Facile oxygen intercalation between full layer graphene and Ru(0001) under ambient conditions

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ABSTRACT

Graphene coatings have been widely considered as protection layers on metal surfaces to prevent surface oxidation and corrosion in gaseous atmospheres. Here, using in-situ ambient pressure X-ray photoelectron spectroscopy we demonstrate that oxygen intercalation readily occurs at full monolayer graphene/Ru(0001) interfaces in 0.5 Torr O_2 around 150 °C, resulting in decoupling of the graphene overlayer from the Ru surface and oxidation of the metal surface. Moreover, oxygen intercalation has been observed even upon illumination of the graphene/Ru(0001) surface with an infrared lamp in air. These results indicate that the stability of graphene/metal interfaces under ambient conditions should be taken into consideration for future applications.

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1. Introduction

Graphene (Gr), a single layer of sp^2-bonded carbon arranged in a honeycomb lattice, presents many outstanding physical and chemical properties [1–5]. Among them, its low chemical reactivity, impermeability to gases, and excellent mechanical strength and stiffness allow the material to be used as protection layers for metal surfaces, inhibiting surface oxidation in O_2 atmosphere or corrosion in air [6–15]. It has been demonstrated that reactive metals, such as Fe, Ni, and Cu, coated by graphene layers are resistive against oxidation or electrochemical corrosion reactions under ambient conditions [7,9,11]. Surface science studies confirm that Gr/Pt(100), Gr/Ru(0001), and Gr/Rh(111) surfaces remain intact when exposed to air at room temperature (RT) [13–15].

Recent experiments, however, show that many gases can intercalate under graphene flakes grown on metal surfaces [16–29]. Particularly, oxygen intercalation at the graphene/metal interfaces in O_2 atmosphere and at elevated temperatures has been reported [16–19]. For example, we found that oxygen intercalation occurs at submonolayer Gr/Ru(0001) interfaces when treating the sample in 1.6×10^{-6} mbar O_2 at 600 K [16]. Sutter et al. used low energy electron microscopy to monitor in-situ O_2 adsorption on graphene islands and confirmed the formation of an O-adlayer at the Gr/Ru(0001) interface [17]. A similar phenomenon was also observed by Starodub et al. and Liao et al., in which the oxygen adsorption at the Gr/Ru interface happens in 10^{-6} Torr range O_2 and above 300 °C [18,19]. Using scanning tunneling microscope (STM) and X-ray photoelectron spectroscopy (XPS), Larciprete et al. and Granas et al. demonstrated the oxygen intercalation

on an extended layer of graphene on Ir(111) in 10^{-3} mbar O_2 and around 500 K [20,21].

The contrasting results from protective coating of graphene under ambient conditions versus oxygen intercalation of graphene in ultrahigh vacuum (UHV) and at elevated temperatures raise the following questions: To which degree can graphene layers protect metal surfaces from oxidation and corrosion? Are there any temperature and pressure limits for the graphene coating effect? In the present work, taking Gr/Ru(0001) as the model system we study O_2 adsorption on the full graphene layer under near ambient conditions. In-situ ambient pressure XPS (AP-XPS) was applied to study the surface oxidation of Ru(0001) covered by a full graphene layer in 0.5 Torr O_2, where we observe clear evidence for oxygen intercalation and the onset of Ru oxidation around 150 °C. Moreover, oxygen intercalation was also observed in air under an infrared lamp, which means that the interface reaction process indeed takes place in air and slightly above RT. Considering that the future graphene-based devices and materials may work in warm ambient environments, the facile oxygen intercalation at the graphene/metal interfaces may affect their performance significantly and should be taken into consideration.

2. Experiment

XPS and ultraviolet photoelectron spectroscopy (UPS) measurements were performed in an Omicron multiprobe UHV system, which consists of a preparation chamber, a spectroscopy chamber, and a microscopy chamber [16,30]. In addition, a high pressure cell has been attached to the UHV system, where gases with pressure up to 4 bar can be dosed and samples be heated [31,32]. Samples treated in this cell were transferred back to the UHV chambers for further surface science measurements without exposing them to air. XPS spectra were

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acquired using Mg Kα ($h\nu = 1253.6$ eV) radiation with an electron analyzer pass energy of 30 eV. UPS spectra were recorded using normal emission with He I ($h\nu = 21.2$ eV) and He II ($h\nu = 40.8$ eV) radiation. A full monolayer graphene overlayer (1 ML Gr) was obtained via exposure of the clean Ru(0001) surface to 5.2×10^{-7} mbar C_2H_4 at 827 °C for 10 min [16]. O_2 titration at 1.3×10^{-6} mbar O_2 was applied to make sure that the Ru(0001) surface was fully covered by the graphene overlayer. O_2 intercalation on the Gr/Ru(0001) surface under ambient condition was conducted in the high pressure cell. In addition, O intercalation was also attempted by putting the 1 ML Gr/Ru(0001) sample in air with and without an illumination by an infrared lamp. The treated sample was then loaded back into the UHV system for subsequent XPS/UPS measurements.

AP-XPS investigations were performed at beamline 11.0.2 at the Advanced Light Source, using an ambient pressure XPS endstation described in detail in Ref. [33]. The full monolayer graphene on Ru(0001) was prepared using the same recipe as that in the Omicron system. High purity O_2 was leaked into the analysis chamber through a high precision leak valve. Ru 3d and O 1 s spectra were in-situ acquired using 390 and 638 eV photons, respectively. The Fermi edges were measured at each of the photon energies, which were used to calibrate the binding energy positions. In high pressure O_2 atmosphere each measurement was carried out at a new sample position to avoid any potential beam damage.

STM images were acquired in a Createc low-temperature STM (LT-STM) system. The O-intercalated Gr/Ru(0001) surfaces were first obtained by exposing the 1 ML Gr/Ru(0001) surfaces to 0.5 Torr O_2 at 200 °C in the high pressure cell. The samples were then taken out from the Omicron system and transferred to the Createc LT-STM system. Before imaging, the sample was annealed at 250 °C for 5 min to remove any surface contaminations during transfer in air. STM measurements were conducted at liquid nitrogen temperature in constant current mode using an electrochemically etched W tip.

3. Results and discussions

We started our investigations of O_2 intercalation at the 1ML Gr/Ru(0001) surface using AP-XPS, and the same O_2 adsorption experiments were made on a clean Ru(0001) for comparison (Fig. 1). It has been shown that the Ru $3d_{5/2}$ peak of the clean Ru(0001) surface is composed of a bulk component (Ru_B) at 280.10 eV reflecting the emission from the Ru atoms below the first layer, and a surface component (Ru_S) at 279.80 eV originating from the top Ru layer [34,35]. Covering Ru(0001) surface by graphene may change the Ru $3d_{5/2}$ line shape significantly due to the strong interaction of graphene carbon atoms with Ru surface atoms [36–38]. Nevertheless, a strong shoulder peak at the lower binding energy position compared to that of the bulk component is still present, which is attributed to the surface Ru atoms interacting strongly with graphene (noted as interface component/Ru_I) [35,38]. Moreover, the Ru $3d_{3/2}$ peaks have been overlapped with newly appearing C 1 s peaks. The C 1 s signals have been analyzed carefully, showing that two C 1 s components with the energy separation by 0.60 eV and relative ratio of 5:1 can be identified [29,38]. Here, we also observed a larger C 1 s component at 285.00 eV (noted as C1) attributed to C atoms interacting strongly with the surface Ru atoms and a smaller component at 284.35 eV (noted as C2) assigned to the nonbonding C atoms with the surface Ru atoms (Fig. 1(a)).

The 1 ML Gr/Ru(0001) surface was exposed to 0.5 Torr O_2 while the sample temperature was ramped from RT to 350 °C. This pressure was taken since it is close to the upper limit of the gas pressure applied in the AP-XPS endstation for in-situ experiments. Shown in Fig. 1(a) and (b) are the recorded AP-XPS Ru 3d and O 1 s spectra. We can see that there is no obvious O 1 s signal at the temperatures of RT and 100 °C. Note that the small signal at 531.1 eV may be due to the weak functionalization of graphene by oxygen [39]. At 150 °C a strong peak at 529.9 eV appears, which can be attributed to atomic oxygen species

adsorbed on the Ru(0001) surface [16,40]. In addition, a new component at 283.64 eV appears in the Ru 3d spectrum with the binding energy lower than that of the metallic Ru $3d_{3/2}$ peak. When the surface was further heated to 200 °C the O 1 s peak intensity continues to increase, and the 283.64 eV component becomes much stronger. The same O_2 exposure onto the clean Ru(0001) surface already results in strong surface oxidation, forming new components at higher binding energy positions in both Ru $3d_{5/2}$ and Ru $3d_{3/2}$ peaks (Fig. 1(c) and (d)). Accordingly, the component appearing at 283.64 eV on the O_2-exposed Gr/Ru(0001) surface above 150 °C should not be from any oxidized Ru components but can only be attributed to the C signal (noted as C3). Similar to our discussion about CO-intercalated Gr/Ru(0001) surface [29], the C3 component is from the graphene C atoms, which are decoupled from the Ru surface by the oxygen intercalation. Both C1 and C2 components now shift down to the same low binding energy position due to the weaker interaction of graphene with the O-Ru(0001) surface than that between graphene and Ru(0001). It should be noted that the binding energy shift from C1 to C3 is as large as − 1.36 eV, which demonstrates the strong effect of the interfacial O intercalation on the electronic state of graphene C atoms. When heating the 1 ML Gr/Ru(0001) surface in 0.5 Torr O_2 to 200 °C and eventually reaching to 350 °C, the C3 component almost stays unchanged, which implies that the surface C atoms remain stable under the present oxidation condition.

On the basis of the comparative studies in O_2 exposure of the 1 ML Gr/Ru(0001) surface and the clean Ru(0001) surface, a few notable differences can be identified concerning the oxidation of the Ru surface with and without the graphene cover. In the low temperature regime (RT – 150 °C), strong oxygen adsorption has been observed on the clean Ru(0001) surface even at RT, in which the Ru 3d surface component cannot be observed any more due to the saturation of surface Ru atoms by adsorbed oxygen atoms. However, for the 1 ML Gr/Ru(0001) surface no big change was observed in the Ru 3d and O 1 s spectra below 150 °C. Only upon heating to 150 °C has the Ru_I component been strongly attenuated. This result implies that graphene can protect the Ru surface from oxidation under mild oxidation conditions, for instance, 0.5 Torr O_2 at temperatures below 150 °C here. In the intermediate temperature regime (150–300 °C), the ratio of O 1 s peak area to Ru $3d_{5/2}$ peak area calculated on the two surfaces (Fig. 1(e)) shows that the amount of oxygen increases slowly on the 1 ML Gr/Ru(0001) surface between 150 and 350 °C, while the oxidation proceeds continuously on the clean Ru(0001) surface. Above 300 °C, the O1s peak from the O_2-exposed Ru(0001) surface shows an obvious broadening, and a shoulder component at 529.5 eV appears, which is due to RuO_2 (Fig. 1(b)) [40–43]. At 350 °C the bulk metallic Ru 3d signal almost disappeared and the Ru $3d_{5/2}$ peak is now located at 280.7 eV, which is from RuO_2 phase grown on the Ru(0001) surface. In contrast, both Ru 3d and O 1 s spectra acquired from the Gr/Ru(0001) surface indicate that only a small part of the surface Ru species have been transformed into RuO_2 even at 350 °C. Obviously, the quicker oxidation of Ru surface region occurs on the bare Ru(0001) surface than the Gr/Ru(0001) surface.

From the O-intercalated Gr/Ru(0001), oxygen desorption was measured by temperature-programmed heating in UHV combined with in-situ XPS measurements. The bottom curve in Fig. 2 is from the O-intercalated sample, which was prepared by heating the 1 ML Gr/Ru(0001) surface in 0.5 Torr O_2 at 200 °C and then annealing in UHV up to 194 °C. On the O-intercalated surface, the graphene layer is almost completely freestanding with C 1 s binding energy at 283.64 eV (C3). The Ru $3d_{5/2}$ peak consists of the bulk Ru component at 280.1 eV and a component due to Ru bonded to surface and subsurface oxygen species (281.0 eV, RuO_x). There is no obvious change in the spectra when heating from RT to 418 °C. Above 418 °C both the RuO_x and C3 components become weaker and, simultaneously, the intensity of the Ru_B and C1 components increases. At 472 °C the C3 component has been completely converted into the C1 and C2 components. Meanwhile, the RuO_x component disappears and the Ru $3d_{5/2}$ peak reassumes its original shape consisting of Ru_B and Ru_I components. These results indicate
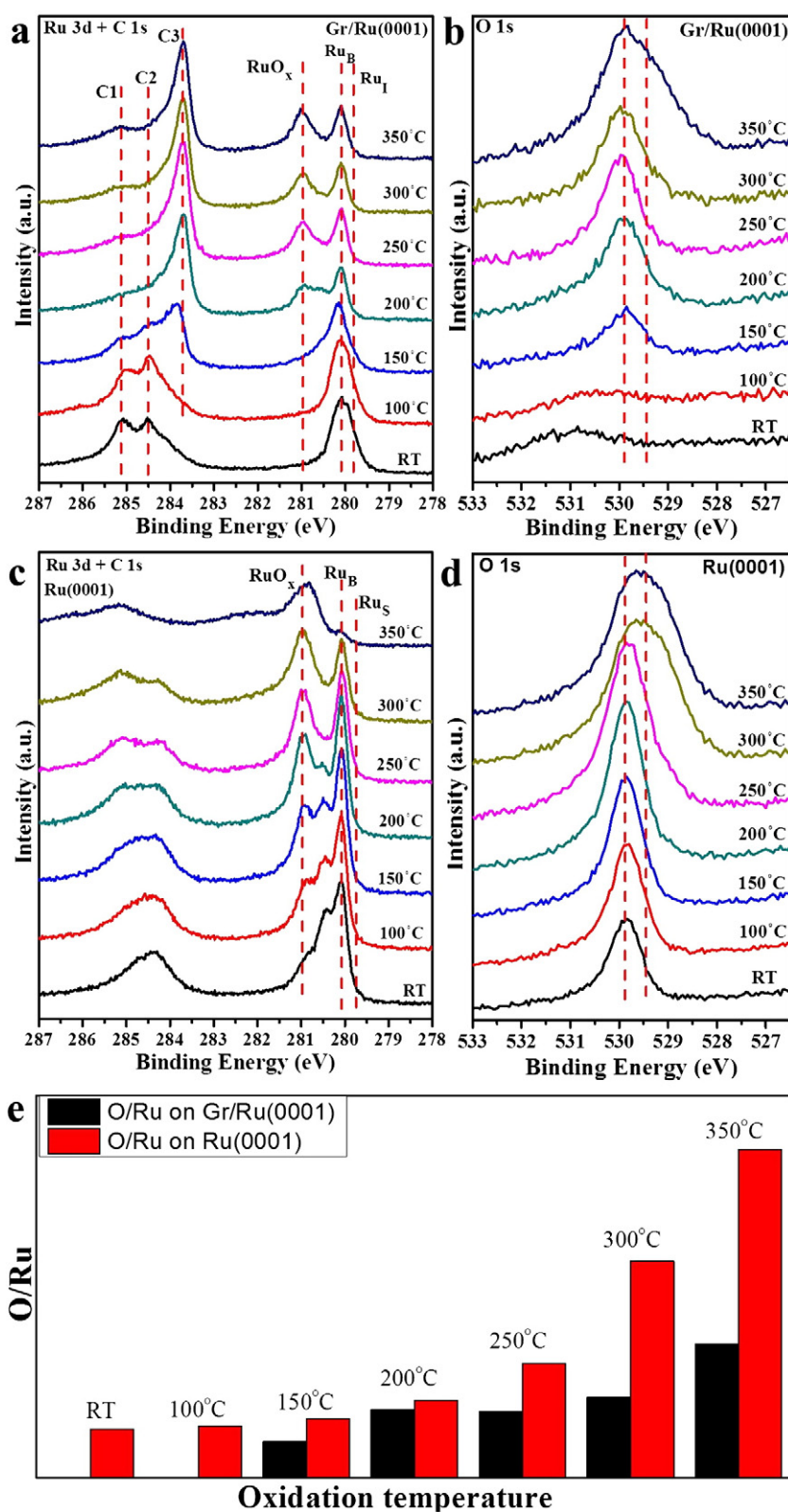
Fig. 1. In-situ AP-XPS Ru 3d + C 1 s spectra (a, c) and O 1 s spectra (b, d) of the 1 ML Gr/Ru(0001) (a, b) and clean Ru(0001) (c, d) surfaces exposed to 0.5 Torr O_2 at various temperatures. (e) O 1 s/Ru $3d_{5/2}$ intensity ratios of the 1 ML Gr/Ru(0001) and clean Ru(0001) surfaces treated in 0.5 Torr O_2 at the indicated temperatures.

that the graphene overlayer has gained its strong interaction with the Ru surface due to complete oxygen desorption. The oxygen desorption experiment also confirms that the interaction of the graphene overlayer with the Ru substrate can be reversibly tuned by intercalation/desorption of oxygen atoms at the Gr/Ru interface.

Moreover, it is noticed that oxygen atoms desorb from the Ru surface in a facile way, i.e. between 420 and 470 °C. In contrast, oxygen desorption from the O-saturated Ru(0001) surface necessitates an annealing temperature as high as 1000 °C. The easier oxygen desorption from the Gr/Ru interface can be attributed to the confinement effect of the
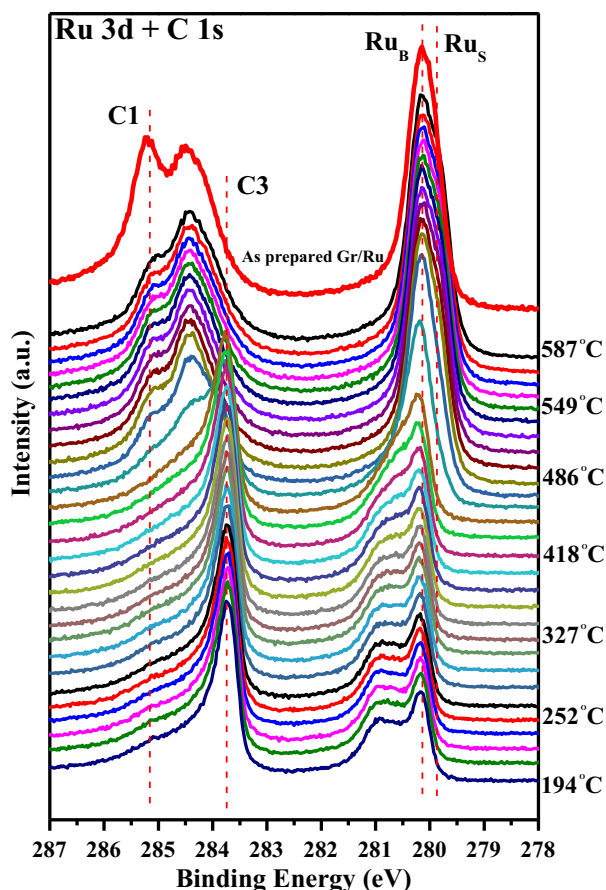
Fig. 2. In-situ AP-XPS Ru 3d + C 1 s spectra acquired from the O-intercalated 1 ML Gr/Ru(0001) surface annealed in UHV at increasing temperatures from RT to 587 °C with the heating rate of 15 °C/min. Because of no change observed at low temperature range, the spectra were given between 194 and 587 °C. For comparison, a spectrum of the as-prepared 1 ML Gr/Ru(0001) surface was included (the top red line).

Fig. 3. He II UPS spectra of the 1 ML Gr/Ru(0001) surface treated in 0.5 Torr O_2 at different temperatures. For comparison, a spectrum of the O-intercalation Gr/Ru(0001) surface annealed in UHV at 523 °C was also included.

graphene cover, which destabilizes adsorbates at the Gr/metal interfaces [17,24,29]. On the other hand, the possibility that oxygen removal is facilitated by the oxidation of surface C atoms cannot be excluded [17, 20]. The top curve in Fig. 2 was taken on the fresh 1 ML Gr/Ru(0001) surface. Compared to the spectrum from the surface subjected to the oxygen intercalation and oxygen desorption processes, the relative intensity of the C1s peak becomes lower, which means that a substantial part of surface C atoms have been etched by oxygen.

The oxygen adsorption and desorption processes were also investigated by UPS. As described above, the 1 ML Gr/Ru(0001) sample was treated in the high pressure cell in 0.5 Torr O_2 at different temperatures and then transferred to the UHV chambers for measurements. The heating in the high pressure cell was done as follows: the temperature was first ramped to the set point value, and then the heater was switched off. At the same time, the high pressure gas was quickly introduced in the cell. Thus, the real temperature of the sample surface in high pressure O_2 may be lower than the set point value. Fig. 3 shows the UPS He-II spectra acquired under various treatment conditions. The main feature at 9.5 eV is characteristic for the graphite-derived π state [44,45]. Increasing the temperature to 200 °C, we observed an obvious shift of the main peak to a lower binding energy position. After heating at 250 °C, the peak at 7.0 eV becomes dominant, which is similar to the π state of the bulk graphite surface [46,47]. Similar to the XPS results, the UPS data confirm the decoupling of the graphene overlayer induced by the oxygen intercalation. After annealing the O-intercalated Gr/Ru(0001) surface at 523 °C in UHV, the UPS spectrum almost
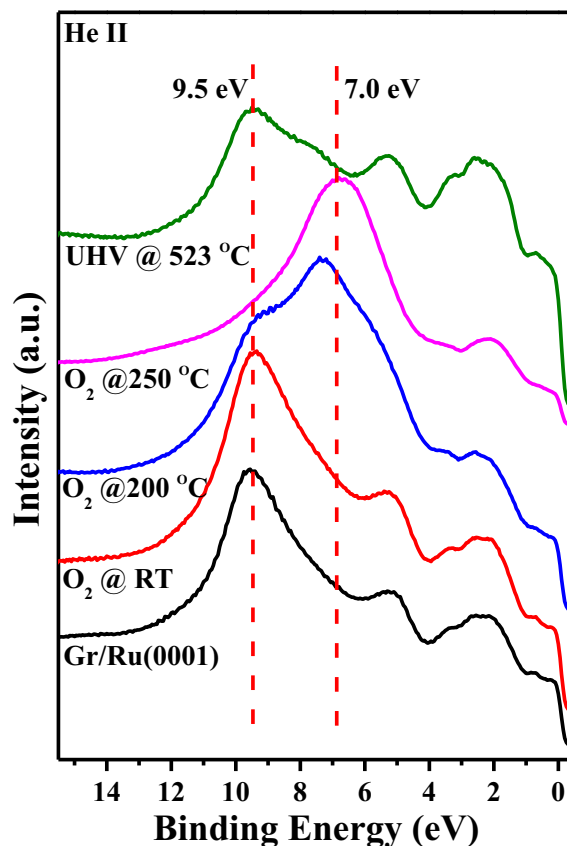
resembles the line shape and line position of the clean Gr/Ru surface, suggesting that the intercalated oxygen species have completely desorbed.

It is known that STM images of monolayer graphene grown on the Ru(0001) surface present a typical moiré pattern due to the strong Gr-Ru interaction and the lattice mismatch between Gr and Ru(0001) [48–52]. However, the O-intercalated Gr/Ru(0001) surface shows much lower corrugation and the characteristic moiré patterns are no longer observed due to the structural decoupling of the graphene from the substrate surface (Fig. 4(a)) [16,17]. The atomically resolved STM image demonstrates the perfect graphene lattice (Fig. 4(b)). After annealing the O-intercalated Gr/Ru(0001) surface in UHV at 523 °C, the moiré patterns were recovered on the surface (Fig. 4(c)). Moreover, high resolution STM image indicates the presence of surface defects in the graphene lattice, probably due to the etching of carbon atoms by oxygen. Both UPS and STM results are consistent with the AP-XPS experiments.

Compared to the previous works which demonstrate the occurrence of oxygen intercalation in 10^{-6} Torr range O_2 and around 300 °C, our present work shows that lower intercalation temperature are needed at higher O_2 pressures, here 0.5 Torr. Therefore, it is expected that the oxygen intercalation may happen at even lower temperatures in higher pressure O_2, such as in ambient pressure O_2. To test this hypothesis, the 1 ML Gr/Ru(0001) surface was illuminated by an infrared lamp in air (200 mbar O_2), which gave a sample temperature well below 100 °C. The subsequent XPS and UPS measurements of the illuminated surface (Fig. 5) show that a strong O 1 s peak with a binding energy of 529.9 eV appears which is attributed to atomic oxygen species absorbed on Ru(0001). In addition we observe a downshift of the graphite-derived π state from 9.5 to 7.0 eV. On the basis of the above discussions, these results confirm oxygen intercalation of the graphene overlayer,
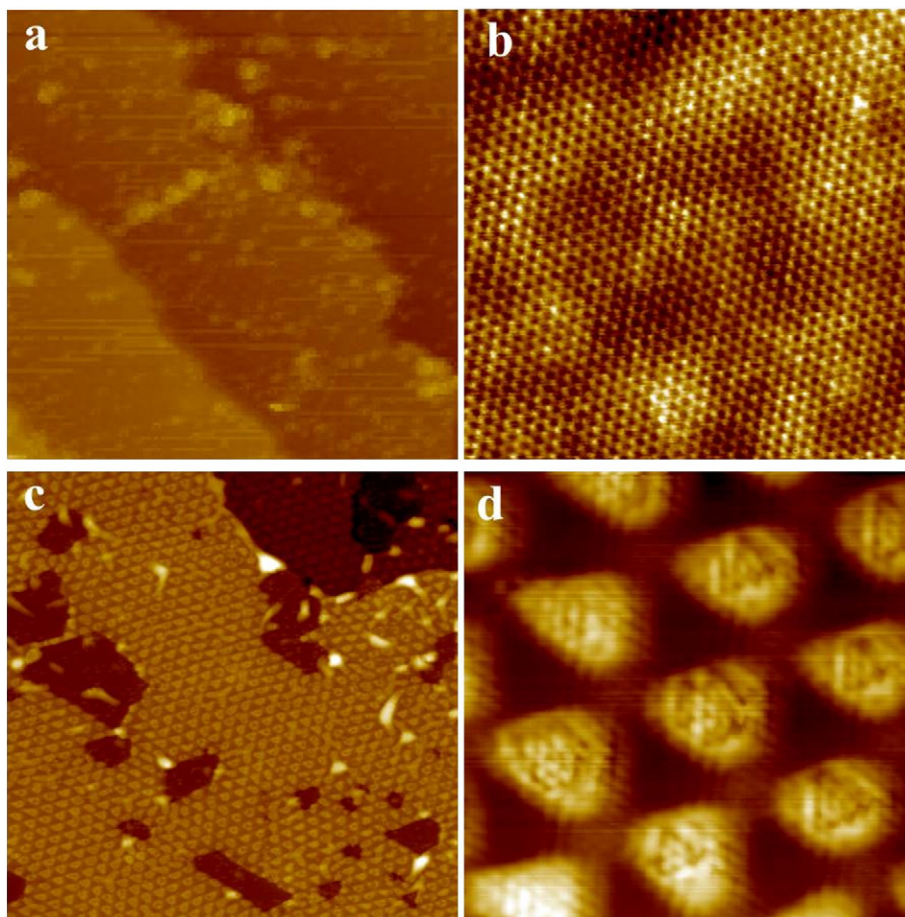
Fig. 4. LT-STM images from the O-intercalated 1 ML Gr/Ru(0001) surface (a, 100 nm × 100 nm; b, 10 nm × 10 nm), and the surface annealed in UHV at 523 °C (c, 100 nm × 100 nm; d, 10 nm × 10 nm).

resulting in decoupled graphene on Ru (0001). The O-intercalation process has been illustrated by Fig. 6. After annealing the O-intercalated 1 ML Gr/Ru(0001) surface in UHV at 523 °C, most of the surface oxygen

species has been removed. At the same time, the peak at 7.1 eV shifts back to 9.5 eV, i.e. to the position of that for the clean Gr/Ru(0001) surface. The result indicates that the higher O_2 partial pressure the
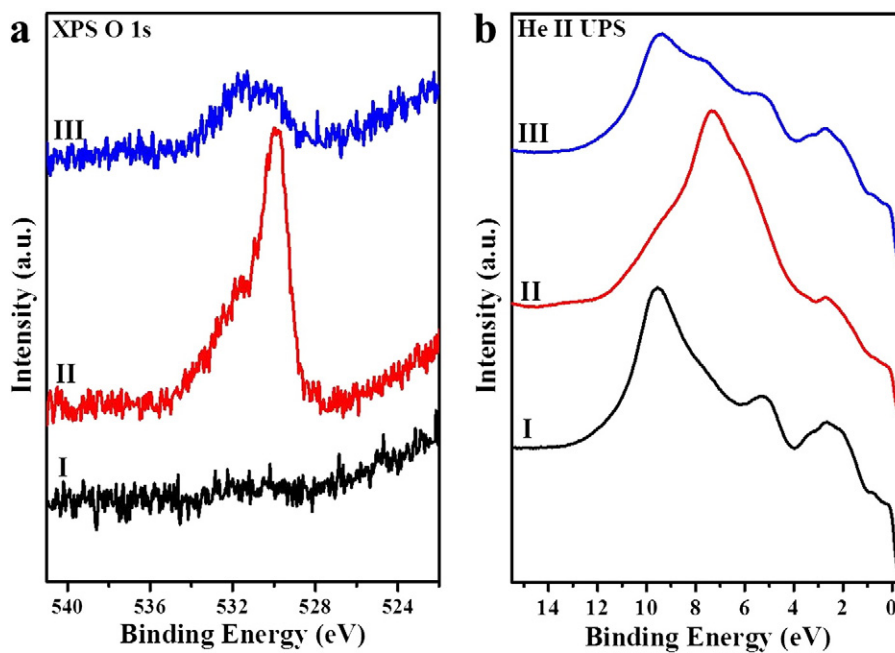
Fig. 5. XPS O 1 s spectra (a) and He II UPS spectra (b) of the 1 ML Gr/Ru(0001) surface illuminated by an infrared lamp in air for 5 h. I: the as-prepared Gr/Ru(0001) surface; II: illuminated surface, III: the surface annealed in UHV at 523 °C.

lower temperature needed for the oxygen intercalation. It should be noticed that the simple exposure of the Gr/Ru(0001) surface to air without the illumination does not produce any changes in XPS/UPS results, consistent with the previous report [14]. However, the oxygen intercalation can be activated at temperatures slightly above RT. At ambient atmosphere and close to RT, the space between the graphene cover and the Ru(0001) surface acts as a two-dimensional container, in which gases can be strongly confined like gas adsorption between single-layer SiO_2 membrane and Ru(0001) [53].

4. Conclusions

We demonstrate that O_2 can intercalate into the interface between a 1 ML graphene overlayer on the Ru(0001) substrate in 0.5 Torr O_2 at a temperature of 150 °C. The oxygen intercalation weakens the interaction between graphene and Ru(0001), leading to a downshift of the C 1 s binding energy by -1.36 eV and resulting in a free-standing graphene structure. The intercalated O atoms completely desorb from the Gr/Ru interface below 527 °C, which may be attributed to the confinement effect of the graphene cover as well as the etching of C atoms. The oxygen intercalation can also take place in air with the aid of an infrared lamp for illumination, showing that the Gr/metal interfaces may not be stable enough at ambient atmosphere and slightly above RT. Future graphene-based devices and materials often work in warm ambient environments, such as under direct sunshine and close to a heating source, where the facile oxygen intercalation at the Gr/metal interfaces may affect their performance and should be considered.

Acknowledgments

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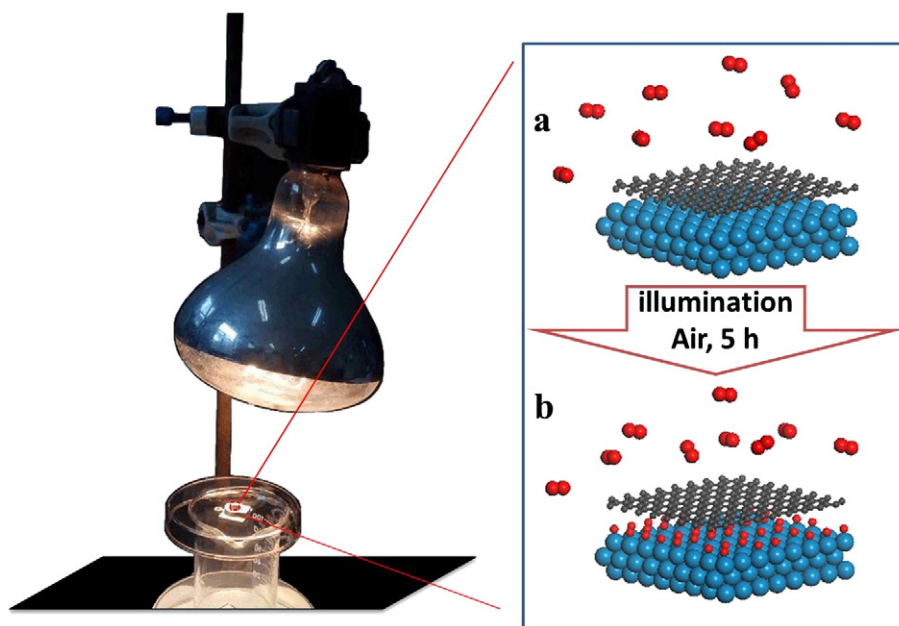
Fig. 6. Schematics for O_2 intercalation of 1 ML Gr/Ru(0001) surface in air under an infrared lamp illumination. (a) Before illuminating the 1 ML Gr/Ru(0001) surface in air; (b) after illumination for 5 h in air. Cyan ball: Ru; black ball: C; red ball: O.

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