CONSPICUOUS: Graphitic carbons are important solid materials with myriad applications including electrodes, adsorbents, catalyst support, and solid lubricants. Understanding the interaction between water and graphitic carbons is critically important for both fundamental material characterization and practical device fabrication because the water–graphite interface is essential to many applications. Research interests in graphene and carbon nanotubes over the past decades have brought renewed interest to elucidate wettability of graphitic carbons and understand their interaction with the surrounding environment. Research on this topic can be traced back to the 1940s, and the prevailing notion has been that graphitic carbons are hydrophobic. Although there have been different voices, this conclusion is supported by many previous water contact angle tests and well accepted by the community since sp² carbon is nonpolar in nature. However, recent results from our groups showed that graphitic surfaces are intrinsically mildly hydrophilic and adsorbed hydrocarbon contaminants from the ambient air render the surface hydrophobic. This unexpected finding challenges the long-lasting conception and could completely change the way graphitic materials are made, modeled, and modified. With several other research groups reporting similar findings, it is important for the community to realize the importance of airborne contamination on the surface-related properties of graphitic materials and revisit the intrinsic water–graphite interaction.

This Account aims to summarize our recent work on water wettability of graphitic surfaces and discuss future research directions toward understanding the intrinsic water–graphite interaction. Historical perspective will first be provided highlighting the long accepted notion that graphite is hydrophobic along with a few reports suggesting otherwise. Next, our recent experimental data will be presented showing that pristine graphene and graphite are mildly hydrophilic; chemical analysis showed that hydrocarbons adsorb onto the clean surfaces thus rendering them hydrophobic. These results are further rationalized by analyzing the change in surface energy of the graphitic surfaces before and after hydrocarbon contamination. Facile methods to remove hydrocarbons from a contaminated surface will be discussed along with a convenient water treatment method that we developed to inhibit hydrocarbon adsorption onto a pristine graphitic surface. Implications of contamination will be illustrated through comparing the electrochemical activity of pristine and contaminated graphite. Lastly, consequences of these findings and future research directions to address a few important unanswered questions will be discussed.
ultrahigh vacuum (UHV). He further proposed that previously reported higher WCA values are due to hydrophobic organic contamination. Nevertheless, since water readily evaporates under UHV causing the WCA to be artificially low, Schrader’s conclusion was not well accepted by the community. It is worth pointing out that in Schrader’s work, extensive effort was made to ensure that a clean surface was used for the wetting measurement; this was not the case in the vast majority of previous studies and may be one of the sources of the inconsistent results.

EFFECT OF HYDROCARBON CONTAMINATION AND INTRINSIC WATER CONTACT ANGLE

To avoid the evaporation issue related to UHV, we have studied the time evolution of WCA on fresh graphene and graphite (HOPG) in the ambient environment. Our experimental results showed a clear time dependence of the WCA upon ambient air exposure. As shown in Figure 1a, WCA of single-layer graphene on copper was only 44° when tested within 10 s of removal from the chemical vapor deposition (CVD) chamber. WCA steadily increased to 60° within 20 min and approached 80° within 1 day of air exposure. Multilayer graphene on nickel exhibited similar behavior. WCA of the freshly exfoliated HOPG surface was 64.4° and approached 91.0° within 2 days of aging in ambient air as shown in Figure 1b.

Time-dependent WCA in the ambient air has been reported for other materials and attributed to airborne hydrocarbon contamination. Gold is a prime example for which the majority of earlier studies showed that the surface is hydrophobic. Not until the early 1980s was clean gold unequivocally considered hydrophilic, and the previously reported hydrophobic behavior was attributed to the adsorption of airborne hydrocarbon contaminants. Ceramics such as silica and rare earth oxides also exhibit contamination dependent WCA. Does the time-dependent WCA that we observed also result from the airborne hydrocarbon contamination? To answer this question, we have characterized the graphitic surfaces with attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), and ellipsometry.

Figure 2a shows ATR-FTIR data for fresh and air-aged graphene surfaces. Methylene (−CH2−) stretching peaks are evident on the graphene sample within 10 min of being exposed to ambient air. Methylene is a significant component of hydrocarbons indicating that hydrocarbons are adsorbed onto the sample surface. The intensity of these peaks continues to increase with exposure to ambient air and plateaus after 70 min. The inset of Figure 2a shows the integrated area of each peak, which initially increases rapidly then plateaus. The WCA and ATR-FTIR data show similar trends: (1) the fresh surface has low WCA and weak methylene peaks; (2) WCA and methylene peaks increase as the sample is exposed to ambient air; (3) WCA and methylene peaks plateau after about 60 min of exposure to ambient air; (4) WCA and methylene peaks continue to increase very slowly and approach an upper limit. Carbon 1s XPS spectra taken on fresh and 2-week air-aged graphene are shown in Figure 2b. The strong peak near 285 eV is from the carbon atoms of graphene. The differential spectrum shows a positive peak at 285.7 eV and a shoulder at 287.6 eV, both indicative of hydrocarbon adsorption. The peak area of the aged sample is 19% larger than that of the fresh one.

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**Figure 1.** Water contact angle (WCA) data on graphene/copper, graphene/nickel, and graphite (HOPG). Panel a reproduced with permission from ref 30. Copyright 2013 Nature Publishing Group. Panel b reproduced with permission from ref 31. Copyright 2014 Elsevier.
Since the samples were subjected to UHV conditions in XPS measurement, desorption of some contamination is likely, and the XPS data will not quantitatively correlate to WCA and ATR-FTIR data taken at ambient pressure. Nevertheless, the XPS data indicate that hydrocarbons do adsorb onto the fresh graphene surface.30 Figure 2c shows ATR-FTIR data collected on HOPG, both freshly exfoliated and aged for 2 days. Similar to graphene, strong methylene stretching peaks are observed on the aged graphite whereas the fresh surface does not yield any methylene signal.31 This result indicates that for both graphene and graphite, the surface after synthesis/exfoliation is hydrocarbon-free and exposing the sample to ambient air causes hydrocarbons to adsorb.

Ellipsometry is a nondestructive optical technique that allows real-time monitoring of the hydrocarbon adsorption. The hydrocarbon film thickness was modeled using the Cauchy dispersion model with fixed index of refraction \( n = 1.45 \).31 The initial data point on a fresh sample is taken as zero hydrocarbon thickness and adsorption of the hydrocarbon layer was monitored as a function of exposure time in air. As shown in Figure 2d, there is conspicuous growth of an adsorptive layer on HOPG, which from ATR-FTIR and XPS results is known to be airborne hydrocarbons. Initial adsorption occurs relatively rapidly and plateaus after about 30 min for HOPG. Theoretical modeling shows that only 2 monolayers of \(-\text{CH}_2-\) (\(\sim 7\) Å) can cause the WCA of HOPG to increase from 64.4° to 96°–105°, which compares well to ellipsometry measurements showing that ca. 6 Å of hydrocarbons adsorb onto the pristine graphite surface.31 Moreover, the WCA- and ellipsometry-measured adsorption show almost the same trend. The ATR-FTIR, XPS, and ellipsometry results indicated that the graphitic surfaces are intrinsically mildly hydrophilic. Adsorption of hydrocarbons from the ambient environment renders the surface hydrophobic.

### SURFACE ENERGY OF CLEAN AND CONTAMINATED SURFACES

Surface energy (\(\gamma_s\)) is the most important surface property of a solid, which not only determines wettability but also greatly impacts adhesion, friction, and other surface or interface performance. Testing the contact angle of different liquids with known polar and dispersive components on the same solid allows for the surface energy to be determined using Young’s equation along with various models. We have used three common models, Neumann, Fowkes, and Owens–Wendt, to calculate the surface energy of fresh and aged graphitic surfaces based on the contact angles from four testing liquids.37 Figure 3 shows the surface energies for fresh and aged graphene and graphite (HOPG). The upper graphs show total surface energy and the lower graphs show the dispersive (\(\gamma_d\)) and polar (\(\gamma_p\)) components of surface energy assuming that \(\gamma_s = \gamma_d + \gamma_p\) (an assumption intrinsic to the Fowkes and Owens–Wendt models). The Neumann model is based on the equation of state assumption and does not differentiate between dispersive and polar components. All three models have intrinsic assumptions, and there is no consensus among the community...
favoring one over another. Therefore, there is merit in comparing the results from all three models.

As shown in Figure 3, the total surface energy of graphene and HOPG clearly decreases as the sample is exposed to ambient air. The salient feature of the result is that surface energy is the greatest on the fresh surface and the least on the aged surface. The aforementioned ATR-FTIR, XPS, and ellipsometry results show that the fresh surface is mildly hydrophilic and free of hydrocarbon contaminants. With exposure to ambient air, airborne hydrocarbons adsorb onto the surface. The results of the total surface energy indicate that the thermodynamic driving force of the adsorption process is to lower the total surface energy.

A detailed analysis on the dispersive and polar components of the total surface energy, that is, $\gamma_d$ and $\gamma_p$, provided more insight into the intrinsic water wettability of both graphene and HOPG. As shown in Figure 3, $\gamma_d$ of fresh graphene/copper and HOPG are similar, 43.5 ± 2.4 vs 45.6 ± 1.6 mJ/m². After 1-day exposure to the ambient, $\gamma_d$ of graphene decreases by 13%, while $\gamma_d$ of HOPG decreases by 10%. Interestingly, $\gamma_p$ of fresh graphene is higher than that of HOPG, ca. 14.0 ± 2.0 vs 8.0 ± 2.7 mJ/m². Moreover, after 1-day exposure to the ambient, $\gamma_p$ of graphene decreases by 74% while $\gamma_p$ of HOPG decreases by 99%. This data suggests that the fresh graphitic surface has an intrinsic polar affinity for water and the adsorbed airborne hydrocarbons block the polar forces so that the water "sees" only the dispersive hydrocarbon layer.

Graphene presents an interesting case because of its atomic thickness and possible contribution from the underlying copper substrate. Previously, it has been suggested that water could interact directly with the copper substrate under the graphene via van der Waals interactions, that is, complete or partial wetting transparency.38,39 Other work also showed that a monolayer of graphene blocks 70% of the van der Waals interactions from the substrate.40,41 Therefore, the higher $\gamma_p$ of the fresh graphene/copper sample could be attributed to the copper substrate. Our results suggest that partial wetting transparency could still apply for uncontaminated graphene though more research is required to fully demonstrate this effect and differentiate it from factors such as charge transfer doping from the substrate. Upon contamination, the WCA will approach 90° as the adsorbed hydrocarbons completely "shield" water from interacting with the substrate underneath graphene.

### REMOVING AND INHIBITING HYDROCARBON ADSORPTION

Due to the 2D nature of graphene, it has to be integrated with other surfaces in many important applications, for example, the graphene-based heterostructure field-effect transistor (FET) that is regarded as a candidate device for post-CMOS (complementary metal-oxide semiconductor) electronics.42,43 It has been reported that such multilayer structures often trap hydrocarbon contaminants between constituent sheets, which could reduce the adhesion at the interface and negatively impact the fabrication process. Moreover, performance of FET...
devices made of graphene degraded significantly due to exposure to the ambient environment, and vacuum annealing is required to achieve the best performance.\textsuperscript{45–47} Our studies\textsuperscript{30,31,37} explained why hydrocarbons easily adsorb on the graphene surface based on the finding that the graphitic surface is intrinsically hydrophilic and has higher surface energy than previously believed. However, from the practical viewpoint, it is critical to develop cost-effective and scalable methods for removing and inhibiting hydrocarbon contaminants.

We have studied various methods to address this challenge.\textsuperscript{30,31,48} We showed that annealing a contaminated graphene sample at 550 °C in Ar causes WCA to drop to 55° and subsequent exposure to ambient air allows WCA to recover back to 80°.\textsuperscript{30} ATR-FTIR showed that the $-\text{CH}_2-$ peak decreased by 50% after thermal annealing; however, a weak D peak was observed in the Raman spectra indicating damage occurred to the graphene.\textsuperscript{30} We also found that UV/O$_3$ treatment of contaminated graphene for 5 min resulted in a precipitous WCA decrease to ca. 45°, the value on fresh graphene. ATR-FTIR showed a 62% decrease in $-\text{CH}_2-$ peak intensity, while XPS showed a decrease in C–H species and an increase in oxygen content. Along with the weak D peak observed in the Raman spectra, this result suggests that exposure to UV/O$_3$ causes slight graphene oxidation.\textsuperscript{30} Exposing freshly exfoliated graphite to UV/O$_3$ for 5 min results in a WCA of 32°, which is substantially lower than the 64.4° observed without UV/O$_3$ treatment. Moreover, a WCA of 32° was also observed for a well-contaminated graphene sample that was exposed to UV/O$_3$ for 5 min. These results indicate that UV/O$_3$ treatment removes adsorbed contaminants but also damages the graphitic surface. For comparison, another experiment showed that UHV can remove adsorbed contaminants with WCA recovering to ca. 65°.\textsuperscript{31}

Inhibiting hydrocarbon adsorption onto a fresh surface is difficult because hydrocarbons are present in nearly every practical working environment. We have developed a convenient method for preserving the pristine graphitic surface through a water treatment technique.\textsuperscript{48} Placing the fresh sample in a low temperature environment (−15 °C) causes a nanometer thick water layer to form on the graphitic surface that inhibits hydrocarbon adsorption. Figure 4 shows WCA of freshly exfoliated graphite stored at room temperature and low temperature. WCA of the sample stored at low temperature increased from 60° to 70° within the first 15 min after exfoliation but then remained constant for 2 h. This result shows that continuous exposure to low temperature will significantly inhibit hydrocarbon adsorption on fresh graphitic surface. Removing the sample from low temperature and exposing to room temperature causes WCA to slowly increase and plateau at ca. 85° after 20 h of ambient air exposure.\textsuperscript{48} ATR-FTIR, XPS, and ellipsometry data all show that an ice-like layer of water forms on the graphitic surface upon low-temperature treatment and inhibits hydrocarbons from adsorbing. This water layer even persists at room temperature for 2−3 h. With continued exposure to ambient air, the water will desorb and slowly be replaced by airborne hydrocarbons, although at a rate about 20× slower than in the absence of water treatment. The role of water was also verified by placing a low-temperature treated sample in a desiccator to desorb water. As expected, hydrocarbons adsorbed quickly onto the surface as water desorbed with WCA approaching ca. 90°. Furthermore, 2 min steam treatment of freshly exfoliated graphite results in WCA less than 70° for nearly 2 h followed by a slow increase as water desorbs and hydrocarbons adsorb.\textsuperscript{48} These findings indicate that the simple water treatment, which is cost-effective and scalable, is effective in inhibiting airborne hydrocarbon contamination on graphitic surfaces.

**EFFECT OF HYDROCARBONS ON THE ELECTROCHEMICAL ACTIVITY**

It has been long believed that electron transfer (ET) between graphite and solution redox couples occurs favorably at step edges, and that the basal plane is electrochemically inert due to its low density of states (DOS) and lack of adsorption of the redox couples.\textsuperscript{49} Interestingly, Unwin and co-workers\textsuperscript{2,50} recently reported the basal plane of graphite to be electrochemically active and attributed this high electrochemical activity to stronger than expected adsorption of redox couples along with a higher than expected DOS at the energy region of the redox couple. Aside from the controversy concerning basal plane activity, there is evidence of temporally dependent ET kinetics on the graphite surface. Amemiya and co-workers showed that the electrochemical activity decreases as the graphitic surface is exposed to ambient air, implicating hydrocarbon adsorption as the cause of decreasing ET rate.\textsuperscript{51}

We conducted cyclic voltammetry (CV) measurements on freshly exfoliated graphite to show the efficacy of the low temperature treatment in preserving the electrochemical...
activity of HOPG. Figure 5a shows CV measurements for graphite exposed to RT for up to 3 days. The fresh surface has a potential peak separation ($\Delta E_{p}$) of 59 meV indicating reversible behavior; however, aging causes $\Delta E_{p}$ to substantially increase indicating an irreversible ET process. Furthermore, current of the aged sample is reduced by about 50% compared to the fresh sample. Low-temperature treatment of freshly exfoliated graphite maintains the reversible electrochemical behavior up to 1 day as shown in Figure 5b. These CV measurements showed that low temperature treatment of freshly exfoliated graphitic surfaces preserves its intrinsic electrochemical behavior. Moreover, because the sample was exposed to the ambient air and water this data provides further evidence that hydrocarbon adsorption does negatively impact electrochemical behavior of pristine graphitic surfaces. Recent work from the Amemiya lab has confirmed these findings using nanogap electrochemical microscopy method.62

**CONCLUSIONS AND OUTLOOK**

Our WCA, FTIR, XPS, and ellipsometry results showed that graphene and graphite are intrinsically mildly hydrophilic. The pristine surface spontaneously attracts hydrocarbons from ambient air to reduce its surface energy, which was supported by the surface energy analysis based on the contact angle data. More recently, the temporal evolution of WCA on graphite and graphitic surfaces in ambient air has been confirmed by other research groups.51,53–60 In these studies,51–58 the WCA of fresh HOPG ranges from 45° to 70°, which reasonably agrees to our reported value, ~64°, when the sample variances as well as local conditions that impact hydrocarbon adsorption kinetics is taken into consideration. Interestingly, Chiesa et al.53,55 proposed that both adsorbed hydrocarbons and water contribute to the increase of WCA. Gomez-Herrero et al.60 showed that freshly exfoliated HOPG has a WCA of 70° that increases to 95° with time due to hydrocarbon adsorption and the surface potential decreases when the contamination occurs. Since WCA data is often used to calibrate force fields for molecular dynamics simulations, the WCA of clean graphitic surfaces should provide new insight into the graphite–water interaction, and this effort has just started and will require more systematic investigation.61

Though the results from others and us clearly indicate the effect of hydrocarbon contamination on the WCA, the molecular process of the hydrocarbon contamination is still not well understood. Previously, Cao et al.62 showed that water preferably adsorbs to step edges on HOPG, which suggests that hydrocarbon adsorption could also start from the defect. What will happen when water and hydrocarbon coexist in the ambient air? Our recent WCA work indicated that the competition between water and hydrocarbon adsorption on the HOPG is highly dependent on temperature and humidity.48 However, molecular-level characterization is highly desirable in the future to uncover the mechanism though this is very challenging.

An important question remaining unanswered is why are graphitic surfaces, which have a nonpolar sp$^2$ carbon structure, not hydrophobic? Water has been shown to have increased affinity for conjugated molecules and preferentially adsorb with the hydrogen atoms pointing toward graphene, suggesting π-hydrogen bonding could contribute to the stronger-than-expected water–graphite interaction.53–66 Carefully designed experiments with airborne hydrocarbon contamination taken into consideration are essential to fully uncover the nature of graphite–water interaction. Moreover, high energy defect sites on the graphitic surface, for example, step edges on graphite and wrinkles on graphene, could attract water causing the surface to appear more hydrophilic,30,62,67 and the quantitative governing mechanisms require further research.

From the practical viewpoint, airborne hydrocarbon contamination could impact not only wettability but also adhesion and adsorption of graphitic surfaces. The research on these topics has not yet started and will be fundamentally interesting and practically important. Last but not least, developing effective methods for removing and inhibiting hydrocarbon contamination is critical for manipulating the graphitic surfaces. We found that UV/O$_3$ treatment and thermal annealing are effective in removing the hydrocarbons but cause damage to the graphitic surface. Interestingly, adsorbed water protects the graphitic surfaces from hydrocarbon contamination. Currently, other methods are being explored,68,69 and future breakthrough in this direction is expected to greatly facilitate the successful fabrication of graphene-based devices in many applications.

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**Figure 5.** Cyclic voltammograms of (a) freshly exfoliated graphite exposed to room temperature and (b) low temperature (−15 °C). (c) shows the time evolution of the separation between oxidation and reduction peaks. The electrolyte solution contains 1 mM Fe(CN)$_6^{4-}$ in 1.0 M KCl. Reprinted with permission from ref 48. Copyright 2016 American Chemical Society.
Author Contributions

A.K. and F.Z. contributed equally.

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Notes

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