Pd overlayer on Oxygen pre-covered Graphene/Ru(0001): Thermal Stability

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Abstract

The behaviors of metal atoms on graphene and graphene oxide are quite important since the composite materials consisting of graphene and transition metal(s) can be employed in numerous technological applications. Despite that the great importance of metal particles on graphene or graphene oxide substrates, fundamental studies of the physical and chemical properties of metal clusters on graphene or graphene oxide are still needed. In this study, in order to elucidate the properties of metal on graphene (GR) and oxygen-precovered graphene (O-GR), the systems consisting of Pd deposited either on to pristine graphene or oxygen-precovered graphene layers have been investigated. The oxygen-precovered graphene was prepared by hot filament method under oxygen atmosphere. Exposure of the graphene layer to atomic oxygen resulted in both intercalation of oxygen between the graphene layer and the Ru(0001) substrate and functionalization of the graphene layer (mainly epoxide formation). Pd deposited onto the oxidized graphene layer interacted strongly with the intercalated oxygen, resulting in intercalation of some of the deposited Pd even at lower temperature than we have seen for Pd on pristine graphene. At the low coverage of 0.25 MLE, Pd mainly formed large planar domains (spreading of Pd on the oxidized graphene layer) and intercalated between the graphene layer and the Ru substrate at lower temperature due to the interaction between Pd and intercalated

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oxygen. At higher temperatures, both systems experience the same phenomenon, i.e., the intercalation of all of palladium between the graphene layer and Ru substrate. The intercalated Pd desorbed from the substrate at temperatures >1100 K. At higher Pd coverages, some of the Pd intercalated between the GR and the Ru substrate, while small Pd particles spread on the surface. The structure of the Pd overlayer after the 800 K annealing cycle seems to be very different from that observed at 300 K. The Pd that was present in small clusters spread out on the graphene surface due to the interaction with the intercalated Pd layer through the graphene layer. This interaction stabilized the Pd and even after 1000 K annealing the metal film was stable. After even higher temperature annealing all the Pd intercalated, and then desorbed above 1100 K. The graphene layer preserved its perfect structure (i.e., continuity) without any damage after the intercalation and desorption of Pd.

1. Introduction

Graphene is a two-dimensional single atomic layer with a honeycomb structure consisting of sp^2 -hybridized carbon. It is recently applied in many fields [1], such as mechanical, electrical, and optical materials, due to its remarkable electronics properties. Composite materials consisting of graphene and transition metal(s) are attracting a great attention for numerous technological applications in the fields of electronics, material science, catalysis, and so on [1, 2]. Therefore, a lot of experimental and theoretical studies have recently focused on the deposition of transition metal(s) onto graphene support and the interfaces between graphene and transition metals [1-5]. Moreover, graphene oxide was previously attracting a great attention mainly for the mass production of high-quality graphene through the reduction of graphene oxide [6]. However, many recent studies are focused on the inherent properties of graphene oxide because graphene oxide can modify the properties of graphene by controlling the functional groups related to oxygen and the defect site [6]. Chen et al. [7] and Wang et al. [8] have recently reported the synthesis of palladium nanoparticles on graphene oxide and shown clean and well-dispersed Pd nanoparticles due to the strong anchoring of Pd onto a graphene oxide surface that prevents agglomeration of Pd clusters.

Despite the great recent interest in metal particles on graphene or graphene oxide substrates, fundamental studies of the physical and chemical properties of metal clusters on graphene or graphene oxide are still needed. Investigations on well-defined model systems can greatly aid the understanding of the properties of metal overlayers on graphene or graphene oxide support. Epitaxial and high-quality graphene has recently been grown on various substrate surfaces, such as metals and inorganic materials [1, 2, 9] and, as a result, the systems of various metals on epitaxial graphene have been investigated. It has recently been shown that metal

overlayers deposited onto metal-supported graphene layers can intercalate between the metal substrate and the graphene film at elevated temperatures [10, 11]. Up to now, two distinct intercalation mechanisms of metals under the graphene layer have been proposed, based on the strength of interaction between metal and carbon [12]. While metals weakly interacting with carbon atoms in the graphene layer are shown to intercalate through extended defects (open edge and/or domain boundaries), metals strongly interacting with carbon atoms prefer to intercalate via an exchange mechanism [12]. The intercalation via exchange mechanism needs higher temperature than that through extended defects. Although graphene oxide has been known for a long time and several graphene oxide models have been proposed, its detailed structure and reaction between oxygen atoms and graphene are still not well-understood [13].

In this study, palladium was deposited onto oxygen-precovered graphene/Ru(0001) surfaces prepared by a hot filament method at room temperature. The thermal behavior and the properties of palladium clusters were then investigated with x-ray photoelectron spectroscopy (XPS) and infrared reflection absorption spectroscopy (IRAS) using adsorbed CO (pressure of $\text{CO} = 1.0 \times 10^{-6}$ Torr) as a probe molecule. Under low temperature annealing in vacuum, palladium clusters on oxygen-precovered graphene mainly form large planar domains and some of the palladium are intercalated between the graphene layer and Ru substrate. However, with further annealing to above the desorption temperature of oxygen, phenomena similar to that of Pd supported on pristine graphene layer are observed. Annealing at high temperature, the intercalation of all palladium between the graphene layer and Ru substrate was observed, and then Pd desorbed from the substrate at temperatures above 1100 K. Even though the annealing induces the intercalation of palladium between graphene and ruthenium substrate and desorption

of palladium, the topmost graphene layer remained intact similar to the system of Pd on pristine graphene.

2. Experimental

The detailed experimental setup and the data acquisition procedures have been discussed elsewhere [11, 14-16]. All the experiments were performed in an ultrahigh vacuum (UHV) surface analysis chamber equipped with x-ray photoelectron spectroscopy, low-energy electron diffraction (LEED), quadrupole mass spectrometry (QMS), and connected to an elevated-pressure cell with KBr windows for infrared reflection absorption spectroscopy measurements. The base pressure in both chambers was $\sim 1 \times 10^{-10}$ Torr. The Ru(0001) single crystal (Princeton Scientific Corp., diameter = 10 mm and thickness = 1 mm) was spot-welded onto a U-shaped Ta wire (0.030 in. diameter) and a C-type thermocouple was spot-welded to the backside of the single crystal to measure the sample temperature. The Ru(0001) single crystal was cleaned by repeated cycles of Ar ion sputtering, oxidation at 1000 K and annealing up to 1900 K in UHV by electron beam bombardment, and the cleanliness of the surface was verified with XPS. The high quality epitaxial graphene layer was obtained by pyrolysis of ethylene on the clean Ru(0001) surface. The Ru substrate was annealed at 1400 K for 300 sec and then the sample was rapidly cooled down under ethylene atmosphere (1×10^{-6} Torr). The quality of graphene layer was monitored with LEED and it was also confirmed with IRAS and temperature programmed desorption (TPD) with the adsorption of CO. Palladium was deposited at room temperature onto the graphene layer supported on Ru(0001) using a resistively heated palladium wire (Alfa Aesar; diameter = 0.25 mm; 99.99%) and the palladium coverage was calibrated with respect to clean Ru by the break point of XPS peak ratio (Pd/Ru) [17]. Atomic oxygen was deposited to the

clean graphene surface with the hot-filament method in oxygen atmosphere (the pressure of oxygen = 5×10^{-6} Torr). The coverage of oxygen was estimated by the integration of the O 1s XPS feature. XPS spectra were analyzed by XPSPeak 4.1 software. Infrared spectra were collected at 4 cm^{-1} resolution using a grazing angle of approximately 85° to the surface normal. All the IR spectra collected were referenced to a background spectrum acquired from the sample prior to gas adsorption and taken under CO atmosphere (1×10^{-6} Torr) after saturation.

3. Results and Discussion

First of all, the quality of the prepared graphene layer was investigated by XPS and LEED in UHV as well as with IRAS of adsorbed CO. The infrared spectrum obtained from the graphene layer after CO exposure (1×10^{-6} Torr of CO) at room temperature showed no CO vibrational features [11]. Carbon monoxide is one of the best probe molecules to identify defect sites on metal surfaces. Due to the strong interaction of CO and Ru, the vibrational features of CO should appear once the graphene layer is defective and Ru sites are exposed through the “holes” in the graphene. The frequency of CO feature in IRAS is $\sim 2055 \text{ cm}^{-1}$ at saturation CO coverage on Ru(0001) as shown in the sample annealed at 1400 K in Figures 2 and 4. It indicates full coverage and continuous layer of carbon on the Ru substrate. In order to investigate the behavior of atomic oxygen on graphene/Ru(0001), XPS and IRAS were performed after deposition of atomic oxygen. Figure 1 (a) shows O 1s XP spectra of atomic oxygen on graphene/Ru(0001) as a function of atomic oxygen deposition time. Atomic oxygen was deposited onto graphene through a hot-filament method at a sample temperature of $\sim 300 \text{ K}$. The broad peak of O 1s XPS feature was observed and the peak maximum centered at $\sim 530.7 \text{ eV}$ at low coverage of atomic oxygen. With further deposition of atomic oxygen the peak shifts to

lower binding energy values and the feature becomes asymmetric. After 40 minutes of atomic oxygen deposition, the XPS feature shifts to 530.2 eV. A control experiment with corresponding amount of molecular oxygen at room temperature was performed in order to confirm the occurrence of molecular oxygen adsorption and/or reaction. No oxygen feature in XPS was observed on the perfect graphene layer after exposure to molecular oxygen. Our previous results [11] and data from other references [18, 19] substantiated that the graphene layers supported on metals or inorganic substrates show no adsorption of gas molecules such as CO at room temperature when the graphene layer fully covers the support. It indicates that the graphene layer is inert and stable and acts as a protective layer for the support. In addition, recent studies [20-24] reported that oxygen adsorption or intercalation at the graphene/metal interface happens at elevated temperature in molecular oxygen atmosphere. Specifically, Liao et al. [21] and Starodub et al. [22] observed oxygen adsorption at the graphene/metal interface in the range of oxygen pressure of 10^{-6} Torr and above 300 °C. Recently, Dong et al. [20] observed oxygen intercalation at graphene/Ru(0001) interface at and above 150 °C at an oxygen pressure of ~0.5 Torr and the XPS binding energy of intercalated oxygen was 529.9 eV which is in good agreement with our observation (530.2 eV). Vinogradoc et al. [25] reported that the binding energy of O in epoxy group formed on highly ordered pyrolytic graphite (HOPG), graphene/Ir(111), and Pt(111) is 531.1 eV after deposition of atomic oxygen. Moreover, they observed that some of the atomic oxygen deposited onto supported graphene are intercalated between graphene and metal substrate and the binding energy of intercalated oxygen is lower than that of epoxy group [25]. From our results and from previous publications [20, 25], it is unambiguous that the broad O 1s XPS feature at low coverage of atomic oxygen is the combination of oxygen atoms on/in graphene layer and oxygen intercalated between graphene

and Ru(0001) substrate. As the population of oxygen atoms increases, the intercalated oxygen feature is more intense. Figure 1 (b) shows IRAS spectra taken at room temperature as a function of annealing temperature. The background spectrum was taken at 300 K after deposition of atomic oxygen. It means that the background spectrum already contains information about oxygen and graphene, and, therefore, the variation of negative features as a function of annealing temperature represents the change from as-deposited atomic oxygen on graphene/Ru(0001). Up to the annealing temperature of 700 – 800 K, the two features at 1063 and 997 cm^{-1} gradually decrease and then they are saturated at higher temperature annealing. From previous reports on graphene oxide [26-28], these two features at 1063 and 997 cm^{-1} are assigned to C–O stretching and epoxy group vibrations, respectively. In summary, atomic oxygen deposition on GR/Ru(0001) at 300 K resulted in both the intercalation of oxygen between the graphene film and the Ru(0001) substrate and the formation of functional groups on the graphene layers (primarily in the form of epoxides).

Figure 2 shows normalized XPS intensities of Pd, Ru, and Pd/Ru collected during stepwise annealing of 0.25 monolayer equivalent (MLE) Pd/ graphene/Ru(0001) (panel (a)) and 0.25 MLE Pd/O-graphene/Ru(0001) (panel (b)). After the desired amount of Pd was deposited onto the graphene (GR) or oxygen-precovered graphene (O-GR) layer at room temperature, the sample was annealed step-wise and changes in the two different systems were monitored by XPS and IRAS of adsorbed CO. The samples were kept at each annealing temperature for 5 minutes, and then cooled down to ~300 K. Figures 2 shows the series of infrared spectra collected during CO exposure (1.0×10^{-6} Torr of CO) of the 0.25 MLE Pd on graphene layer (panel (c)) and on oxygen-precovered graphene (panel (d)) as a function of annealing temperature, respectively. The two series of IR spectra collected after annealing up to 1300 K show no evidence of CO

adsorption on either system (pristine and oxygen-precovered graphene layers) and it indicates that the graphene layers did not experience any damage and remained intact up to that temperature. As the XPS results in Figure 2 (a) reveal, in the temperature range of 300 – 900 K, the XPS intensity of Pd on the graphene layer gradually decreases with increasing annealing temperature. As we have previously discussed it in detail [11], this phenomenon can be explained by the agglomeration of Pd clusters deposited onto the graphene layer. As the sample temperature was increased, the mobility of Pd was sufficiently high due to the weak interaction between palladium and graphene to form large clusters. In the 300-900 K temperature range, as shown in Figure 2 (c), the IRAS of adsorbed CO shows gradual decrease of the CO intensity, which is a strong evidence for the agglomeration of Pd clusters. Above 900 K annealing temperature, however, the XPS intensity of Pd abruptly increases and continues to increase up to 1100 K and, concomitantly, that of Ru gradually decreases. The IRAS spectrum of adsorbed CO shows a significant reduction in intensity after annealing at 1000 K and the CO vibrational feature completely disappears at 1100 K. Even though the CO feature is completely disappeared in the IRAS, the XPS intensity of Pd restores almost to the same value as its original intensity was, as shown in Figure 2 (a). These observations provide direct evidence that Pd clusters deposited onto the graphene layer intercalate between the graphene layer and the Ru substrate without any damage of the graphene layer at high annealing temperatures (~1000 K). The gradual decrease in the intensity of Ru XPS signal demonstrates that spreading of the intercalated palladium layer occurred on the Ru substrate under the graphene layer. Further annealing above 1100 K results in the reduction of Pd and the increase in Ru XPS intensities due to the onset of Pd desorption at this temperature [29, 30]. Therefore, the increase in the intensity of Ru XPS

signal above 1100 K is attributed to the desorption of palladium, and, ultimately, the dissolution of the GR layer in the Ru substrate above 1300 K.

The behaviour of the Pd overlayer (~0.25 MLE) on the oxygen-precovered graphene layer is quite different from that of Pd on the pristine graphene layer. The XPS intensity of Pd and the Pd to Ru intensity ratio are both maintained at the constant values up to 1000 K, whereas the XPS intensity of Ru gradually increases up to 800 K and then decreases until 1200 K, as shown in Figure 2 (b). The slight increase of Ru XPS signal intensity up to 800 K originates from the oxygen desorption from the graphene layer and the intercalation of Pd between the graphene and the Ru substrate. On the other hand, the XPS intensity of Pd fluctuates with annealing at low temperature (up to 500 K) and then maintains at a constant value. This phenomenon may be related to the initial intercalation of Pd between graphene and Ru substrate. The IRAS spectra in this temperature range unambiguously show the evidence of intercalation. The IR spectrum of adsorbed CO on the as-deposited Pd at 300 K shows two distinct features at 2090 and 1945 cm^{-1} corresponding to CO adsorption on large planar Pd domains. As previously mentioned, the atomic oxygen deposited onto pristine graphene forms two types of oxygen; one is on or in graphene (e.g., epoxy groups) and the other is intercalated. The oxygen on or in the graphene layer plays the role of anchoring site for Pd and palladium forms large planar domains on graphene. As a result, the IR spectrum recorded just after Pd deposition resembles that obtained after CO adsorption on Pd(111). This IR spectrum is consistent with that reported by Freund and co-workers [31] for the SFG signal of CO (pressure = 10^{-6} mbar) on Pd(111) at 250 – 300 K and by Goodman and co-workers [32]. The latter group observed that the coverage of CO on Pd(111) at 190 and 350 K are 0.63 and 0.50 ML and CO preferentially occupied bridge-bound sites at the coverage of CO higher than 0.5 ML. However, the possibility of the formation of

defect-rich, planar Pd domains and/or large Pd domains consisting of small clusters cannot be ruled out completely, as a broad IR band is observed at $2000 - 1900 \text{ cm}^{-1}$. Even though the IR band observed at $\sim 1980 \text{ cm}^{-1}$ is one of the evidence of a defect-rich surface and/or small metal cluster [31, 33], the peak intensity is much lower in comparison with CO/0.25 MLE Pd/GR at 300 K. It indicates that the deposited Pd on oxidized graphene generally forms smooth planar domains with some defects and the populations of defects, steps and/or particle edges are much lower in the Pd/GRO systems than in the Pd/GR systems. However, after annealing at 400 K, the intensity of this CO vibrational feature is significantly reduced, as shown in Figure 2 (d), and the XPS intensity of Pd is concomitantly reduced. Palladium that initially formed large planar domains intercalate between the graphene layer and the Ru substrate even at this low sample temperature. Surface oxygen species formed during atomic oxygen deposition strongly interact with the as-deposited Pd cluster. With further annealing to a higher temperature, the intercalated palladium spreads between the graphene and Ru before it desorbs above 1100 K. As a result, IRAS spectra for the sample annealed above 500 K do not show any CO vibrational feature (all the Pd were intercalated). This observation indicates that there is no Pd on the graphene layer and the graphene layer does not have any defect sites at all that might have formed during the intercalation or subsequent annealing. With the annealing at very high temperature (above 1300 K), a CO vibrational feature at 2055 cm^{-1} appears with high intensity as shown in Figure 2 (d) because the annealing at 1400 K causes the dissolution of graphene into Ru [11], just as we have seen it for the Pd/GR/Ru(0001) system above.

The thermal behavior of Pd clusters on pristine and oxygen-precovered graphene were further investigated at higher Pd coverages. Figure 3 (a) – (d) show the normalized XPS intensities of Pd and Ru as well as the Pd/Ru intensity ratio for two different coverages of Pd (1

and 2 MLE) on graphene (panel (a) and (b)), and on oxygen-precovered graphene (panel (c) and (d)), as a function of annealing temperature. Despite the different Pd coverages, the variation of XPS intensities of Pd shows a similar trend; for Pd on graphene, it gradually decreases with increasing annealing temperature in the temperature range of 300 – 900 K and for Pd on oxygen-precovered graphene, it slightly increases and then remains nearly constant. Eventually, in both cases, annealing at high temperatures (at and above 1100 K) results in the desorption of palladium as evidenced by a steep decrease in the XPS intensity of Pd.

Figures 4 (a) – (d) show the corresponding series of IRAS spectra of adsorbed CO on Pd/GR/Ru(0001) (panels (a) and (b)) and on Pd/O-GR/Ru(0001) (panels (c) and (d)) systems with different coverages of palladium (1 and 2 MLE) under CO atmosphere (1.0×10^{-6} Torr). All the spectra were obtained at a sample temperature of 300 K. For the systems of Pd supported on pristine graphene layer similar IRAS results as those of 0.25 MLE of Pd/GR/Ru(0001) are seen. At annealing temperatures of ~ 1000 K, CO vibrational features are still visible, but their intensities decrease with increasing annealing temperature. For these systems, CO vibrational features at and below 800 K were not changed except their intensities. It indicates that the properties of Pd clusters are almost the same until palladium completely intercalates between graphene and Ru support. The intensity of the vibrational feature of adsorbed CO decreases dramatically after annealing the sample to 1000 K, and it completely disappears between 1100 and 1300 K, even under CO atmosphere. After annealing at 1400 K, a new, high intensity feature appears at 2055 cm^{-1} , which can be assigned to CO on Ru(0001), due to the dissolution of carbon into Ru [11].

For the systems in which Pd is supported on oxygen-precovered graphene, the IRAS spectra of adsorbed CO at higher coverages of Pd are somewhat different from that of 0.25MLE

Pd/GR/Ru(0001) system, as shown in Figures 4 (c) for 1 MLE Pd and (d) for 2 MLE of Pd. After the deposition of Pd at room temperature on O-GR/Ru(0001), IRAS shows a pattern similar to that of adsorbed CO on Pd supported on pristine graphene and the only difference between the two systems is that the intensity is greatly reduced in the system in which Pd is deposited onto an oxygen-precovered graphene surface. At low Pd coverage (e.g. 0.25 MLE Pd) on the oxygen-precovered graphene, the amount of oxygen on the surface is sufficient to enable all the Pd to form 2D (planar) rafts. Surface oxygen present on the system primarily in the form of epoxides plays the role of anchoring sites for Pd, therefore, guiding the incoming palladium atoms to form 2D planar domains, instead of three-dimensional clusters. However, as the coverage of palladium increases, the amount of oxygen on the graphene surface becomes limited, i.e., the number of incoming Pd atoms exceeds that of surface oxygen species. This will ultimately results in the formation of a Pd overlayer in which the metal is present in two distinct forms: some of the palladium is anchored to oxygen atoms, while the excess palladium forms three-dimensional clusters, similarly to those we observed for Pd deposition onto a pristine graphene layer. Therefore, the IRAS patterns of adsorbed CO for higher coverages of Pd are very similar to those observed for Pd on pristine graphene, although the integrated intensities are greatly reduced. Significant changes in the IR spectra of adsorbed CO are observed for the Pd/O-GR/Ru(0001) systems with high Pd coverage (≥ 1 MLE) in the 300 – 600 K temperature range. In this temperature range, the intensities of the IR features of Pd cluster-adsorbed CO are reduced, and new bands appear at 2080 and 1940 cm^{-1} , similar to IR features of adsorbed CO on Pd(111). The possibility of the formation of PdO [34] cannot be ruled out completely, but no evidence from XPS measurements substantiates the formation of PdO (after 600 K annealing practically no intensity of the O 1s XPs feature was observed). In addition, because the new

IRAS features appearing during low temperature (up to 600 K) annealing are stable up to 1000 K that is higher than the decomposition temperature of PdO (720 – 850 K) [35]. The Pd overlayer structure formed in the 300 – 700 K, however, seems to be different from that present after annealing at 800 and 1000 K. The main difference in the samples in these two temperature regimes is the presence (300 – 700 K) and complete absence of oxygen (800 – 1000 K). The Pd clusters formed during deposition at 300 K form 2D rafts on the GR layer and this Pd overlayer is primarily responsible for the development of the IR feature of adsorbed CO at $\sim 1940\text{ cm}^{-1}$. Above 700 K annealing all the intercalated oxygen is removed, and the Pd overlayer on the graphene layer interacts strongly with the intercalated Pd layer uniformly spread over the Ru substrate. This Pd overlayer is responsible for the IR feature of adsorbed CO at $\sim 2075\text{ cm}^{-1}$. Interestingly, this Pd layer is more thermally stable than Pd clusters deposited onto a pristine graphene layer. This is manifested in the higher temperature needed for the intercalation of the 2D Pd layer between the graphene layer and Ru substrate in this latter case. Annealing the samples above 1100 K brings about the onset of the desorption of intercalated Pd, and above 1300 K the dissolution of graphene into the Ru substrate.

4. Conclusions

The thermal behavior of Pd on pristine graphene and atomic oxygen-exposed graphene on Ru(0001) support have been investigated in the temperature range of 300 – 1400 K by XPS and IRAS of adsorbed CO. IRAS spectra of the oxygen-exposed GR/Ru(0001) surface suggest that atomic oxygen exposure results in the formation of epoxy groups primarily. The oxygen-precovered graphene/Ru(0001) surface was prepared by the hot filament method under oxygen atmosphere at 300 K of substrate temperature. Palladium clusters on pristine graphene

agglomerated as the annealing temperature increased and intercalated between the graphene layer and the metal substrate starting above 900 K. On the oxygen-precovered graphene, Pd at the low coverage of Pd (0.25 MLE) mainly formed large planar domains (spreading of Pd on the oxidized graphene layer) and intercalated between the graphene layer and the Ru substrate at lower temperature due to the interaction between Pd and intercalated oxygen (no adsorbed CO on Pd was observed above 400 K annealing). At higher temperatures, both systems experience the same phenomenon, i.e., the intercalation of all of palladium between the graphene layer and Ru substrate. The intercalated Pd layer desorbed from the substrate at temperatures >1100 K. The IR spectra of adsorbed CO at Pd coverages ≥ 1 MLE showed identical features regardless whether the graphene layer was exposed to atomic oxygen or not. The much lower intensities of the IR features of adsorbed CO on the as-deposited Pd on the oxidized GR/Ru(0001) system, in comparison to that on the pristine graphene, indicated that the Pd particles were much smaller on the O-GR layer than on the pristine graphene. Annealing these samples from 300 to 700 K seems to result in significant changes in the structure of the Pd overlayer on the oxidized GR layer. Similarly to that we have seen for the 0.25 MLE Pd/O-GR/(Ru(0001)) system, some of the Pd (that formed a spread layer on the O-GR) intercalated between the GR and the Ru substrate, while the small Pd particles spread on the surface. The structure of the Pd overlayer after the 800 K annealing cycle seems to be very different from that observed at 300 K. The Pd that was present in small clusters spread out on the graphene surface due to the interaction with the intercalated Pd layer through the graphene film. This interaction stabilized the Pd film and even after 1000 K annealing the metal film was stable. After even higher temperature annealing all the Pd intercalated, and then desorbed above 1100 K. Interestingly, after the intercalation and desorption of Pd, the graphene layer preserved its perfect structure (i.e., continuity) without any

damage. Annealing at and above 1350 K, the graphene layer is dissolved into Ru bulk and, as the result, bare Ru site is exposed.

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Figure Captions

Figure 1. (a) O 1s XP spectra: atomic oxygen deposition on graphene/Ru(0001). (b) IR spectra of oxygen-precovered graphene/Ru(0001) as a function of annealing temperature. (The background spectrum was taken at 300 K after the deposition of atomic oxygen and the series of spectra were taken after cooling the sample down to room temperature.)

Figure 2. Summary of XPS measurements (a) 0.25 MLE of Pd on pristine graphene and (b) 0.25 MLE of Pd on oxygen-precovered graphene as a function of annealing temperature, and the corresponding series of IRAS spectra ((c) and (d)) under CO atmosphere ($P(\text{CO}) = 1 \times 10^{-6}$ Torr) taken at room temperature.

Figure 3. Summary of XPS spectroscopy of (a) 1.0 MLE of Pd and (b) 2.0 MLE of Pd on pristine graphene and (c) 1.0 MLE of Pd and (d) 2.0 MLE of Pd on oxygen-precovered graphene as a function of annealing temperature.

Figure 4. A series of IRAS of (a) 1.0 MLE of Pd and (b) 2.0 MLE of Pd on pristine graphene and (c) 1.0 MLE of Pd and (d) 2.0 MLE of Pd on oxygen-precovered graphene. The indicated temperature is the annealing temperature and IRAS were taken under CO atmosphere (pressure = 1×10^{-6} Torr) at room temperature.

Figure 1 (a)
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Figure 1 (b)
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Figure 2 (a)
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Figure 2 (b)
Yi *et al.*

Figure 2 (c)
Yi *et al.*

Figure 2 (d)
Yi *et al.*

Figure 3 (a)
Yi et.al

Figure 3 (b)
Yi et.al

Figure 3 (c)
Yi *et al.*

Figure 3 (d)
Yi *et al.*

Figure 4 (a)
Yi et.al

Figure 4 (b)
Yi et.al

Figure 4 (c)
Yi et al.

Figure 4 (d)
Yi *et al.*

Figure S1
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