Water Chemistry beneath Graphene: Condensation of a Dense OH–H₂O Phase under Graphene

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ABSTRACT: Room temperature oxygen hydrogenation below graphene flakes supported by Ir(111) is investigated through a combination of X-ray photoelectron spectroscopy, scanning tunneling microscopy, and density functional theory calculations using an evolutionary search algorithm. We demonstrate how the graphene cover and its doping level can be used to trap and characterize dense mixed O−OH−H₂O phases that otherwise would not exist. Our study of these graphene-stabilized phases and their response to oxygen or hydrogen exposure reveals that additional oxygen can be dissolved into them at room temperature creating mixed O−OH−H₂O phases with an increased areal coverage underneath graphene. In contrast, additional hydrogen exposure converts the mixed O−OH−H₂O phases back to pure OH−H₂O with a reduced areal coverage underneath graphene.

INTRODUCTION

One promising application of the rich variety of new 2D materials is as model systems for studying catalysis. For example, single atom doping of 2D materials can be used to create new catalytic sites, single atom or substrate doping can be used to alter the catalytic activity of the 2D material itself, the 2D material can be used like a chain armor to protect catalyst materials against harsh reaction conditions, the 2D material can be used as membrane that only allows for example protons to penetrate while more bulky ions or molecules are blocked, or the confined space between the 2D material and its metal substrate can be used to create new reaction pathways.

Examples of this last application were reviewed extensively in 2017 by Fu and Bao covering elemental and molecular intercalation both from gas and liquid phase as well as undercover growth and reactions. Since then an impressive amount of literature has been published within the area of “undercover catalysis”, and it has for example been demonstrated that defective graphene on Pt(111) can increase rates for the hydrogen evolution reaction by 200% as compared to bare Pt(111).

Many intercalation studies of atoms and molecules under graphene have been published in the past and they have given an excellent starting point for understanding undercover reactions. For example, oxygen, CO, and hydrogen intercalation has been studied in detail for graphene (Gr) grown on a number of metal surfaces including Ru(0001), Pt(111), and Ir(111) with experimental surface science techniques as well as density functional theory. These studies have given unprecedented understanding of intercalation of molecules under Gr, the intercalation mechanisms, the phases formed under the Gr cover and their experimental fingerprints. Also, it has been shown that Gr intercalation can be controlled by gas pressure, temperature, and the morphology of the epitaxial Gr on its substrate.

In contrast to the rich amount of intercalation studies under Gr fewer studies report on undercover gas-phase reactions. The best studied system is CO oxidation under Gr grown on Pt(111). Low electron energy microscopy (LEEM) studies performed at low pressures in the group of Bao revealed that wrinkles in the graphene layer function as one-dimensional gas inlets for oxygen and CO. A modified CO adsorption structure and a lowered CO desorption temperature result from the Gr layer above. Furthermore, it was demonstrated how in situ LEEM can be used to follow CO oxidation of rows of CO molecules trapped below Gr close to the Pt step edges. More recently the same group used a combination of polarization-modulated infrared reflection absorption spectroscopy (PMIRRAS) and ambient pressure XPS (APXPS) to study CO oxidation below the submonolayer and one monolayer Gr on Pt(111) in a pressure range from 10⁻⁹ to 40 mbar.
Interestingly, these experiments revealed that the Gr overlayer weakens the CO-Pt interaction and thereby lowers the activation energy for CO oxidation. The authors even demonstrated that it is possible to run the CO oxidation reaction over a Pt(111) surface fully covered by Gr. CO oxidation below graphitic shells has also been demonstrated for Pt nanoparticles where a lower activation energy was demonstrated.23

Some of the authors of this paper investigated CO oxidation over an oxygen saturated Ir(111) surface below Gr flakes at elevated temperatures, using in situ XPS at low pressures (5 × 10⁻⁹ mbar) of CO and elevated temperatures (490 K).15 At these conditions, our study showed that the oxygen atoms below the Gr flakes work as a reservoir from which oxygen is expelled. Consequently, CO oxidation only takes place at the bare Ir(111) patches.

For hydrogen oxidation using Gr flakes supported by Pt-group metals, we are only aware of some evidence for formation of H₂O and/or OH on Pt(111) under Gr upon subsequent oxygen and hydrogen dosing based on O 1s and C 1s XP spectra.15 However, no detailed analysis or discussion was presented. In contrast, hydrogen oxidation below freestanding SiO₂ bilayer film supported by Ru(0001) was recently studied in detail by Prieto et al.24 In this study, it was demonstrated that the apparent activation energy determined from a front velocity analysis of LEEM images is reduced by a factor of 2 for the confined reaction.

Here, we report on a detailed study of H₂ oxidation on Ir(111) with and without Gr. At room temperature and without Gr, water forms and desorbs instantaneously, while the identical reaction performed under the Gr cover leads to trapping of a dense mixed OH–H₂O structure. Furthermore, we demonstrate how the Gr doping level together with C 1s reference values for intercalated structures19 give a novel tool to follow uncover reactions in situ. Using this new tool we follow how the dense OH–H₂O structure increases its areal cover underneath Gr once O atoms are dissolved into it and subsequently reduce its areal coverage upon converting the dissolved O atoms to OH and H₂O once H atoms are dissolved into the structure.

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**EXPERIMENTAL DETAILS**

XPS experiments were collected in normal emission with an angular acceptance of ±5° at the now closed beamline 131125 at the MAX IV Laboratory. Photon energies of 120 eV for Ir 4f, 390 eV for C 1s, and 625 eV for O 1s were used. Reproducible C 1s core level shifts (CLS) as small as 20 meV can be measured on this beamline making it ideally suited for characterizing the sharp and intense C 1s peak of graphene. STM and TPD measurements were carried out at the TUMA-III Laboratory in Cologne. All STM imaging was conducted at room temperature and the STM topographs were postprocessed in the WxSM software.26 The base pressures of the XPS and STM setups were below 1 × 10⁻¹⁰ mbar. Details of the TPD experiments are explained in the Supporting Information when discussing Figure S3.

Gr was grown on a Ir(111) single crystal with the same recipe as described in previous publications.15 Oxygen exposure onto Gr is conducted in an O₂ pressure of 5 × 10⁻⁶ mbar (200 L) if not specified otherwise. The dose of 200 L is more than an order of magnitude larger than what is necessary to reach saturation coverage of oxygen on Ir(111)27,28 and full intercalation of 0.5 ML Gr on Ir(111). H₂ exposure is conducted at 5 × 10⁻⁷ mbar (100 L), if not specified otherwise. No further change in the C 1s spectrum was seen at higher hydrogen doses.

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**CALCULATIONAL DETAILS**

Density functional theory calculations were performed using an evolutionary search algorithm39,40 to determine the structure and stability for OH–H₂O mixed phases intercalated under an idealized (4 × 4) graphene covered (2√3 × 2√3)Ir(111) surface unit cell. A five layer Ir slab was used with four of the layers being fully relaxed. The calculations were performed with the real-space projector augmented wave GPAW code41 using the “dispersion-aware” M06-L functional42 which has proven successful in describing, e.g., the bonding in layered compounds43 and the hydrogenation of graphene over Ir(111).44 Throughout, the graphene lattice constant of 2.45 Å was used together with (2 × 2) k-points in the surface Brillouin zone and a grid-spacing of 0.175 Å. For calculating
the core level shifts (CLSs), the fully screened core hole approximation was used, meaning that the self-consistent total energy of the system including the core hole was evaluated, thus including final state effects. The reported shifts are referenced to a C atom in nonintercalated graphene on Ir. In practice this was done by calculating the shift in each system (nonintercalated or intercalated graphene) with respect to a single C atom attached to the bottom side of the Ir slabs. Subtraction of these shifts then yields the relative shift of each system with respect to the nonintercalated reference. With the used sign convention, a positive CLS corresponds to a shift to higher binding energies in the experiment.

### RESULTS AND DISCUSSION

Before H₂ oxidation under Gr is discussed, we briefly describe the oxidation without Gr on Ir(111). Figure 1a shows from bottom to top the O 1s spectra of Ir(111): (0) after cleaning, (1) after oxygen exposure until saturation which results in a p(2 × 1)-O structure with O atoms adsorbed in the 3-fold hollow sites, and (2) after subsequent hydrogen exposure reacting the adsorbed oxygen to water, that instantaneously desorbs. Due to the rapid desorption of the product water at the reaction temperature of 300 K, atomic oxygen (with a binding energy of 530.0 ± 0.05 eV for the O 1s core level) is the only oxygen containing species we observed. Oxygen was in these experiments initially dosed at 107 K to test for water formation and trapping at temperatures of 107 and 170 K, respectively, caused by 100 L H₂ exposure. In contrast to the final H₂ exposure at 300 K, these experiments left the oxygen phase untouched.

The process is dramatically different when Ir(111) is half covered by Gr flakes (0.5 ML), as can be seen in panel b. Prior to hydrogen dosing, the sample was saturated with oxygen by dosing 200 L of O₂ at 450 K. A slightly elevated sample temperature is needed to facilitate oxygen intercalation under the Gr flakes. As established in our previous work, the mobile O atoms resulting from dissociative chemisorption are pushed under the Gr flakes until these are completely delaminated and a p(2 × 1)-O structure forms on the entire sample, both on the bare Ir(111) and under the flakes. As the O atoms bind downward to Ir(111) the O 1s binding energy position is the same for oxygen atoms with and without the Gr cover. However, the delamination of the Gr flakes is clearly signaled by a C 1s peak shift −0.47 eV compared to pristine graphene, here called C₀, in agreement with our previous work and the work of Laciprete et al. Upon H₂ exposure, the molecular hydrogen adsorbs dissociatively on the areas not covered by Gr. The H atoms can now follow two different reaction paths in which they titrate away atomic O. They either (i) react with O on Ir(111) patches not covered by Gr or they (ii) react with O atoms under Gr. For reaction path i, we already demonstrated that water will form and desorb directly. Reaction path ii would lead to OH and/or H₂O molecules being formed, and possibly trapped, under Gr.

Comparing the spectra in panel b, before (1) and after (2) H₂ exposure, it is obvious that the O₀ and C₀ components disappear, giving evidence that the p(2 × 1)-O structure is fully removed. Furthermore, new oxygen components develop at 530.4 ± 0.1 eV, O₌, and 531.9 ± 0.1 eV, O₄, respectively, simultaneously with the reappearance of the C₀ component (59%) signaling nonintercalated graphene, and a new component C₂ at 284.37 eV (41%). Shavovsky et al. previously studied low temperature water adsorption and desorption on oxygen covered Ir(111) with high resolution XPS and assigned similar O 1s components observed at 530.5 and 531.5 eV to a mixed phase of OH and H₂O on Ir(111). Based on the simultaneous appearance of the new C₂ component and the OH and H₂O components of the mixed phase, we conclude that trapped OH and H₂O formed under 41% of the graphene flakes via reaction path ii and caused the new C₂ component. Evidence for H atoms following reaction path i comes from the finding that H₂ dosing leads to a reduction of the O 1s intensity to 35 ± 10% of the initial coverage of the p(2 × 1)-O structure.

The local coverage of the mixed OH–H₂O phase causing the C₂ component can be found from the absolute intensities of the OOH and O₄H₂O components and the relative intensity of the C₂ component. To obtain a precise value for the coverage of the mixed OH–H₂O phase we dosed hydrogen onto O-intercalated Gr flakes without moving the sample and while measuring the C 1s and O 1s regions simultaneously (see Figure S2). From this experiment we find that the mixed OH–H₂O phase has a surprisingly high local density of 0.8 O-containing molecules per Ir surface atom. This density is almost the double of the experimentally determined O-density for the p(2 × 1)-O structure (0.44 O atoms per Ir surface atom). The high density implies that O atoms trapped under Gr condense into a dense mixed OH–H₂O phase upon reaction with hydrogen. The reappearance of the C₀ component in panel 2 of Figure 1b is a necessary consequence of the higher oxygen density of the dense OH–H₂O phase.

Further support for the formation of OH and H₂O under Gr comes from a temperature-programmed desorption (TPD) experiment in which 0.5 ML Gr on Ir(111) was exposed sequentially to O₂ and H₂. The H₂O desorption peak temperature of 440 K (see Figure S3) is significantly higher than the desorption peak temperature of the pure H₂O bilayer (170 K) or a mixed OH–H₂O phase (210–235 K) formed on bare Ir(111) by dosing water onto an O precovered Ir(111) surface at low temperatures. Possible reasons for the much increased desorption temperature for the phase formed under Gr are discussed below.

The formation of the dense OH–H₂O phase under oxygen-intercalated Gr can be followed in real time by acquiring scanning tunneling microscopy (STM) movies during H₂ exposure. Panels a–c of Figure 2 show snapshots from such a movie taken during exposure to S × 10⁻⁹ mbar of H₂ at room temperature (the full movie can be seen in the Supporting Information), while panels d and f of Figure 2 show schematic representations of panel a and c, respectively. Upon H₂ exposure the formation of OH–H₂O islands beneath Gr is visible as bright areas. After the H₂ intercalation has terminated Gr appears in two heights as evident by the linescans in Figure 2e. The lower areas arise from Gr that is no longer intercalated and thus is laminated to the Ir substrate, while the 1.5 Å higher areas arise from the dense OH–H₂O phase (see also Figure 2f). The phase boundary between the OH–H₂O phase and the nonintercalated Gr is sharp and follows the moire pattern as visible in Figure 2e. Apparently, the chemical inhomogeneity of Gr's binding to Ir(111) affects the shape of the OH–H₂O phase formed beneath.

Based on our XPS, TPD, and STM results, we conclude that room temperature hydrogen dosing onto O-intercalated Gr flakes leads to a mixed dense OH–H₂O phase exclusively formed and trapped under Gr. The intercalated OH–H₂O phase remains trapped under Gr up to a temperature of 440 K.
In contrast, upon room temperature H2 exposure of oxygen adsorbed to bare Ir(111) the reaction products desorb instantaneously.

Our finding of an intercalated dense OH−H2O mixed phase is supported by the density functional theory calculations summarized in Figure 3. The stoichiometry and density of the densest structures shown in Figure 3, parts e and f. In Figure 3 is also shown the calculated average adsorption potential energies of the H atoms relative to H in the hydrogen molecule. These calculations reveal that the energy gain per H atom increases from 0.78 eV to more than 0.9 eV as the structures develop from a 1:1 H:O ratio and no contraction to denser and more H-rich structures. We note that by using the evolutionary search algorithm for the structural search (covering several hundred different structural candidates per stoichiometry and density) our computed structures are unbiased by any expectations or experimental knowledge. We thus attribute significance to the finding at mid-densities—Figure 3c,d—of atomic O species dissolved in the OH−H2O network and to the finding of alternating OH and H2O rows in the most dense structure, Figure 3f. For this O12H18 phase (formally a p(2 × 1)−OH−H2O phase), we find a DFT calculated core level shift (CLS) of +0.18 to +0.22 eV (the CLS is slightly different for the different C atoms in graphene) agreeing relatively well with the experimentally observed shift of +0.28 eV for the C2 component. Furthermore, the finding in DFT of a preference for highly dense phases fits well with the experimental observations of a local coverage of the OH−H2O structure (0.8 ML), which is approximately double that of the p(2 × 1)-O structure (0.44 ML), as well as with the partial relamination of the Gr flakes that occurs in the oxygen-intercalated regions once the oxygen leaves these regions upon forming the dense phases.

At this point, it should be underlined that we did not perform a complete structural characterization of the intercalated OH−H2O phase here. This would require structural information on the intercalated phase, which we did not observe in our STM imaging. Most plausible, the OH−H2O dense phase below graphene flakes is at room temperature not perfectly ordered and displays slight local density variations. Nevertheless, the thermodynamic driving force for the formation of dense OH−H2O phases below graphene found in DFT explains the formation of the dense OH−H2O phase observed experimentally.

Comparing the DFT-calculated energies of the dense O12H18 phase with and without Gr, we determine an intercalation cost of 0.14 eV per OH−H2O unit. Thus, from the adsorption enthalpies alone we also expect preferential formation of the dense OH−H2O structure on bare Ir(111) patches in apparent contradiction to our experimental observations.

To explain this apparent contradiction, we studied the stability of various phases adsorbed on bare Ir(111) with respect to desorption of a water molecule. We assume that the barrier for water desorption can be described by the DFT-calculated desorption energy alone; i.e., we neglect any additional kinetic barriers. This should be a good approximation since water adsorption is typically a nonactivated process. Desorption of a water molecule from the dense O12H18 structure costs 1.36 eV, which according to the Redhead formula would correspond to a desorption temperature of 462 K and a residence time of 2.4 × 10^8 s at 300 K if first order desorption, a frequency factor of 2.9 × 10^{14} s^{-1/3} and a heating rate of 5 K/s are assumed.

The dense O12H18 phase is therefore clearly stable on bare Ir(111) at room temperature. For comparison, we also considered the H-poor O6H2 phase as a model for the very first phases that would form upon the initial exposure of the p(2 × 1)-O structure to H2. The most stable structure found

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(see Figure S5 in the Supporting Information) consists of a single water molecule surrounded by atomic O. Desorption of this water molecule now costs only 0.77 eV, giving rise to a desorption temperature of 266 K and a residence time of 30 ms at 300 K. This phase is therefore clearly unstable with respect to water desorption at room temperature.

From these results, it is now evident why the dense O12H18 does not form at room temperature on bare Ir(111): As hydrogen is dosed onto p(2 × 1)-O without Gr, less dense phases containing water molecules surrounded by atomic O initially form. Since in these phases there is no possibility for attractive hydrogen bonding to neighboring OH groups or other water molecules (in contrast to the case of the denser phases shown in Figure 3), the O-surrounded water molecules are highly unstable and immediately desorb at 300 K. Thus, upon H2 exposure of the p(2 × 1)-O structure, the oxygen is simply titrated away, and the denser phases never have a chance to form, in perfect agreement with our experiments. Beneath Gr, the O6H2 phase also forms initially, but since it is impossible for water to desorb through the Gr film, the phase will be trapped. Continued hydrogen dosing and contraction will lead to the formation of the denser and highly stable phases such as O12H18.

Comparing the DFT-calculated desorption temperature of water from O12H18 on bare Ir (462 K) with the experimental desorption temperature of water from O12H18 trapped beneath Gr (440 K) we find a very good agreement. We note that the above-mentioned previous studies of water desorption from a mixed OH–H2O phase formed on bare Ir(111) found much lower desorption temperatures of around 210–235 K, but an explanation is hampered by the fact that no detailed characterization of the formed phases were given. A likely explanation for the lower desorption temperature in these previous studies is that H2O was dosed onto O-precovered Ir(111) while here the OH–H2O phase was formed by dosing H2 onto O-precovered Ir(111) with Gr islands. As OH can be formed without consuming surface oxygen if H2O is dosed onto O–Ir(111) the structures formed upon water dosing are expected to host also atomic oxygen. As discussed below this will lower the desorption temperature.

We have now found that one cycle of O intercalation and subsequent H2 exposure leads to formation of a dense OH–H2O structure exclusively intercalated under Gr. Next we will demonstrate that it is possible to dissolve oxygen into this structure, already at room temperature, leading to a less dense mixed structure containing: atomic oxygen, H2O, and OH. Furthermore, we will demonstrate how the C 1s signal of graphene can be used to probe the undercover reaction and, in particular, how this can be used to distinguish mixed and coexisting phases very easily.

In Figure 4a, we compare O 1s and C 1s spectra of Gr partly intercalated by the dense OH–H2O structure before and after an additional room temperature oxygen exposure cycle. Focusing first on the C 1s spectra it is clear that the C2 component assigned to the dense OH–H2O structure is removed upon the oxygen dosing and replaced by a broad C3 component located at 283.95 eV and thus shifted −0.14 eV, with respect to pristine graphene. No C1 component shifted by −0.47 eV and signaling the p(2 × 1)-O phase intercalated under Gr are observed. Therefore, formation of this phase is exclude. In contrast to the significant changes in the C 1s spectra, the OH and H2O components in the O 1s spectra are essentially unaffected by the oxygen dosing as demonstrated by

Figure 4. O-uptake in the superdense OH–H2O phase studied with XPS and STM. (a) O 1s and C 1s spectra of Gr exposed to (2) one cycle of (O2 + H2), (3) an additional O2 exposure, and (4) after two cycles of (O2 + H2). (b) Left STM image: UHV, after 4 cycles of (O2+H2). Right STM image: During additional exposure to 1 × 10−2 mbar of O2 after approximately 30 min (265 L). Image size 60 × 70 nm, U = −1 V, and I = 1 nA. Schematic representation of the STM images are shown below. The colors used are in line with those used for the XPS components and the black lines show Ir step edges. (c) Relative area of the C2 component versus the number of (O2 + H2) cycles obtained from XPS experiments.

Figure 4a and in additional in situ experiments shown in Figure S2. The simplest scenario required to reconcile these observations is that O dissolves into the OH–H2O structure, thereby modifying the OH–H2O interaction (turning C2 into C3), while keeping the amount of OH–H2O unchanged. Further, Figure 4a nicely demonstrates how the Gr doping level can be used to follow the reaction under cover. The disappearance of the C2 and the appearance of the C3 component are, for example, crucial for concluding that oxygen dissolves into the OH–H2O structure.

The in situ experiments in Figure S2 further reveal that the Opre-coverage is reduced to half of the coverage of the p(2 × 1)-O structure, suggesting that the majority of the oxygen adsorbs on bare Ir(111) patches and only a small fraction is dissolved into the OH–H2O structure. Since the dense OH–H2O structure intercalated under Gr initially covers all Ir sites, we expect an intercalated O–H2O–OH structure to increase its coverage underneath the Gr cover causing more intercalation
and less nonintercalated Gr. Both our XPS and STM data agree with this picture. In the XPS experiments we observe that the area of the C₆ component is reduced by 23% when the dense OH−H₂O structure is saturated with oxygen at room temperature (compare points 2 and 3 in Figure 4a), and inspection of the STM images in Figure 4b shows that the C₆ marked areas are reduced by 34% (upper right corner) and 20% (lower left corner), respectively.

When the intercalated O−H₂O−OH structure is exposed to H₂ again we find that the dissolved oxygen can be fully converted to OH and H₂O causing the C₆ component to reappear with increased intensity. In more detail we observe that the C₄ component, signaling the mixed O−OH−H₂O phase, disappears upon H₂ dosing while the C₂ component, signaling the dense OH−H₂O phase, reappears with a 10% increase in relative intensity (Figure 4, parts a and c). Upon continued cycles of subsequent O₂ and H₂ dosing at room temperature the relative intensity of the C₂ component increases more and more for each cycle as shown in Figure 4c. The increase for each cycle is moderate, in agreement with our previous conclusion that only a smaller amount of oxygen atoms are dissolved into the OH−H₂O phase upon room temperature oxygen dosing.

The formation of the less dense O−H₂O−OH structures under Gr upon O uptake in the dense OH−H₂O phase is supported by our DFT calculations and the evolutionary search algorithm. Analogously to the calculations of the H uptake, the stoichiometry and density of O−H₂O−OH structures were varied from the density of the O₂H₁₀ phase with a 3:2 H₂O ratio down to half of that H density and a 9:10 H₂O ratio. Our calculations, shown in Figure 5 together with the average adsorption potential energies of the O atoms given relative to O in the oxygen molecule, reveal that 1.6 to 1.3 eV per O atom is gained when oxygen dissolves in the dense OH−H₂O phase and converts it to a more open structure. The best agreement between the measured C₄ component and the DFT calculated adsorption energy per O atom in eV upon adsorption from the gas phase along with the degree of expansion of the structure with respect to the superdense OH−H₂O phase are included in the figure.

CLS is found for the O₁₀H₁₂ and O₁₀H₉ phases. For these phases we find DFT calculated CLSs of −0.09 ± 0.01 (O₁₀H₁₂) and −0.17 ± 0.01 O₁₀H₉ close to the experimental position of the C₄ component at −0.14 eV. The observed reduction of the nonintercalated Gr area of 20−34% in our STM and XPS experiments translate into a 29−49% increase of the intercalated area fitting best with the expected 50% increase of the areal coverage when the O₁₀H₁₂ structure is formed upon O-uptake.

**CONCLUSIONS**

We investigated Ir(111) fully covered with chemisorbed oxygen and partly covered with Gr flakes where the oxygen is intercalated. Upon room temperature hydrogen exposure, adsorbed oxygen is titrated away from the bare Ir(111), while underneath graphene oxygen is hydrogenated giving rise to a dense OH−H₂O phase. Ab initio calculations show that this dense phase is thermodynamically more stable than dilute OH−H₂O phases. Experimentally, the dense OH−H₂O phase is not observed on bare Ir(111), as its formation requires going through the dilute OH−H₂O phases that simply desorbs without the confining cover of the Gr. We have demonstrated that the dense OH−H₂O phase facilitates oxygen intercalation under Gr already at room temperature and by using the Gr doping level as an additional probe we showed that O atoms are dissolved into the OH−H₂O phase making it less dense and increasing its areal coverage. Subsequent hydrogen dosing leads to the formation of more OH and H₂O, and cycles of O₂ and H₂ dosing can therefore be used as an effective method to increase the area of the OH−H₂O phase below the graphene flakes. We expect that many other molecules can be dissolved into the dense OH−H₂O phase trapped below graphene. This finding paves the way for future studies of reactions taking place in dense OH−H₂O phases mimicking the first layer of a water film on metal surfaces in simple room temperature experiments.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c10289.

STM movie corresponding to Figure 2 (MP4)

Ir 4f spectra corresponding to Figure 1, O 1s and C 1s spectra recorded in situ while exposing the sample to O₂ and H₂, temperature-programmed desorption of the OH−H₂O formed under Gr, O 1s and C 1s spectra acquired as a function of cycles of subsequent oxygen and hydrogen dosing, model of the most stable structure of the H-poor O₉H₉ phase (PDF)

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Notes
The authors declare no competing financial interest.

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