it, respectively, and \(\beta\) is the tunneling decay coefficient. Tunneling studies using redox centers tethered to organic molecules (with typical lengths of 5–50 Å) on metals revealed a \(\beta\) of 1.0–1.2 Å\(^{-1}\) for alkanethiol chains,\(^{37,38}\) 0.4–0.6 Å\(^{-1}\) for π-conjugated chains,\(^{39,40}\) and 0.2–0.3 Å\(^{-1}\) for aromatic chains.\(^{41–43}\) Tunneling through vacuum between two metals typically yields a \(\beta\) of 2.0–2.5 Å\(^{-1}\.\(^{18}\)

Consequently, one could be tempted to perform a linear fit of the data in Figure 3a by adopting eq 1 for \(k_{\text{ET,hBN}}\). Doing so
would yield a $\beta$ of 0.4—0.5 Å$^{-1}$, which is somewhat smaller than expected for a wide-band-gap insulator such as hBN. In fact, it is evident from Figure 3a that the distance dependence of $\ln(k_{\text{ET}}^{\text{hBN}})$ is not linear and decays more slowly as $x$ increases, as seen for ≥3L hBN. When only 1L and 2L hBN are considered for the linear fit, reasonable $\beta$ values of 1.2 and 1.1 Å$^{-1}$ for $[\text{IrCl}_6]^{3-}$ and $[\text{Ru(NH}_3)_6]^{3+}$ are obtained. The deviation from eq 1 at large $x$ becomes very apparent when the data are normalized to $k_{\text{ET}}^{\text{hBN}}$, as shown in Figures 3b and c. When 0L, 1L, and 2L data are used for the fitting, $\beta$ values of 1.1 and 1.0 Å$^{-1}$ for $[\text{IrCl}_6]^{3-}$ and $[\text{Ru(NH}_3)_6]^{3+}$ are obtained and the linear fits pass within ±0.2 Å from the origin, as they ought to, since for $x = 0$ $\ln(k_{\text{ET}}^{\text{hBN}}) = \ln(1) = 0$. This data normalization also has the noteworthy advantage of canceling out the effects of solvent, electrolyte, and impurity adsorption at the electrode surface.

Let us now review the quantitative aspects of electron transfer formalized by the Marcus—Hush theory. The following formalism for $k_{\text{ET}}$ is usually invoked, describing the electron transfer as a temperature-activated process:44–46

$$k_{\text{ET}} = \nu_n \kappa_n \kappa_0$$

where $\nu_n$ is the effective nuclear vibration frequency, $\kappa_n$ is the electronic transmission coefficient, and $\kappa_0$ is the nuclear reorganization factor, typically expressed in terms of the standard free energy of activation ($\Delta G^\ddagger$):18

$$\kappa_n = e^{-\Delta G^\ddagger/k_0T}$$

where $k_0$ is the Boltzmann constant and $T$ is the temperature. Of all the above quantities, $\kappa_0$ is the only source of the exponential decay with distance:

$$\kappa_0(x) = \kappa_0(0)e^{-\beta x}$$

where $\kappa_0(0)$ and $\kappa_0(x)$ are the $\kappa_0$ values at the electrode surface ($x = 0$) and at a distance $x$ from it, respectively. In the adiabatic regime of strong electronic coupling, $\kappa_0(x) \rightarrow 1$, which manifests itself by the independence of the rate constant on distance.18 At larger distances, the electronic coupling weakens, $\kappa_0(x) < 1$, and even an initially adiabatic reaction becomes nonadiabatic and independent of the nuclear dynamics since $\kappa_0(x)$ is reduced to $\kappa(x)$ in agreement with reported values
for the basal plane graphite, while the \( \rho^0 \) of \( 5.4 \times 10^{-4} \) atom\(^{-1} \) eV\(^{-1} \) for \([\text{IrCl}_6]^{3-}\) is closer to the edge plane graphite, consistent with the above discussion.\(^{36}\)

**Manifestation of the Marcus–Hush Theory of Electron Transfer.** We observe further anomalies in the other two electrochemical parameters determined from the voltammetric fitting, namely, the transfer coefficient and limiting current density, which are plotted in Figure 4 as a function of the tunneling distance. Figure 4a and b show that bare graphite yields an average \( (1 - \alpha) \) of 0.36 for \([\text{IrCl}_6]^{3-}\) and average \( \alpha \) of 0.58 for \([\text{Ru(NH}_3)_6]^{3+}\), both of which are reasonable values, indicating a high symmetry of the reduction/oxidation reactions.\(^{18}\) However, a progressive decrease of an initially constant \( (1 - \alpha) \) of 0.51 is observed for \([\text{IrCl}_6]^{3-}\) oxidation for >3L hBN. \([\text{Ru(NH}_3)_6]^{3+}\) reduction on hBN does not exhibit as clear a decrease in \( \alpha \) with the tunneling distance but yields unusually small values of \( \alpha \) between 0.13 and 0.27. Another striking observation shown in Figure 4c and d is that the \( j_{\text{lim}} \) on hBN (\( j_{\text{lim}}^{\text{hBN}} \)) as a function of the tunneling distance for \([\text{IrCl}_6]^{3-}\) and \([\text{Ru(NH}_3)_6]^{3+}\), respectively, normalized to \( j_{\text{lim}}^{\text{gra}} \) does not reach the expected unity maximum at large potentials.

![Figure 4](image-url)

**Figure 4. Dependence of the transfer coefficient and limiting current density on tunneling distance.** (a, b) \( (1 - \alpha) \) and \( \alpha \) as a function of the tunneling distance for \([\text{IrCl}_6]^{3-}\) and \([\text{Ru(NH}_3)_6]^{3+}\), respectively. Green marks correspond to hBN; black marks to bare graphite. (c, d) Limiting current density on hBN (\( j_{\text{lim}}^{\text{hBN}} \)) as a function of the tunneling distance for \([\text{IrCl}_6]^{3-}\) and \([\text{Ru(NH}_3)_6]^{3+}\), respectively, normalized to \( j_{\text{lim}}^{\text{gra}} \).

Instead of following the Marcus–Hush theory,\(^{5} \) Crucially, the Butler–Volmer model continues to produce a good voltammetric fit, but \( k^0 \) and \( \alpha \) (or \( 1 - \alpha \)) become worse fitting parameters. Consequently, their apparent values increase and decrease, respectively, and the physical value of \( j_{\text{lim}}^{\text{hBN}} \) decreases as Marcus–Hush behavior dominates, much in agreement with our observations. The qualitative conditions necessary to observe these anomalies were identified as large overpotentials, small \( k^0 \), small electrode size, and small \( \lambda \) (i.e., a “fast” redox system). Feldberg argued that such conditions would be difficult to achieve simultaneously in an experiment;\(^{5} \) however, our system favorably meets all of these conditions. For \( \lambda = 1.0 \) eV, the two kinetics models are only distinguishable when \( E - E^0 \geq 0.5 \) V (easily accessible in our system), and 99% of the Marcus–Hush potential-independent \( k^0 \) plateau is reached when \( E - E^0 \geq 1.5 \) V.\(^{5} \) Furthermore, the following distinguishability condition must be met:

\[
\frac{k^0 r}{D} \leq 10^{(1-\lambda/10k_BT)} \tag{9}
\]

where \( r \) is the electrode radius and \( D \) is the diffusion coefficient of the redox mediator. One way to approach this condition is to decrease \( r \) to units of nanometers, a feat demonstrated more than a decade ago;\(^{51} \) however, this leads to complications as \( r \) becomes comparable to the electrical double-layer thickness found at typical aqueous electrolyte concentrations. Basal plane graphite has long been identified as having small \( k^0 \) for outer-sphere redox mediators due to its low DOS, but little effort has been expended toward employing it as an ultramicroelectrode. More crucially, very few systems have values of \( k^0 \) and \( \lambda \) low enough to meet the conditions imposed by eq 9, since \( k^0 \) increases with decreasing \( \lambda \), according to eq 8. Our system is noteworthy, since \( \lambda \) is kept constant, whereas the apparent \( k^0 \) decreases progressively with the tunneling distance due to the weakened electronic coupling. Consequently, the combination of the basal plane graphite ultramicroelectrodes with \( r = 2.5 \) \( \mu \)m and tunneling through hBN, which pushes the apparent \( k^0 \) to below \( 10^{-7} - 10^{-5} \) cm s\(^{-1} \), allows the conditions imposed by eq 9 to be met, subject to the value of \( \lambda \). In fact, we can obtain a rough estimate of \( \lambda \) based on the observed deviation from the expected exponential decay between 2–3L hBN layers (Figure 3). Evaluating \( k^0, r, D \) and \( E \) values against eq 9 thus leads to \( \lambda \approx 1.3 \) eV for \([\text{IrCl}_6]^{3-}\) and \( \lambda \approx 0.7 \) eV for \([\text{Ru(NH}_3)_6]^{3+}\), both in agreement with experimentally determined values of \( \sim 1.2 \) eV\(^{52} \) and \( \sim 0.6 \) eV,\(^{22} \) respectively, though in disagreement with some theoretical predictions.\(^{5} \) This also explains why deviations in \( \alpha \) and \( j_{\text{lim}} \) are only seen at the largest distances for \([\text{IrCl}_6]^{3-}\), while anomalous behavior is observed for \([\text{Ru(NH}_3)_6]^{3+}\) across the entire range of distances. We stress that the above evaluation is very approximate and does not fully explain all the aspects of the observed deviations. However, we believe the above data provide a robust qualitative evidence for the yet unverified Feldberg’s predictions and importantly afford another experimental confirmation of one of the most important treatments of electron transfer: the Marcus–Hush theory.

**Properties of the hBN Tunneling Barrier.** It is instructive to consider the properties of the tunneling barrier and its dependence on the hBN thickness and applied potential. The band diagram in Figure 5a schematically depicts the various energy levels in the graphite/1L hBN/liquid heterostructure and their mutual alignment for the unbiased case prior to contact between the three phases. In reality, the
The internal structure of the tunneling barrier is likely to be more complex, due to the high anisotropy of hBN. Figure 5b shows the tunneling process for the \([\text{IrCl}_6]^{3-}\) oxidation, with a large positive potential applied to the graphite, allowing the electrons to tunnel from the occupied states of \([\text{IrCl}_6]^{3-}\) to the empty states in graphite. Similarly, Figure 5c shows the electron tunneling from the occupied states in graphite to the empty states of \([\text{Ru(NH}_3)_6]^{3+}\), facilitated by the large negative potential applied to the graphite. An important implication of the analysis in Figures 5a–c is that both processes are dominated by the electron/hole tunneling near the valence band maximum (VBM), rather than the conduction band minimum (CBM), of hBN, since this path has a significantly lower tunneling barrier. Furthermore, the barrier for tunneling to/from \([\text{IrCl}_6]^{3-}\) is smaller than that for \([\text{Ru(NH}_3)_6]^{3+}\) thanks to the relative position of the redox levels and VBM of hBN.

The dependence of the electronic band structure, shown in Figure 5d for 1L, on the number of hBN layers is also an important consideration, given the nature of the present study. While little experimental information has so far been offered on this matter, our DFT calculations reveal a strong dependence of the band gap energy on the number of hBN layers, changing from 6.1 eV for 1L to 5.6 eV for 6L, as shown in Figure 5e. However, this ~0.5 eV difference originates from the decrease in the CBM, with the VBM remaining nearly constant. As discussed above, the tunneling occurs via the VBM (rather than the CBM) route for both mediators, and therefore we do not expect the hBN band gap dependence to affect the tunneling processes here.

We also evaluated the distribution of the applied potential across the graphite/hBN/liquid heterostructure. Figure 6a shows the difference between the hBN and graphite half-wave potentials \(E_{1/2}^{\text{hBN}}\) and \(E_{1/2}^{\text{graphite}}\) as a function of the tunneling distance for both mediators. Figure 6b shows the fraction of the applied potential spent within the hBN tunneling barrier for both mediators. Both absolute values (green markers) and values normalized to the hBN thickness (empty markers) are shown.
Briefly, graphene was exfoliated to ca. 10–30 nm thickness onto a 300 nm SiO$_2$/Si substrate. hBN was exfoliated onto a PMMA substrate and then placed on the graphite using the stamp-transfer method.$^{52}$ The resulting hBN/graphene heterostructure was spin-coated with an insulating PMMA layer (130 nm thick), in which two identical circular working electrode openings (typically 5 μm in diameter) over the basal planes of bare graphite and hBN were created using e-beam lithography (Figure 1a,b). Electrical contact was made by scratch-exposing the graphite away from the openings and bonding it to a Cu wire using Ag paint. A Nikon Eclipse LV100ND optical microscope and a DS-Fi2 U3 CCD camera (Nikon Metrology, UK Ltd.) were employed to acquire the optical images (Figure 1c,d). The electrochemical cell was formed by dispensing a microdroplet of a liquid solution (typically 60–100 μm in diameter) around the opening (Figure 1e). The number of hBN layers was determined by a Bruker Dimension 3100 V AFM in tapping mode (Figure 1f). Raman spectra were collected using an inVia spectrometer (Renishaw) with a 532 nm laser excitation, and XPS was measured using a Thermo Scientific Al K-Alpha Theta Probe.

**Electrochemical Measurements.** All electrochemical measurements were performed in 6 M LiCl supporting electrolyte aqueous solution, which minimized the evaporation of the liquid. Dispensation and manipulation of the microdroplets on the surface were controlled using a pneumatic microinjector and a micromanipulator reported previously.$^{50,53}$ The potential was applied to the graphite electrode using a PGSTAT302N potentiostat (Metrohm Autolab), and a scan rate of 100 mV s$^{-1}$ was used in order to achieve a steady-state ultramicroelectrode response without the thin-layer cell diffusion effects (Supporting Figure S5). The $k^*$, $h_{lim}$ and $α$ (or $1 - α$) were determined by fitting the voltammograms with the following empirical function based on a Butler–Volmer model of the electrochemical kinetics:

$$\frac{j}{J_{lim}} = \left( 1 + \frac{\theta}{kθ} \frac{2xθ + 3α}{4xθ + 3α} \right)^{-1}$$

(11)

where $θ$ and $κ$ are defined as follows (for the reduction and oxidation, respectively):

$$\theta = 1 + \frac{D_a e^{-\frac{E}{RT}(E-E^0)}}{D_b} \quad \text{and} \quad \theta = 1 + \frac{D_a e^{-\frac{E}{RT}(E-E^0)}}{D_b}$$

(12)

$$κ = \frac{2xθ}{4D_a} e^{-\frac{E}{RT}(E-E^0)} \quad \text{and} \quad κ = \frac{2xθ}{4D_a} e^{-\frac{E}{RT}(E-E^0)}$$

(13)

where $D_a$ and $D_b$ are the diffusion coefficients of the oxidized and reduced form of the mediator, respectively, $F$ is the Faraday constant, $R$ is the universal gas constant, and all other symbols have the same meaning as defined previously. Equations 11–13, which had been introduced by Oldham and Zoski,$^{54}$ were used by Feldberg to model the Butler–Volmer behavior at disk ultramicroelectrodes. The $D_a$ ($D_b$) values of 2.5 (2.2) × 10$^{-8}$ cm$^2$ s$^{-1}$ for [Ru(NH$_3$)$_6$]$^{3+/2+}$ and 2.4 (2.1) × 10$^{-8}$ cm$^2$ s$^{-1}$ for [IrCl$_6$]$^{3+/2+}$ were determined as averages from cyclic voltammetric and chronoamperometric measurements at a Pt disk electrode (1.1 mm radius), using the Randles–Ševčík and Cottrell equations, respectively.$^{16}$ The $E^0$’s of [Ru(NH$_3$)$_6$]$^{3+/2+}$ and [IrCl$_6$]$^{3+/2+}$ reduction/oxidation were determined from cyclic voltammetry using the same electrode. The potential, measured against a Ag/AgCl reference electrode, was converted to the standard hydrogen electrode (SHE) scale. A large-area Pt counter electrode was used to complete the three-electrode configuration. All measurements were carried out at ambient temperature (20–25 °C).

**DFT Calculations.** Theoretical calculations were performed using the VASP code$^{29}$ in a plane-wave basis. Bulk graphite was approximated with a 6L-thick slab. We used a plane-wave cutoff energy of 600 eV throughout and left at least 20 Å of vacuum space above the 2D sheets in order to model isolated materials. The k-point grid was set to a Γ-centered 12 × 12 × 1 Monkhorst–Pack grid. The local density approximation was used to compute the band structures, ionization energies, and hBN band gaps. A correction to the latter

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**METHODS**

**Device Fabrication and Characterization.** The tunneling devices were prepared by mechanical exfoliation of graphite (NGS Naturgraphit) and hBN (hq graphene), dry stamp-transfer, and e-beam lithography (Zeiss EVO), as described in Supporting Figure S1.

CONCLUSIONS

We studied electron tunneling across an atomically flat hBN barrier sandwiched between a graphite electrode and two outer-sphere redox mediators in a liquid solution. The steady-state voltammetry of [IrCl$_6$]$^{3+/2+}$ oxidation and [Ru(NH$_3$)$_6$]$^{3+/2+}$ reduction obtained on disk ultramicroelectrodes with typical diameters of 5 μm revealed an exponential dependence of the apparent electron transfer rates on the hBN thickness for 1L and 2L hBN. For thicker hBN, deviations in $j_l$ and $α$ were observed, indicating limitations of the Butler–Volmer model of electrochemical kinetics. This behavior is qualitatively consistent with thus far unverified predictions from Marcus–Hush theory for disk ultramicroelectrodes and, as such, provides further confirmatory evidence for one of the most fundamental treatments of electron transfer. Furthermore, the experimental platform developed here could be exploited in a range of diverse scenarios, including studies of long-range electron transfer, electrochemical switching between outer- and inner-sphere reactions, and investigation of electrocatalytic mechanisms. It could be possible to discriminate between outer-sphere and inner-sphere reactions as recently shown for 1L MoS$_2$ on Au,$^{57}$ explore electrocatalytic reactions on hBN/metal heterostructures,$^{8,55}$ and study proton tunneling/transport through 1L hBN.$^{60}$ Such developments are even more likely to succeed, once a reliable control over the thickness and quality of synthetically grown, large-area hBN is established.$^{61}$
quantities was necessary as both of them are underestimated in semilocal DFT. The scissor correction to the band gap and correction to the ionization energy were obtained by recalculating these quantities in the few-layer (≤3L) limit of hBN using the HSE06 functional. We found no dependence of either correction on N and therefore assume that it can be applied to all hBN thicknesses.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nano.9b08308.

Tunneling device fabrication; voltammetry in pure supporting electrolyte; Raman spectroscopy and XPS of hBN and graphite; dielectric breakdown estimation; [IrCl6]3−/2− voltammetry on graphite at varied scan rates (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: matej.velicky@manchester.ac.uk.
*E-mail: robert.dryfe@manchester.ac.uk.

ORCID

Matěj Velický: 0000-0003-4230-3811
Héctor D. Abriuña: 0000-0002-3948-356X
Robert A. W. Dryfe: 0000-0002-9335-4451

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This project has received funding from the UK EPSRC (grant no. EP/K016954/1) and the European Union’s Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement no. 746685. V.Z. thanks the Graphene Flagship Project and the Computational Shared Facility at the University of Manchester for support. P.S.T. thanks the Hungarian Academy of Sciences for an MTA Premium Post Curie grant agreement no. EP/K016954/1) and the European Union. This project has received funding from the UK EPSRC (grant no. EP/K016954/1) and the European Union. This project has received funding from the UK EPSRC (grant no. EP/K016954/1) and the European Union.

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