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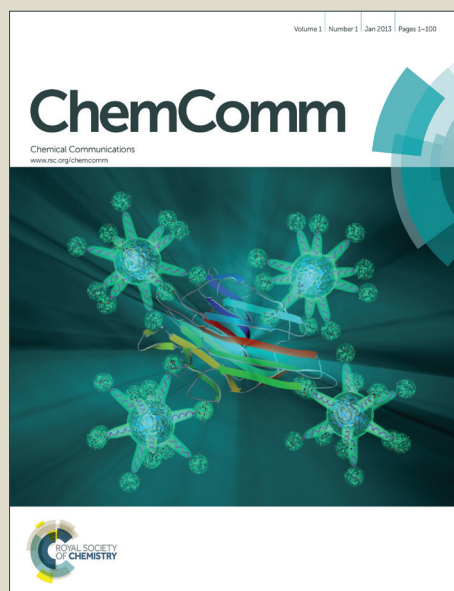
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COMMUNICATION

Support effects in the adsorption of water on CVD graphene: an ultra-high vacuum adsorption study

A. Chakradhar, N. Sivapragasam, M. T. Nayakasinghe and U. Burghaus

Experimental data for water adsorption on CVD (chemical vapor deposition) graphene/SiO_2 and graphene/Cu studied at ultra-high vacuum (UHV) conditions are discussed, focusing on support effects and hydrophobicity. At UHV, it seems that the graphene wettability is inversely related to wetting property of the support. Graphene is not transparent to water wetting on the supports studied here.

The use of carbon based materials for catalysis has grown vastly.[1-4] In addition, a single layer of carbon is a promising material for nanoelectronics,[5-7] energy storage/conversion,[8] sensors,[9] etc. Typically, graphene-based devices are operated in ambient as well as moisture is present in most catalytic processes. Therefore, it is important to consider water-graphene interactions. A UHV study allows for characterizing the intrinsic surface properties of graphene. Despite the ever growing graphene community, surprisingly little kinetics data are available that were obtained at UHV measuring conditions.

Water adsorption on supported graphene has pre-dominantly been studied computationally with controversial results. Density functional theory (DFT) showed that the electronic properties of graphene upon water adsorption were indeed affected by the SiO_2 substrate.[10, 11] However, water adsorption on graphene/h-BN was not influenced by the interaction with the substrate.[12] T. Wehling, et al.,[10] proposed that the presence of dangling-bond defects on SiO_2 substrates could potentially cause doping, as the dipole moments of H_2O adsorbates create local electrostatic fields.[10] However, V. Bermudez, et al.,[11] reported such highly reactive defects on SiO_2 do not exist at a real graphene-SiO_2 interface. In fact, as soon as SiO_2 is exposed to ambient, such defects would be passivated by dissociative adsorption of H_2O vapor.[11] It was reported that the configuration of the adsorbed H_2O may depend on the substrates. These effects are still debated in computational studies.[8] Experimental works on atomically clean graphene are still rare. X. Feng, et al.,[13] studied the adsorption of water on epitaxial

graphene grown on different substrates toward possible water intercalation using scanning tunneling microscopy (STM). Accordingly, chemical properties of the substrate strongly affect the reactivity of the C-C bonds in epitaxial graphene.[13] However, the defect density due to intercalation amounts to only 1% of the graphene film.[13] In addition, scanning tunneling spectroscopy (STS) revealed extensive charge fluctuations which may affect adsorption properties.[14] Little is known about graphene's gas-surface kinetics at UHV.[15-18] The wettability of graphene too is a widely debated topic in surface science and engineering communities. Conclusions reported from contact angle measurements have been contradictory.[19-21] J. Rafiee, et al., published that a graphene monolayer is transparent to wetting,[21] whereas C. Shih, et al., noted that graphene is only partially transparent,[20] and R. Raj concluded the negligible effect of the support on the wettability of graphene.[19] All of these studies were conducted at ambient, therefore, the cleanliness of the graphene samples are rather unknown. In ref.,[22] it was seen that contact angles change over time due to uptake of contaminations from ambient. We use a simple kinetics technique (TDS) to study the effect of the support on hydrophobicity and wettability of graphene at atomically clean UHV conditions. Numerous studies and applications consider epitaxial graphene. Therefore, support effects are paramount.

Recently we characterized water adsorption on graphene/Ru(0001) where the graphene layer was grown in UHV by physical vapor deposition (PVD).[18, 23] According to our experiments, water adsorption kinetics and wettability on a clean ruthenium support and on graphene/ruthenium were very different, i.e., graphene is not "transparent". Several important questions remain unanswered. Do commercial CVD samples, as studied here, deviate from a PVD model system? Does the support affect adsorption properties? In particular, do semiconducting (SiO_2) and metallic (Cu) supports lead to different wetting behaviors? Does the wettability of graphene correlate with the wettability of the support? Thermal desorption spectroscopy (TDS) experiments, as used in this study, are able to address these currently unanswered questions. In addition, the UHV conditions guarantee atomically clean surfaces, i.e., indeed the intrinsic surface properties of CVD graphene will be characterized.

Copper foil and SiO_2, as used here, have vastly been utilized as a support for graphene in other studies,[24, 25] because cheap CVD

Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND 58108, USA. E-mail: uwe.burghaus@ndsu.edu; Web: www.uweburghaus.us

samples are commercially available. In addition, numerous surface science studies have been conducted to study water adsorption on copper and SiO_2 substrates.[26-30] Copper is a complex support, but most of the copper surfaces are hydrophilic with the exception of Cu(111).[30] No TDS data are available for polycrystalline copper. In contrast, hydrophobic adsorption kinetics is reported for water adsorption on SiO_2 surfaces.[27, 28] Nevertheless, blank experiments are shown along with the graphene data.

Water interactions at UHV are usually discussed in regard to sub-monolayer adsorption and water multilayer formation. Amorphous or crystalline water layers form at large exposures, whereas two-dimensional clusters are expected at monolayer exposure.[31-33] In TDS, hydrophilic systems usually show a monolayer structure and a condensation peak. On the contrary, for hydrophobic surfaces, only one water desorption peak is detected that obeys zero-order kinetics.[30, 34, 35] Importantly, for a strictly hydrophobic surface, zero-order kinetics is present already within sub-monolayer coverage. Therefore, TDS allows for distinguishing hydrophobic and hydrophilic surfaces. (A list of hydrophobic and hydrophilic surfaces that have been studied in surface science are listed in Tab. S1; supplemental section).

Similarly, depending on whether the TDS data of the support just mirror the data of the supported graphene, or completely different results are obtained, graphene could be considered "transparent" for water wetting or not. Complications may arise from a possible intercalation of water,[13, 36] which we, however, did not observe.
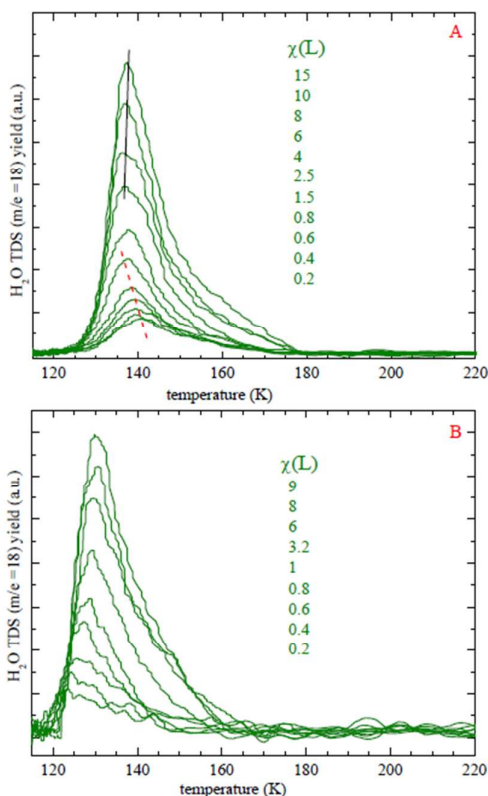

Figure 1. TDS of water as a function of water exposure **A)** on hydrophilic graphene/SiO_2 **B)** on hydrophobic SiO_2 support.

According to our UHV data, CVD graphene/SiO_2 and graphene/Cu are non-transparent for water adsorption similar to

PVD graphene/Ru(0001) studied earlier.[18] Graphene/SiO_2 deviates from graphene/Ru and graphene/Cu in regard to hydrophobicity. Therefore, considering details, the support indeed affects the adsorption properties to some extent.

According to the vendor information,[37] the graphene/Cu sample consists of predominantly crystalline single-layer graphene, grown continuously across copper surface steps and grain boundaries.[37] Graphene is grown on both sides of the copper foil with the advantage for TDS not to obscure the data by a background signal from copper. A graphene film was transferred to a silica wafer using poly-methyl metacrylate as the transferring agent.[37] The graphene/SiO_2 sample consists of a single layer graphene with 5% defects (holes and cracks), consistent with our Raman spectrum of an as-received sample (Fig. S1). In addition, Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were used to characterize the graphene samples (Fig. S2-S5). Note that, as a standard cleaning procedure, graphene samples were annealed at ~650 K in UHV (base pressure $1x10^{-10}$ mbar) before the data were collected. Even greater annealing temperatures may be preferred resulting in even cleaner samples, but greater temperatures damaged the samples. An oxygen AES signal was present, but originates likely from a partially oxidized copper support (according to XPS) rather than oxygen functionalities (see supplemental). Therefore, we believe that the vastly considered CVD graphene samples studied here are as clean as technically possible. Note that these samples are usually studied at ambient pressure; here the samples are at 10^{-10} mbar.

Results of UHV TDS experiments of water on graphene/SiO_2 are depicted in Fig. 1A. (Fig. 1B shows the data for a bare silica support.) These curves correspond to different exposures of water (i.e., to different initial water coverages, 1 sec exposure at $1x10^{-6}$ Torr corresponds to one Langmuir, 1 L). Water desorbs already at low temperatures (~120-180 K), excluding dissociation of water.[31-33] Only one TDS feature is evident. However, in contrast to a hydrophobic surface, initially the TDS peaks shift to lower temperatures with increasing exposure (see red dashed line in Fig. 1A). Low temperature leading edges initially do not align. In fact, an Arrhenius plot yields a straight line at lower exposures, but with positive slope, indicating deviation from zero-order kinetics (Fig. S6). At higher exposures, TDS curves have the same leading edge (Fig. 1A), and shift towards greater temperature with increasing exposure since water starts to condense at large exposures. Moreover, analyzing one of the high exposure (6L) TDS curves (by leading edge method, see inset of Fig. 2) yields a straight line and a heat of condensation of 0.46 eV/molecule, consistent with water condensation (see detailed calculation in supplemental section). Therefore, graphene/SiO_2 does not resemble the properties of a hydrophobic surface (Fig. 1A), although the support is hydrophobic (Fig. 1B). For bare silica (Fig. 1B), the TDS curves align starting at the lowest (sub-monolayer) exposures. Similar results were reported for water adsorption on thin silica films grown on Mo surfaces.[27, 28] This result for graphene/SiO_2 is in contrast to PVD graphene/Ru(0001), where the water adsorption kinetics showed many features expected for zero-order kinetics, indicating mostly hydrophobic interactions. Thus, support effects are evident. In addition, we can conclude that graphene/SiO_2 does not mirror the water desorption kinetics of the SiO_2 support. Therefore, graphene/SiO_2 is not transparent to water wetting.

ChemComm

Based on our Raman data (Fig. S1, where I_D/I_G ~0.08) and vendor information, the defect density of graphene/SiO$_2$ is relatively low (<5%). Since the SiO$_2$ support is hydrophobic, it appears very unlikely that defects (e.g. due to water intercalation) would cause hydrophilic properties of graphene/SiO$_2$. Furthermore, the ratio of I_D and I_G in Raman spectra before and after water adsorption shows variations as large as seen when scanning a pristine surface. In addition, the Raman spectra rule out an uptake of large amounts of amorphous carbon.
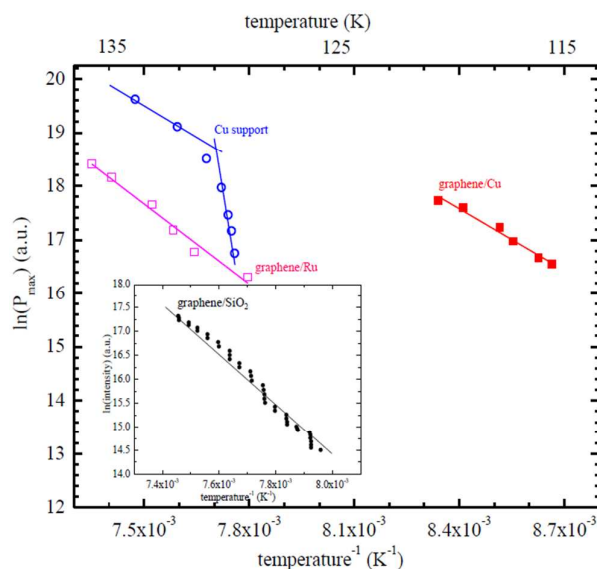

Figure 2. Kinetics parameter for water on ■ graphene/Cu, ○ Cu support, and □ graphene/Ru. Inset shows kinetics parameter for water on graphene/SiO$_2$ at 6L exposure.

Results of UHV TDS experiments for water on graphene/Cu are depicted in Fig. 3. Similar to graphene/Ru,[18] only one TDS peak is evident which shifts slightly to greater temperatures with increasing exposures. The exponential rise at low temperature and common leading edges are all indicative of the sublimation of ice and approximate zero-order kinetics. In addition, the Arrhenius plot in Fig. 2 yields a straight line. No further monolayer desorption features ("wetting structures") are seen in the TDS data (Fig. 3). Therefore, graphene/Cu is hydrophobic, in contrast to graphene grown on the semi-conductor support. The TDS maximum shifts simply because it takes longer to heat off the water when the starting concentration of water is increased.

In the case of water adsorption on polycrystalline Cu, a single broad TDS feature is evident (Fig. S7). Moreover, the low temperature leading edges of TDS curves don't align, as it would be expected for zero-order kinetics. In addition, the Arrhenius plot in Fig. 2, assuming zero-order kinetics, does not yield a single straight line. Thus, bare polycrystalline Cu is not hydrophobic (as most copper surfaces) and graphene/Cu does not mirror the water desorption kinetics of copper. Therefore, graphene also is not transparent to water wetting using a copper support. Comparing three samples (graphene/SiO$_2$, graphene/Cu, and graphene/Ru), it appears clear that the graphene surface chemistry is indeed influenced by the support (e.g. oxides/semi-conductor vs. metals).

The high temperature edges of the TDS curves (Fig. 1 & 3) do not drop abruptly to zero as expected for strictly zero-order

kinetics. Similar feature was seen for graphene/Ru and identified as intrinsic to graphene/Ru.[18] Readsorption and/or pumping speed limitations could be ruled out by dosing water with a molecular beam system. The desorption rate may become coverage-dependent below a critical water concentration which decreases its desorption rate and results in the high temperature-low coverage tail of the TDS curves[13] (as also seen for water adsorption on HOPG[38]).

Not all of our findings may be consistent with all prior works. Although contact angle measurements result in important insights, these studies are limited to ambient pressure. As also noted by others,[22, 39] airborne contaminations can affect the wettability of graphitic systems. Intrinsically a UHV study should result in cleaner measuring conditions, although if special care is taken, contact angles can be determined on clean samples.[22]
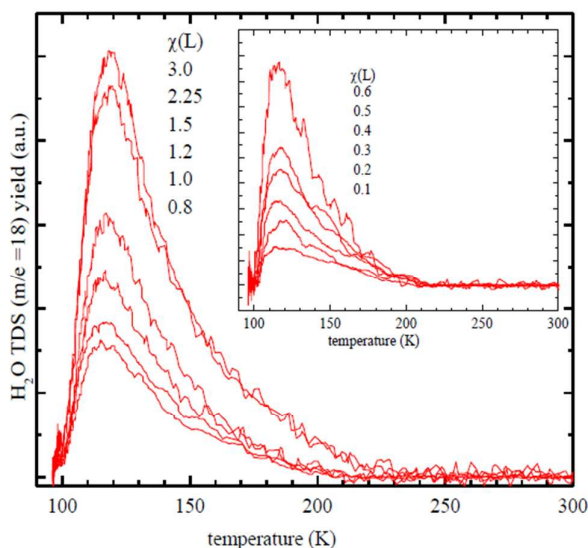

Figure 3. TDS data of water on graphene/Cu as a function of water exposure. Inset shows data for lower exposures.

In summary, adsorption kinetics of water on CVD graphene/SiO$_2$ and graphene/Cu was investigated at clean UHV conditions. Water adsorption on graphene/SiO$_2$ shows a deviation from zero-order desorption kinetics at lower exposures, suggesting a hydrophilic interaction and wetting of the surface.[22] On the contrary, water adsorption on graphene/Cu is consistent with hydrophobic interactions, similarly to graphene/Ru. Graphene is not transparent to water wetting on both copper and silica supports. Graphene grown on metallic supports (Cu and Ru) showed hydrophobic properties in contrast to graphene grown on the semi-conducting support (SiO$_2$). For the cases studied here, the graphene wettability appears inversely related to wetting property of the support, i.e., if the support is hydrophobic, graphene shows wetting behavior (becomes hydrophilic) and if the support is hydrophilic, graphene shows non-wetting behavior (is hydrophobic). These results provide an experimental proof of support effects for water adsorption on graphene and are in agreement with ref.,[10, 11] where DFT calculations showed that water adsorption on graphene is indeed perturbed by the support. However, according to ref.[40]

only 30% of the van der Waals interactions of the support are transmitted through the graphene layer.

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