Remarkably High Heterogeneous Electron Transfer Activity of Carbon Nanotube-Supported Reduced Graphene Oxide

Xianwen Mao, Fei Guo, Esther H. Yan, Gregory C. Rutledge and T. Alan Hatton*

Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts, 02139, USA
* E-mail: tahatton@mit.edu

ABSTRACT: Enhancement of the heterogeneous electron transfer (HET) activities of graphene materials toward redox-active molecules assumes a crucial role in numerous graphene-based electrochemical technologies. Here we discover that carbon nanotube-supported reduced graphene oxide (rGO/CNT) exhibits unusually higher HET activities (including electrocatalytic performance towards dopamine, electron transfer kinetics with Ru(NH$_3$)$_6$$^{3+/2+}$ and Fe(CN)$_6$$^{3-/4-}$, and direct electron transfer efficiencies with cytochrome c and horse radish peroxidase) than does CNT-free rGO with an identical electrochemical surface area and surface chemistry. Through examination of the electronic structure combined with Gerisher-Marcus calculations, the critical factors responsible for this anomalous enhancement of the HET activities in rGO/CNT are identified to be a high density of π electronic states, up-shifting of the Fermi level, and appearance of a pronounced quantum capacitance-dominating character. These results indicate a general strategy to improve the HET properties of graphene by using a π electron-rich substrate to modulate electronic structure, and provide insight into the importance of the quantum capacitance in graphene electrochemistry.

INTRODUCTION

Graphene-based electrode materials, such as chemical vapor deposition-produced graphene and chemically or electrochemically reduced graphene oxide (rGO), are having a huge impact on numerous electrochemical technologies.$^{1,2}$ Heterogeneous electron transfer (HET) at solid electrodes, including graphene, is the subject of many theoretical and methodological studies in electrochemistry.$^3$ Enhancement of the HET activity of graphene materials is key to realizing their potential applications in myriad important areas such as energy storage/conversion,$^{4,6}$ molecular sensing,$^{7,8}$ and electrocatalysis.$^{9,11}$ Moreover, there is growing interest in developing a deeper understanding of the fundamental electron transfer behavior of graphene materials, particularly the HET kinetics.$^{12-14}$ One of the most important factors governing the HET activities of an electrode material is its electronic structure; the efficiencies of electron exchange at an electrode/electrolyte interface depend strongly on the overlap between the energy levels of the electrode material and the redox states in solution.$^{3,15,16}$ Hence an effective strategy to enhance the HET activity of graphene materials would appear to be through manipulation of their electronic properties. Control over electronic structure of graphene materials has been achieved previously by strategies such as potassium deposition,$^{17}$ surface functionalization by alkylsilanes,$^{18}$ variation of graphene stacking configurations,$^{19}$ and use of different substrates including SiO$_2$, Al$_2$O$_3$ and hexagonal boron nitride.$^{20}$ However, none of these studies focused on the HET properties of the related material systems.

Here we report unusually high HET activities for carbon nanotube (CNT)-supported rGO (denoted as rGO/CNT hereafter), with a major focus on elucidating how the nanotube substrate-induced variation in electronic structure of rGO influences its electrochemistry. The base control against which comparisons were made was the rGO electrode without the CNT support (denoted as rGO-ctrl hereafter). First, we demonstrate that, compared to rGO-ctrl, rGO/CNT exhibited a significantly higher sensitivity towards detection of dopamine, an important neurotransmitter that assumes a crucial role in human metabolism, cardiovascular, central nervous, renal, and hormonal systems.$^{21-22}$ and can shed light on the treatment of schizophrenia, Huntington’s disease and Parkinson’s disease.$^{23-25}$ Remarkably, rGO/CNT exhibited an extremely low detection limit of 0.07 µM, one of the best performance numbers reported to date (see Supporting Information (SI) Table S1). Next, using two benchmark diffusional redox mediators, Ru(NH$_3$)$_6$$^{3+/2+}$ and Fe(CN)$_6$$^{3-/4-}$, we show that rGO/CNT exhibited significantly higher standard HET rates than did rGO-ctrl. Additionally, we investigated experimentally the electronic valence band structures of rGO/CNT and rGO-ctrl, and performed theoretical Gerischer-Marcus calculations,$^{26-27}$ at the classical and quantum capacitance-dominated (QCD) limits.$^{28-29}$ Furthermore, we find that, compared to rGO-ctrl, rGO/CNT exhibited significantly higher direct electron transfer (DET) efficiencies with two enzymes of great interest in biotechnology, cytochrome c and horse radish peroxidase.$^{30-33}$ Development of electrodes having high DET efficiencies with redox enzymes is of great interest in various potential applications such as biosensors,$^{33}$ bioelectronics,$^{34}$ enzyme catalysts$^{35}$ and biofuel cells.$^{36}$

Our study is the first investigation of the HET activities of rGO/CNT, a novel graphene system, and indicates its potential application in various electrochemical technologies. Even after controlling for the effects of surface chemistry and electroactive surface area, rGO/CNT exhibited unexpectedly high HET activities compared to those of rGO-ctrl, which we attribute to the marked variation in electronic structure of the top rGO layer caused by the CNT substrate. We identify three key factors that account for the exceptional performance of rGO/CNT: an increase in the density of π electronic states, shifting of the Fermi level, and emergence of a pronounced QCD character. This report suggests a general strategy to enhance the HET activity of graphene by using a π electron-rich substrate to modulate electronic structure, and provides new insights into the importance of the quantum capacitance in graphene electrochemistry.
RESULTS AND DISCUSSION

Synthesis of rGO/CNT. The rGO/CNT samples were prepared under a facile and controllable synthesis protocol that consisted of a two-step sequential deposition process and subsequent electrochemical reduction (Figure 1a; for details, see SI Section 1.2). Briefly, a CNT/CH₃Cl suspension was deposited onto a circular confinement zone with a specified geometric surface area on a patterned conductive substrate. Next, a GO/H₂O suspension, composed of mostly single-layer graphene oxide (GO) sheets, 37-38 as confirmed by atomic force microscopy (AFM) imaging (Figure 1b), was carefully drop-cast onto the nanotube mat, resulting in a CNT-supported GO film (denoted as GO/CNT). During the electrochemical reduction of the GO component, the highly conductive CNT support transferred electrons easily from the substrate to the GO layer above, generating reduced graphene oxide in close proximity to the nanotubes. The rGO-ctrl samples were prepared similarly by the one-step deposition of a GO/H₂O suspension directly on the substrate followed by electrochemical reduction.

Scanning electron microscopy (SEM) imaging showed that rGO-ctrl (Figure 1c) had an almost flat surface, consistent with the morphology of electrochemically reduced graphene oxide reported previously. 39-40 By contrast, the rGO/CNT hybrid (Figure 1d) exhibited an interesting and markedly different morphology, in which the rough surface of the CNT mat was coated conformally by a thin rGO film. High-resolution SEM (HR-SEM) imaging (Figure 1e) revealed clearly the presence of carbon nanotubes under the rGO layer. For comparison, an HR-SEM image of CNTs without rGO is shown in Figure 1f. SEM imaging of different locations on the rGO/CNT sample suggested that the nanotube support was covered completely by rGO; the complete surface coverage was also verified by spectroscopic and electrochemical measurements, as discussed later.

The successful conversion of graphene oxide to rGO in the hybrid was confirmed by X-ray photoelectron spectroscopy (XPS) measurements. Representative wide-range XPS survey scans of GO/CNT and rGO/CNT are shown in Figure 1g. The intensity of each spectrum was normalized to that of the carbon peak at 284 eV. It is readily apparent that the relative intensity of the oxygen peak at 532 eV decreased significantly after electrochemical reduction. Quantitatively, the O/C ratio of GO/CNT was 0.59 ± 0.07, in agreement with that of graphene oxide produced by exfoliation of graphite oxide 39 and the theoretical value of completely oxidized graphite from density functional theory (DFT) calculations. 41 In contrast, the O/C ratio of rGO/CNT was significantly reduced to 0.08 ± 0.02, in accord with previously reported experimental 42 and modeling 43 results for reduced graphene oxide. The O/C ratio for rGO-ctrl was 0.07 ± 0.01, very close to the value of rGO/CNT, indicating that both systems had similar surface chemistries.
Additionally, we observed that prior to reduction, GO/CNT showed an XPS spectrum that was the same as that of GO (SI Figure S1a) but markedly different from that of as-received CNTs (SI Figure S1b), which had almost no oxygen content. This observation confirms, in accord with the SEM analysis, that the surface of GO/CNT was completely covered by GO and no CNTs were exposed.

To gain insights into the detailed surface chemistries of GO/CNT and rGO/CNT, high-resolution core-level C 1s scans were carried out. Representative C 1s spectra for GO/CNT and rGO/CNT are shown in Figure 1h and Figure 1i, respectively. The core-level spectra were deconvoluted into graphitic carbon (C=C at 284.5 eV), alkylic carbon (C–C at 286.1 eV), and oxygen-containing bonds (C–O at 286.8 eV, C=O at 288.2 eV, and O–C=O at 290.1 eV). It is clear that GO/CNT contained abundant oxygen-containing groups, a large fraction of defect-like sp³ carbon (i.e., C–C), and a low sp³ concentration. In contrast, rGO/CNT had much lower concentrations of C–O, C=O, and O–C=O, indicating effective removal of the oxygen groups. Additionally, a significant increase in the sp² fraction suggested that the π-conjugated carbon bonds were restored upon electrochemical reduction.

Electrocatalysis against Dopamine. rGO/CNT and rGO-ctrl were first compared by examining their electrocatalytic performances against dopamine (DA). The extensively-documented performance of dopamine sensing devices provides a good basis for assessment of electrochemical activities of the material systems developed here. Figure 2a shows the cyclic voltammograms (CVs) in 1 mM DA in 0.1 M H₂SO₄ obtained on rGO-ctrl and rGO/CNT. The rGO/CNT system exhibited significantly higher current densities than those observed with rGO-ctrl, suggesting that the former had a much stronger electrocatalytic activity toward dopamine. The increased current response was not due to exposure of the nanotube component to the solution, since SEM and XPS analyses indicate a full coverage of the CNT support by rGO; this conclusion was further corroborated by our observation that CNTs alone showed clear CV peaks characteristic of DA but, when covered by an insulating GO layer, these peaks became almost negligible (SI Figure S2). Mechanistically, the interplay between DA and an electrode can be probed by examining the magnitudes of CV peak currents (Iₚ) of the electrode at various scan rates (ν). The slope of an ln Iₚ – ln ν plot is 0.5 when the electrochemical reaction of DA is diffusion controlled; the slope is 1 when this reaction is surface limiting. Figure 2b displays the CV profiles of rGO/CNT in 1 mM DA at different ν, with the corresponding ln Iₚ – ln ν data shown in Figure 2c. Note that in Figure 2c we used the magnitude of the current (i.e., absolute value). The slopes for the anodic and cathodic currents were 0.56 and 0.63, respectively, suggesting that the electrochemical reaction of DA on rGO/CNT was more diffusional than surface limiting.

Next we investigated the dopamine sensing capabilities of rGO-ctrl and rGO/CNT using differential pulse voltammetry (DPV) to detect the amperometric responses at a series of different DA concentrations. Figure 3a shows the representative anodic DPV curves obtained on rGO/CNT when the dopamine concentration was varied from 0.1 to 201 μM. The corresponding calibration curve (i.e., DPV peak current versus dopamine concentration) with the concentration axis on linear and log scales is shown in Figure 3b and Figure 3c, respectively. The results for rGO-ctrl are shown in Figure 3d – f. For both rGO/CNT and rGO-ctrl, well-defined anodic DPV profiles were observed. The magnitude of the peak current increased with increasing dopamine concentration, from which it can be concluded that both electrodes were able to detect dopamine electrochemically. Notably, at the same DA concentrations, rGO/CNT exhibited significantly higher current densities than did rGO-ctrl. Additionally, even over the extremely low concentration range from 0.1 to 1 μM, rGO/CNT displayed well-resolved DPV profiles, whereas rGO-ctrl showed almost overlapping DPV curves with poor resolution (SI Figure S3). For rGO/CNT, there existed an excellent linear relationship between the DPV peak current and the dopamine concentration over the range from 0.1 to 11 μM (Figure 3b and 3c). In contrast, the linear range for rGO-ctrl began at a higher concentration of 3 μM (Figure 3e and 3f), indicating an inability of rGO-ctrl to detect dopamine reliably at low concentrations. Linear regression produced a much larger slope for rGO/CNT (6.96 μA/μM) than for rGO-ctrl (0.027 μA/μM). For rGO/CNT and rGO-ctrl, the linear fits over the high dopamine concentration range (>11 μM) generated calibration curves with different slopes (SI Figure S4). This behavior is associated with current saturation for electrodes with limited electroactive surface areas, and has also been observed for other carbon nanofiber- and graphene-based DA sensors. The limit of detection (LOD) values for rGO/CNT and rGO-ctrl were determined from the equation:

\[
\text{LOD} = \frac{3\sigma}{S}
\]

where σ is the standard deviation of five measurements of the blank solution from one electrode, and S is the slope of the linear regression equation over the low concentration range. Using more than twenty different samples for each, the LOD for rGO-ctrl and rGO/CNT were found to be 1.1 ± 0.05, and 0.07 ± 0.01 μM, respectively. The LOD of rGO-ctrl was comparable to that of the DA sensor based on non-functionalized graphene (2.64 μM). Remarkably, the extremely low LOD of rGO/CNT represents one of the highest sensitivities among the many previously-reported DA sensors based on carbon materials, including graphite-, CNT-, and
graphene-based systems (SI Table S1). It should be noted that the synthesis conditions affected the sensing performance of the resulting rGO/CNT electrode and reproducibility of the data. For a detailed discussion, see SI Section 3.4. After being stored in an open laboratory atmosphere for three months, 97.6% of the initial DPV response of rGO/CNT to 0.1 mM DA remained, suggesting good sensor stability. The good stability and ease of storage were attributed to the non-enzymatic nature of the rGO/CNT electrode.46-50

In addition, rGO/CNT could selectively detect DA in the presence of interfering species that commonly coexist with dopamine in biological samples, including Cl−, Br−, CO32−, K+, Zn2+, Ca2+, ascorbic acid and uric acid (see SI Section 3.6).

**Electroactive Surface Area.** From our earlier discussion, we already eliminated the possibility that the surface chemistry or the exposure of CNTs to the DA solution led to the difference in DA sensing performance between rGO/CNT and rGO-ctrl. We suspect that one contributing factor should be the large electroactive surface area (ESA) of rGO/CNT due to its undulating and porous surface character. Therefore, we measured the ESAs of rGO/CNT and rGO-ctrl using the Randles-Sevcik method31 (for details, see SI Section 4). The ESA of rGO-ctrl was estimated to be 0.37 ± 0.04 cm2, close to the geometric surface area of 0.28 cm2, while the value for rGO/CNT was found to be significantly higher (2.55 ± 0.19 cm2). Note that rGO/CNT had an approximately five-fold higher ESA relative to that of rGO-ctrl, but exhibited a ~40 to 50-fold increase in Ip at the same dopamine concentration (see Figure 3a and Figure 3d).

To control carefully for the effects of ESA, we fabricated a series of rGO/CNT electrodes with different ESAs by changing the deposition volume and simultaneously varying the size of the patterned circular confinement (SI Section 4). Figure 4 shows the ESA of rGO/CNT (purple squares) as a function of the deposition volume, together with the recorded DPV peak current (green circles) in 100 µM dopamine. For comparison, the peak current and ESA of rGO-ctrl prepared using a deposition volume of 50 µL are also shown in Figure 4 (right panel). A good linear relationship between the ESA and the deposition volume for rGO/CNT was observed, indicating that the fabrication procedure developed here allowed systematic adjustment of the ESA of the electrode. We found that the current response decayed with a decreasing ESA, as expected. More importantly, we found that a rGO/CNT sample with a smaller ESA (0.24 ± 0.05 cm2) than that of rGO-ctrl (0.37 ± 0.04 cm2) still showed a significantly higher current (61 ± 5 µA) compared to the value for rGO-ctrl (3.1 ± 0.2 µA). Therefore, this finding strongly indicates that, in addition to ESA, there must be other important factors that contribute to the superior electrochemical activity of rGO/CNT relative to that of rGO-ctrl.

**Heterogeneous Electron Transfer Kinetics.** We suspect that another contributing factor to the difference in electrocatalytic activities observed between rGO/CNT and rGO-ctrl may have been the density of electronic states (DOS); carbon electrodes with a high DOS have been found to exhibit excellent dopamine sensing performance.2-46 It has been reported previously that hybridization of graphene and carbon nanotubes, either by electrospray deposition of graphene onto CNT yarns57 or by CVD growth of graphene on nanotube-coated Cu foils,55 leads to an increase in the DOS near the Fermi level (D(EF)), i.e., density of π states) compared to that of graphene alone. In our rGO/CNT system, it appears plausible that the density of π electronic states in the top rGO layer may be increased by the CNT substrate, which contains abundant π electrons and is strongly electron-donating. Information on the DOS of

Figure 3. DA sensing performance. (a) Typical DPVs of rGO/CNT corresponding to different DA concentrations from 0.1 to 201 µM. (b) DPV peak current versus the DA concentration for rGO/CNT. (c) Data in panel b with the x-axis on a log scale. (d) Typical DPVs of rGO-ctrl corresponding to different DA concentrations from 0.1 to 201 µM. (e) DPV peak currents versus the DA concentration for rGO-ctrl. (f) Data in panel e with the x-axis on a log scale.

Figure 4. ESAs (purple squares) and DPV peak currents (green circles) in 100 µM DA as a function of deposition volume. Left panel: rGO/CNT. Right panel: rGO-ctrl. The solid line is a linear fit between the ESA and the deposition volume for rGO/CNT.
electrode materials can be inferred from their heterogeneous electron transfer kinetics; although some discrepancies exist regarding the manner in which the DOS affects the HET kinetics, the general consensus is that a higher DOS near $E_F$ results in a larger HET rate.\textsuperscript{33, 34-55} If the hypothesis were true that the DOS for rGO/CNT was larger than that of rGO-ctrl, we should expect to observe faster electron transfer kinetics on rGO/CNT. To test this hypothesis, we studied the HET kinetics of the two material systems.

Ru(NH$_3$)$_6^{3+/2+}$ and Fe(CN)$_6^{3-/4-}$ were chosen as the redox mediators to evaluate the HET kinetics because they are one-step electron-diffusional systems with physically meaningful Butler-Volmer (BV) parameters that can be related to Gerisher-Marcus (GM) theoretical calculations,\textsuperscript{28-29} and they have been widely accepted as benchmark systems for comparison of electrode activities.\textsuperscript{33} For the kinetic study, we fabricated rGO/CNT and rGO-ctrl electrodes with identical ESAs of 0.37 cm$^2$ each. The required deposition volume for rGO/CNT was 7.3 µL, determined from the linear relationship between the ESA and the deposition volume shown in Figure 4. The two systems prepared in this way had the same surface chemistries and ESAs, so the DOS should have been the only factor that would influence the HET kinetics. We measured the HET kinetics of Ru(NH$_3$)$_6^{3+/2+}$ and Fe(CN)$_6^{3-/4-}$ through sampled-current voltammetry (SCV)\textsuperscript{56} (see SI Section 5). Significantly larger HET rate constants were obtained with rGO/CNT ($k_{\text{HET}}^0 = 0.11 \pm 0.02$ cm/s for Ru(NH$_3$)$_6^{3+/2+}$ and $k_{\text{HET}}^0 = (2.3 \pm 0.3) \times 10^{-4}$ cm/s for Fe(CN)$_6^{3-/4-}$) than with rGO-ctrl ($k_{\text{HET}} = (7.7 \pm 0.4) \times 10^{-4}$ cm/s for Ru(NH$_3$)$_6^{3+/2+}$ and $k_{\text{HET}}^0 = (9.1 \pm 0.6) \times 10^{-4}$ cm/s for Fe(CN)$_6^{3-/4-}$). The $k_{\text{HET}}^0$ values on rGO-ctrl are consistent with the values obtained on the basal plane of highly oriented pyrolytic graphite (HOPG),\textsuperscript{33} although it has been recently recognized that the history of HOPG basal plane influences its HET activity significantly.\textsuperscript{57-58} The $k_{\text{HET}}^0$ values obtained on rGO/CNT are in general agreement with the values obtained on graphite edge sites\textsuperscript{59} and nitrogen-doped nanocrystalline diamond,\textsuperscript{15} while larger rate constants have been obtained on nanosized carbon electrodes using scanning electrochemical microscopy techniques.\textsuperscript{60-61} Our HET kinetic study suggests that there was a significant difference in DOS between rGO/CNT and rGO-ctrl.

**Electronic Structure.** We used ultraviolet photoelectron spectroscopy (UPS) to probe directly the electronic structure of rGO/CNT and rGO-ctrl, and performed theoretical calculations based on the GM theory to elucidate the effects of electronic structure on the electron transfer kinetics, as discussed in the following section. Figure 5a shows the overall UPS spectra of rGO/CNT and rGO-ctrl normalized by the total integrated intensity ($E_F$ denotes the Fermi level of the electrode system). Both materials exhibited graphite-like valence band structures: the intensities from 0 – 2, 2 – 13, and > 13 eV arise from $p_x$, $p_y$, and $s$ states, respectively.\textsuperscript{62} Detailed UPS spectra in the high binding energy range and near the Fermi level are shown in Figure 5b and Figure 5c, respectively. Notably, the high binding energy cutoff ($E_{\text{HBC}}$) was higher for rGO/CNT (18.6 eV) than for rGO-ctrl (17.7 eV) (Figure 5b), which further indicated that the work function ($\Phi = E_{\text{ photons}} - E_{\text{HBC}}$, where $E_{\text{ photons}}$ is the incident photon energy) was smaller for rGO/CNT than for rGO-ctrl. This observation may be attributed to type doping of the rGO component in the hybrid through the electron-donating feature of the CNT support, which led to a lower work function. Our result is consistent with a recent finding that surface functionalization of reduced graphene oxide by electron-donating chemical groups led to a decrease in $\Phi$.\textsuperscript{58} Additionally, we found that the DOS from 0 to 2 eV (i.e., the density of $\pi$ electronic states) for rGO/CNT was significantly higher than that of rGO-ctrl (Figure 5c), which validated our earlier conclusion from the kinetic study that rGO/CNT exhibited a larger $D(E_F)$ than did rGO-ctrl. Since a higher density of $\pi$ electronic states could also be inferred from a higher electrical conductivity, we measured the conductivities of the rGO-ctrl and rGO/CNT films using the four-point probe method. It was found that rGO/CNT indeed had a higher conductivity (140 ± 13 S/cm) than rGO-ctrl (35 ± 6 S/cm). Compared to high-quality pristine graphene, reduced graphene oxide usually exhibited lower conductivities due to the presence of functional groups and defects that could impede the charge carrier transport.\textsuperscript{63}

**Gerisher-Marcus Calculation.** To delineate the effects of electronic structure on HET kinetics, we modeled the electrochemistry at rGO/CNT and rGO-ctrl surfaces using the Gerisher-Marcus (GM) formalism.\textsuperscript{26-27} Based on the GM theory, electron transfer is dependent upon the DOS of the electrode and the distribution of redox states in solution, and is not merely restricted to the Fermi positions of reacting species. The energy distribution functions of the occupied and unoccupied states ($W_{\text{red}}(\lambda, E)$ and $W_{\text{ox}}(\lambda, E)$) of a redox mediator in solution are described by Equations 3 and 4, respectively.\textsuperscript{26-27}

\[
W_{\text{red}}(\lambda, E) = \frac{1}{\sqrt{4\pi k_B T \lambda}} \exp \left( -\frac{(E - E_{F,\text{redox}} + \lambda)^2}{4k_B T \lambda} \right)
\]

\[
W_{\text{ox}}(\lambda, E) = \frac{1}{\sqrt{4\pi k_B T \lambda}} \exp \left( -\frac{(E - E_{F,\text{redox}} - \lambda)^2}{4k_B T \lambda} \right)
\]

where $k_B$ is the Boltzmann constant, $E_{F,\text{redox}}$ is the Fermi level of the redox couple, and $\lambda$ is the solvent reorganization energy, which lies between 0.5 and 1 eV.\textsuperscript{26} The reductive heterogeneous electron transfer (HET) rate is

![Figure 5](image-url)

**Figure 5.** Electronic structure. (a) Full UPS spectra of rGO/CNT and rGO-ctrl. (b) Detailed UPS spectra in the high binding energy regime (16 to 19 eV). Solid black lines show the linear fitting to determine $E_{\text{HBC}}$. (c) Detailed UPS spectra near the Fermi level in the low binding energy regime (0 to 2 eV).
transfer rate constant \( (k_{\text{HET}}) \) for a redox mediator at rGO/CNT or rGO-ctrl depends on the convolution of the valence band DOS of the electrode \( (\rho(E)) \) and the distribution of the unoccupied redox states in solution.\(^{26-29}\)

\[
k_{\text{HET}} = \xi \int_{-\infty}^{\infty} \theta(E) f(E) \rho(E) W_{\text{val}}(\lambda, E, \eta) dE
\]

where \( \xi \) is the prefactor, \( \theta(E) \) is the proportionality function, and \( f(E) \) is the Fermi-Dirac distribution. Usually it is assumed that \( \theta(E) \) is independent of energy and \( \xi \) is not specific to rGO/CNT or rGO-ctrl,\(^{26,29}\) and hence they cancel out when we calculate the relative rate constants. \( \rho(E) \) for rGO/CNT or rGO-ctrl was approximated by the normalized UPS intensities of the valence band near the Fermi level, as shown in Figure 5c.

An important parameter for graphene-based electrodes is the quantum capacitance, which has a significant impact on the manner in which the overpotential affects the band structure and the distribution of electronic states.\(^{29,64}\) Hence we consider two extreme cases in which the electrode behaves as either a classical electrode (i.e., double-layer capacitance-dominated) or a quantum capacitance-dominated (QCD) electrode. Figure 6 illustrates the difference in the alignment and population of electronic states between classical and QCD limits. Figure 6a shows the energy distribution of a redox mediator in solution, as described by Equations 3 and 4. The Fermi level of a redox mediator (i.e., \( E_{F,\text{redox}} \)) can be calculated from its formal potential versus Ag/AgCl (\( E_{\text{redox}}^{0} \)) using \( E_{F,\text{redox}} = E_{\text{redox}}^{0} - 4.8 \text{ eV} - \varepsilon \). Figure 6b depicts the generic electrode band structure without an externally applied potential \( (V_{\text{app}}) \) (filled and empty bars indicate the valence and conduction bands, respectively). The Fermi level of an electrode (i.e., \( E_{F} \)) can be determined from UPS using \( E_{F} = -\Phi = E_{1\text{HBE}} - E_{\text{photon}} \). Generally, \( E_{F,\text{redox}} \) and \( E_{F} \) are not equal. Here we denote the difference between \( E_{F,\text{redox}} \) and \( E_{F} \) as \( E_{\text{diff}} \) (i.e., \( E_{\text{diff}} = E_{F} - E_{F,\text{redox}} \)). \( E_{\text{diff}} \) plays a key role in the HET kinetics for a QCD electrode, as discussed later.

Figure 6c illustrates the energy alignment and population of electronic states of a classical electrode when \( V_{\text{app}} = E_{\text{redox}} \) or \( V_{\text{app}} = E_{\text{redox}} - \eta \), where \( \eta \) is the magnitude of the overpotential. The case for a QCD electrode is shown in Figure 6d. For a classical electrode, when applying an external potential, the positions of the energy bands are shifted as a whole while the relative population of electronic states remains unchanged.\(^{29,64}\) In the case of a QCD electrode, however, the positions of the energy bands remain unchanged while the population of electronic states is changed such that the bands are occupied below \( E_{F,\text{redox}} + \eta \) and unoccupied above \( E_{F,\text{redox}} + \eta \).\(^{29,64}\) The behavior of a real electrode may be in between the classical and QCD limits: upon application of an external potential, the band positions of the electrode could be shifted as a whole together with variation in the relative population of empty/filled states.

Figure 7 presented several examples of GM calculations based on Equation 5. Note these calculations are not for specific redox systems, and the values of the parameters involved such as \( \lambda \) and \( E_{\text{diff}} \) were arbitrarily chosen within their typical ranges (i.e., 0.5 to 1 eV for \( \lambda \) and 1 to 2 eV for \( E_{\text{diff}} \)), in order to demonstrate the effects of these values on HET kinetics. A detailed modeling of the electrophotometry of an electrode requires the theoretical calculation of not just the standard electron transfer rate constant \( (k_{\text{HET}}) \), but also the \( k_{\text{HET}} - \eta \) characteristic \( (k_{\text{HET}}) \) is the rate constant at a nonzero overpotential), which may provide valuable insights into the detailed electronic properties of the electrode systems, such as the fingerprints of the distinct van Hove singularities for single-walled carbon nanotubes.\(^{29,68}\) Calculation of the \( k_{\text{HET}} - \eta \) relationship requires careful specification of the integral function in Equation 5 at varying \( \eta \) values. As an example, Figure 7a illustrates explicitly the

\[ \int_{-\infty}^{\infty} \theta(E) f(E) \rho(E) W_{\text{val}}(\lambda, E, \eta) dE \]

\[ k_{\text{HET}} = \xi \int_{-\infty}^{\infty} \theta(E) f(E) \rho(E) W_{\text{val}}(\lambda, E, \eta) dE \]
calculated integral function (i.e., \( f(E)\rho(E)W_{\text{vol}}(\lambda, E) \)) using \( \rho(E) \) of rGO/CNT and assuming the classical behavior when \( \lambda = 0.5 \) or 1.0 eV. With an increasing overpotential (from blue to pink, also see the arrow direction), the integration range and the integrated area of \( f(E)\rho(E)W_{\text{vol}}(\lambda, E) \) increases, indicating higher \( k_{\text{HET}} \) values. Note that \( f(E)\rho(E)W_{\text{vol}}(\lambda, E) = 0 \) when \( E > 0 \) or \( E < -\eta \).

To further demonstrate the effects of the solvent reorganization energy on electron transfer rates, Figure 7b shows calculated \( k_{\text{HET}} \) values normalized to \( k^0_{\text{HET}} (\lambda = 1 \text{ eV}) \) as a function of \( \eta \) while varying the \( \lambda \) values gradually from 0.5 to 1.0 eV. Calculations were performed using \( \rho(E) \) of rGO/CNT and assuming the classical behavior. It is clear that \( k_{\text{HET}} \) increased with a decreasing \( \lambda \) value. This is because a smaller reorganization energy results in a more significant overlap in energy levels between the redox mediator and the electrode.

To show the effects of electrode DOS on the \( k_{\text{HET}} - \eta \) characteristics, comparative calculations were performed between a high DOS electrode (using \( \rho(E) \) of rGO/CNT) and a low DOS electrode (using \( \rho(E) \) of rGO-ctrl) assuming the classical behavior and using an arbitrarily chosen \( \lambda \) value (1.0 eV). Figure 7c shows calculated \( k_{\text{HET}} \) values normalized to \( k^0_{\text{HET}} \) of rGO-ctrl as a function of \( \eta \). It is apparent that a higher density of electronic states leads to larger \( k_{\text{HET}} \) values. It should be noted that although calculations shown in Figure 7b and 7c were performed assuming the classical behavior, similar effects of \( \lambda \) and DOS on the \( k_{\text{HET}} - \eta \) characteristic are also obtainable using a QCD electrode.

One important consideration of a QCD electrode is the energy difference between the Fermi level of the electrode and that of the redox couple (i.e., \( E_{\text{diff}} \)). For a QCD electrode with a non-trivial DOS distribution (i.e., non-uniform distribution), \( E_{\text{diff}} \) influences significantly the \( k_{\text{HET}} - \eta \) characteristic. For a classical electrode, \( E_{\text{diff}} \) does not affect the \( k_{\text{HET}} - \eta \) characteristic since the band structure is always shifted as a whole by the applied potential. To illustrate the effects of \( E_{\text{diff}} \) for a QCD electrode, we calculated the \( k_{\text{HET}} - \eta \) curves with five arbitrarily chosen \( E_{\text{diff}} \) values (1.0, 1.25, 1.5, 1.75, and 2.0 eV) assuming the QCD behavior and using \( \rho(E) \) of rGO-ctrl. Figure 7d shows calculated \( k_{\text{HET}} \) values normalized to \( k^0_{\text{HET}} (E_{\text{diff}} = 1.0 \text{ eV}) \) as a function of \( \eta \). It can be easily seen that in this case a larger \( E_{\text{diff}} \) resulted in a larger \( k_{\text{HET}} \). This result indicates that for a QCD electrode, the band position plays a significant role in its HET kinetics.

In short, from the discussion above, the important factors in the GM calculations that determine the \( k_{\text{HET}} - \eta \) characteristics include \( \lambda \), DOS, and \( E_{\text{diff}} \) (the last only when the electrode exhibits a QCD behavior).

**Comparison to Butler-Volmer Kinetics.** To further evaluate the effects of electronic structure modulation in a way that is directly relevant to experiments, and to examine the origin of the extremely fast HET kinetics on rGO/CNT, we compared the calculated \( k_{\text{HET}} - \eta \) curves in both the classical and QCD limits to Butler-Volmer (BV)

![Figure 8](image-url). Comparison to BV kinetics. (a) Band structures of rGO-ctrl and rGO/CNT, together with the energy distribution of the occupied and unoccupied states of Ru(NH$_3$)$_6$($^{3+/2+}$ and Fe(CN)$_6$($^{3-/4-}$). (b–c) Calculated \( k_{\text{HET}} - \eta \) characteristics using the Gerischer-Marcus theory in the classical and QCD limits, compared with the \( k_{\text{HET}} - \eta \) relation from the experimentally determined Butler-Volmer kinetic parameters. (b) Ru(NH$_3$)$_6$($^{3+/2+}$ on rGO-ctrl. (c) Ru(NH$_3$)$_6$($^{3+/2+}$ on rGO/CNT. (d) Fe(CN)$_6$($^{3-/4-}$ on rGO-ctrl. (e) Fe(CN)$_6$($^{3-/4-}$ on rGO/CNT.
kinetics at small overpotentials (< 0.3 V), using realistic parameters for Ru(NH₃)₆³⁺/²⁻ and Fe(CN)₆³⁻/⁴⁻. Figure 8a shows the energy diagram on a vacuum scale for rGO-ctrl and rGO/CNT as well as the two redox mediators. As mentioned previously, the positions of Eₚ for rGO-ctrl and rGO/CNT were determined from UPS measurements and the positions of Eₚ,redox for Ru(NH₃)₆³⁺/²⁻ and Fe(CN)₆³⁻/⁴⁻ were converted from their formal potentials. The reorganization energy for Ru(NH₃)₆³⁺/²⁻/⁶⁺ was 0.8 and 0.9 eV, respectively. Figure 8b – c show the calculated HET rate constants using the GM model in the classical and QCD limits (k_HET^Classical and k_HET^QCD), overlaid with the values obtained based on the BV formulation (k_HET^BV) using the experimentally determined k_HET^0 and α values from SCV measurements. All the rate constants were normalized to k_HET^0 of rGO-ctrl, k_HET^Classical and k_HET^QCD were calculated using the parameter values shown in Figure 8a. Again, ρ(E) for rGO/CNT or rGO-ctrl was approximated by the normalized UPS intensities of the valence band near the Fermi level.

For both redox mediators, the k_HET^BV data obtained for rGO-ctrl follow closely the k_HET^Classical values over the range from 0 to 0.3 V (Figure 8b and 8d), suggesting that rGO-ctrl behaved as a classical electrode. However, rGO/CNT exhibited a somewhat different behavior, wherein the k_HET^BV data lay between the k_HET^Classical and k_HET^QCD values (Figure 8c and 8e), indicating that rGO/CNT showed a strong quantum capacitance-dominated character. The DL capacitance (C_DL) of a graphitic material is related directly to ΔEₚ by the Gerischer model: 

$$\frac{1}{C_{DL}} = \frac{1}{C_H} + \frac{1}{\sqrt{E_p \Delta E_p \varepsilon_0 \varepsilon}}$$

where C_H is the Helmholtz capacitance, which is a constant for a given electrolyte, ε is the dielectric constant, ε₀ is the vacuum permittivity, and ε₀ is the electronic charge. Equation 6 suggests that a higher ΔEₚ leads to a larger C_DL. In our case, from UPS measurements, we observed directly a significant increase in ΔEₚ for rGO/CNT compared to that for rGO-ctrl, indicating a larger C_DL for the former. Hence, the overall capacitance of rGO/CNT was more likely to be dominated by the quantum capacitance.

**DET Efficiencies with Enzymes.** Cyt c is a DET-type enzyme studied extensively and it has been shown that conventional carbon electrodes, such as glassy carbon, graphitized carbon fiber, and carbon paste electrodes, show very low DET efficiencies with this enzyme. Figure 9a shows representative background-subtracted voltammograms of 100 µM Cyt c in 100 mM phosphate buffer solution (pH = 7.0) at different scan rates on rGO-ctrl and rGO/CNT with identical ESAs of 0.37 cm² each. Both electrodes exhibited well-defined voltammetric responses towards Cyt c with peak currents located around 0.04 to ~0.06 V versus Ag/AgCl, consistent with the DET-type electrocatalysis of this enzyme.

We observed the electrocatalytic currents immediately upon adding Cyt c into the background electrolyte solution, and little deviation from the initial voltammetric response after multiple subsequent scans. The linear relation between the voltammetric peak current and (scan rate)^1/2 (Figure 9b) suggested a diffusion-controlled charge transfer behavior of this enzyme on both rGO-ctrl and rGO/CNT. Remarkably, compared to rGO-ctrl, rGO/CNT exhibited significantly larger current densities, suggesting a higher DET efficiency. For instance, at a scan rate of 0.05 V/s, rGO-ctrl showed a peak current density of 1.47 µA/cm² whereas rGO/CNT showed a peak current density of 6.57 µA/cm². Notably, the rGO/CNT system exhibited higher electrocatalytic DET efficiencies towards Cyt c than did several advanced carbon systems recently reported: the magnitude of the peak current obtained under similar conditions (i.e., identical scan rate and Cyt c concentration) is 4.18 µA/cm² for nanostructured carbon films with hydrophobic coating and 1.12 µA/cm² for high-DOS tubrostratic carbon nanofibers.

A second DET-type enzyme, horse radish peroxidase (HRP),
was immobilized onto rGO-ctrl or rGO/CNT to investigate if this enzyme may display its desired electrocatalytic activity for H$_2$O$_2$ reduction. Figure 9c shows typical CV curves of HRP-modified rGO-ctrl (blue line) and rGO/CNT (red line) upon introduction of 5 µM H$_2$O$_2$. As controls, CV curves in the absence of H$_2$O$_2$ for rGO-ctrl (black line) and rGO/CNT (green line) are also depicted in the figure. Without H$_2$O$_2$, rGO-ctrl and rGO/CNT exhibited CV responses with similar current densities. Upon introduction of H$_2$O$_2$, rGO/CNT showed a much stronger CV response than did rGO-ctrl: the magnitude of the current at −0.4 V during the anodic scan was 35.8 ± 0.8 µA for rGO/CNT and 10.6 ± 0.8 µA for rGO-ctrl, respectively. To show the dependence of the reductive current on the H$_2$O$_2$ concentration, we recorded the chronocoulometric response of rGO/CNT upon introducing hydrogen peroxide to the electrochemical cell with concentrations up to 65 µM at −0.4 V (Figure 9d). With increasing H$_2$O$_2$ concentration, the magnitude of the recorded current increased. We observed a linear correlation between the current and the H$_2$O$_2$ concentration from 1 to 50 µM (Figure 9e). Figure 9e additionally shows the occurrence of current saturation at high H$_2$O$_2$ concentrations, characteristic of Michaelis-Menten kinetics. The apparent Michaelis-Menten constant ($K_m$) was 898.7 µM, calculated from the electrochemical version of the Lineweaver-Burk plot (Figure 9f) according to the equation:

$$\frac{1}{I_{SS}} = \frac{1}{I_{max}} + \frac{K_m}{I_{max}} \left(\frac{1}{c_0}\right)$$

where $I_{SS}$ is the steady-state current after the addition of the substrate, $c_0$ is the bulk concentration of the substrate, and $I_{max}$ is the maximum current measured under saturated substrate conditions. Using 16 different rGO/CNT samples, the detection limit was found to be 0.39 ± 0.07 µM based on 3σ, with a sensitivity of 4.83 µA/µM. Compared to several previously-reported DET-type sensing systems for detection of H$_2$O$_2$ (SI Table S2), HRP-rGO/CNT exhibited a lower detection limit and a better sensitivity.

CONCLUSIONS

We report extremely high electrocatalytic activities of carbon nanotube-supported rGO, readily synthesized using a two-step protocol involving sequential deposition of carbon nanotubes and graphene oxide, followed by electrochemical reduction of the GO. Compared to rGO-ctrl with a similar ESA and surface chemistry, rGO/CNT exhibits a higher sensitivity towards dopamine detection, faster electron transfer kinetics with Ru(NH$_3$)$_6^{3+/2+}$ and Fe(CN)$_6^{3-/4-}$, and higher DET efficiencies with Cyt c and HRP. Through examination of the electronic structure combined with GM calculations, the critical factors responsible for the anomalously high HET activities of rGO/CNT are identified to be a high density of π electronic states, up-shifting of the Fermi level, and appearance of a pronounced QCD character. Our study suggests a general strategy to enhance the HET activities of graphene by using a π electron-rich substrate to modulate electronic structure, and provides valuable insights into the importance of the quantum capacitance in graphene electrochemistry. The rGO/CNT system may be useful in other important applications, such as fuel cells, metal-air batteries, and field-effect transistors, wherein the graphene electronic properties govern the device performance.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI.

Methods, XPS analysis of GO and CNTs, supplementary information on dopamine detection, determination of electroactive surface area, HET kinetic measurements, and comparison of H$_2$O$_2$ sensing performance.

AUTHOR INFORMATION

Corresponding Author

E-mail: tahatton@mit.edu

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported in part by a grant from the MIT Energy Initiative Seed Fund program. X.M. was supported by a Skoltech Fellowship.

REFERENCES

1. Ambrosi, A.; Chua, C. K.; Bonanni, A.; Pumera, M., Electrochemistry of Graphene and Related Materials. Chem Rev 2014, 114 (14), 7150-7188.
2. Mao, X.; Rutledge, G. C.; Hatton, T. A., Nanocarbon-based electrochemical systems for sensing, electrocatalysis, and energy storage. Nano Today 2014, 9 (4), 405-432.
3. Chen, S.; Liu, Y.; Chen, J., Heterogeneous electron transfer at nanoscopic electrodes: importance of electronic structures and electric double layers. Chem Soc Rev 2014, 43 (15), 5372-5386.
4. Zhu, Y. W.; Muraili, S.; Stoller, M. D.; Ganesh, K. J.; Cai, W. W.; Ferreira, P. J.; Pirkle, A.; Wallace, R. M.; Cychoz, K. A.; Thommes, M.; Su, D.; Stach, E. A.; Ruoff, R. S., Carbon-Based Supercapacitors Produced by Activation of Graphene. Science 2011, 332 (6037), 1537-1541.
5. Wang, Z.; Dong, Y.; Li, H.; Zhao, Z.; Bin Wu, H.; Hao, C.; Liu, S.; Qiu, J.; Lou, X. W., Enhancing lithium–sulphur battery performance by strongly binding the discharge products on amine-functionalized reduced graphene oxide. Nat Commun 2014, 5, doi:10.1038/ncomms6002.
6. Bonaccorso, F.; Sun, Z.; Hasan, T.; Ferrari, A. C., Graphene photonics and optoelectronics. Nat Photon 2010, 4 (9), 611-622.
7. Sun, C. L.; Chang, C. T.; Lee, H. H.; Zhou, J. G.; Wang, J.; Sham, T. K.; Pong, W. F., Microwave-Assisted Synthesis of a Core-Shell MWCNT/GONR Heterostructure for the Electrochemical Detection of Ascorbic Acid, Dopamine, and Uric Acid. ACS Nano 2011, 5 (10), 7788-7795.
8. Schedin, F.; Geim, A. K.; Morozov, S. V.; Hill, E. W.; Blake, P.; Katsnelson, M. I.; Novoselov, K. S., Detection of individual gas molecules adsorbed on graphene. Nat Mater 2007, 6 (9), 652-655.
9. Liang, Y. Y.; Li, Y. G.; Wang, H. L.; Zhou, J. G.; Wang, J.; Regier, T.; Dai, H. J., Co3O4 nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction. Nat Mater 2011, 10 (10), 780-786.
10. Xiao, Y.; Zheng, Y.; Jaroniec, M.; Qiao, S. Z., Origin of the Electrocatalytic Oxygen Reduction Activity of Graphene-Based Catalysts: A Roadmap to Achieve the Best Performance. J Am Chem Soc 2014, 136 (11), 4394-4403.
11. Liu, X.; Antonietti, M., Modulating Black Powder Chemistry for the Synthesis of Doped and Highly Porous Graphene Nanoplatelets and Their Use in Electrocatalysis. Adv Mater 2013, 25 (43), 6284-6290.
12. Güell, A. G.; Ebejer, N.; Snowden, M. E.; Macpherson, J. V.; Unwin, P. R., Structural Correlations in Heterogeneous Electron Transfer at Monolayer and Multilayer Graphene Electrodes. J Am Chem Soc 2012, 134 (17), 7258-7261.
13. Velický, M.; Bradley, D. F.; Cooper, A. J.; Hill, E. W.; Kinloch, I. A.; Mishchenko, A.; Novoselov, K. S.; Patten, H. V.; Toth, P. S.; Valota, A.
