Monitoring the Interaction of CO with Graphene Supported Ir Clusters by Vibrational Spectroscopy and Density Functional Theory Calculations

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TOC GRAPHICS

ABSTRACT

The interaction of carbon monoxide (CO) with graphene supported Ir cluster (Ir/graphene/Ir(111)) and a Ir(111) single crystal surface was studied by infrared reflection-adsorption spectroscopy (IRRAS). The cluster morphology was characterized by scanning tunneling microscopy (STM) and density functional theory (DFT) calculations predicted the adsorption frequencies of CO molecules on Ir single crystal surface and clusters. After exposing the clean Ir(111) surface to CO at 195 K, one intense vibrational band is observed at 2043 cm^{-1} , which is assigned to on top CO species. This band shifts to much higher frequency at 2082 cm^{-1} at higher CO exposure. After exposing clean graphene/Ir(111) to CO at 195 K, no CO band was observed in the IR spectra, which confirms a full graphene layer over Ir(111) surface. However, CO molecules adsorb on Ir clusters supported on graphene/Ir(111) at 195 K. For the 0.05, 0.1, 0.15 and 0.2 ML Ir clusters, two IR bands were observed at 2060 and 2088 cm^{-1} , 2050 and 2070 cm^{-1} , 2048 and 2070 cm^{-1} , and 2052 and 2070 cm^{-1} , respectively. The IR bands at lower frequencies are assigned to the CO on one layer high clusters and the IR bands at higher frequencies are assigned to the CO adsorption on two or more layers high clusters. The IR frequencies of CO adsorbed on clusters are shifted to lower wavenumbers compared to those observed on single crystal surface, which is in agreement with DFT calculations. The IRRAS data recorded after CO adsorption on Ir clusters at different temperatures demonstrate that CO species are stable up to 350 K, although the intensity of CO on top one layer high cluster reduces largely, indicating CO induced cluster sintering.

INTRODUCTION

Graphene supported metal nanoparticles are interesting from both fundamental and technological perspectives due to their unique properties for gas sensors¹, transparent electrodes for displays² and solar cells³. In addition, metal nanoparticles have recently attracted enormous attention because of their important applications in a variety of fields such as catalysis, photocatalysis, chemical reactions, solar cells and electronic devices⁴. Metal supported graphene is known as a template for the growth of highly ordered, hexagonal arrays of d transition metal nanoparticles on the graphene moiré unit cell^{5,6}. It was previously shown that nanoparticles grown through UHV vapor deposition form ordered arrays on graphene substrates. The size of these nanoparticles can be carefully controlled with diameters smaller than 2 nm on graphene/Ir(111) by the amount of deposited material^{5,7,8}.

A detailed research on the adsorption of molecules on small transition metal clusters on graphene is of great general interest to understand the adsorption sites and growth properties of clusters with strongly reduced dimensions. We have demonstrated recently that Ir and Pt nanoparticles in the 1-1.5 nm size regime (40-80 atoms) form a regular and crystalline superlattice on the graphene moiré structure on Ir(111) by a combination of surface diffraction (SXRD), grazing incidence small angle x-ray scattering (GISAXS) and normal incidence x-ray standing waves (NIXSW) measurements. In addition, we observed that one atomic layer high Pt nanoparticles on graphene/Ir(111) undergo reversible changes in their lateral strain state under CO exposure and subsequent CO oxidation at 575 K⁹.

Among the transition metals, Ir nanoparticles dispersed on porous substrates have gained interest in surface science because of their widespread potential applications, especially in heterogeneous catalysis and chemical industry. Ir and Ir alloys are used as catalysts for the activation of C-H bonds^{10,11}, CO_x-free production of hydrogen from ammonia¹², improving automobile catalytic converters by decomposing NO and reducing NO_x with hydrocarbons^{13,14} and electro-oxidation of formic acid and methanol¹⁵.

In a previous theoretical investigation of the adsorption energy of CO on the Ir(111) single crystal surface, it was found that the CO molecules prefer on top sites¹⁶, while the carbon atom is bound to Ir and the molecule is oriented perpendicular to the surface. A binding energy of -2.13 eV per molecule was calculated for a (2x2) cell (0.25 ML) using the PW91 functional, with a CO vibration mode at 2114 cm⁻¹ for on top CO¹⁷. The binding energy for a CO molecule on bridge sites was calculated to -1.70 eV¹⁷. Time resolved infrared reflection-absorption spectroscopy of CO on Ir(111) surface at 440 K shows a CO vibrational band at 2060 cm⁻¹, assigned to on top CO adsorption¹⁷. Thermal desorption spectra (TDS) after various CO exposures at 300 K on Ir(111) show first order kinetics at about 550 K, related to the adsorption of CO in a ($\sqrt{3}\times\sqrt{3}$)R30° superstructure. Increasing CO exposure to higher than 2.5 Langmuir (L) leads to a shift in the CO desorption peak to lower temperatures (about 500 K), representing a ($2\sqrt{3}\times 2\sqrt{3}$)R30° superstructure at saturation coverage of CO on Ir(111) single crystal surface¹⁸. Also, temperature programmed desorption (TPD) spectra of CO on Ir(111) show one desorption peak at 510 K for low CO exposure (1L) and two desorption peaks at about 440 K and 510 K for higher CO coverages¹⁹, which implies coverage dependent adsorption of CO on Ir. However, in most IRAAS experiments a C-O stretching mode at about 2060-2065 cm⁻¹ was observed²⁰, which is about 50 cm⁻¹ lower than the value of 2114 cm⁻¹ from previous theoretical calculations for the p(2x2) CO on top adsorption¹⁷. This significant difference will be revisited in the following section.

It was originally proposed that CO molecules can adsorb on both on top and bridge sites on Ir(111) single crystal surface. A recent study suggests an exclusive occupation of top sites even at higher CO coverages^{21,22}. Schick et al. reported a single absorption IR band at about 2090 cm⁻¹ for CO adsorbed in on top sites on Ir(111), which desorbs between 400 and 600 K²³. Kerpel et al. found similarly only one CO species adsorbed on Ir clusters in the size range of 3-21 atoms in a frequency range of 1962-1985 cm⁻¹, while stretching vibrations at 2030 and

2026 cm⁻¹ assigned to on top CO were reported for the single crystal Iridium(111) and (100), respectively²⁴.

For lower coordinated Ir metal atoms, a red shift in IR frequency was observed for the CO adsorption²⁴. The stronger red shift of the C–O stretching frequency was related to the enhanced C–O bond activation on clusters via the back donation occurring from the interaction of the filled metal *d*-orbitals with the CO π^* -orbital. This effect is expected to be stronger for the lower coordinated clusters atoms.

Recently, CO adsorption was studied on different-sized Pt clusters (0.05-1.5 ML) on graphene/Ir(111) using XPS, STM, infrared-visible sum frequency generation (IR-vis SFG) vibronic spectroscopy and DFT calculations²⁵. The authors determined predominantly on top CO adsorption on the Pt atoms. A stronger red shift was observed for more undercoordinated Pt atoms.

Here we report vibrational spectroscopic studies of the adsorption of CO molecules on Ir clusters on graphene/Ir(111) combined with a morphological characterization by scanning tunneling microscopy. The experimental results are supported by theoretical calculations of the CO adsorption energies and harmonic vibration frequencies for CO adsorbed on Ir(111) single crystal surface and on Ir clusters supported by graphene/Ir(111). Our high-quality IR data show the presence of two vibrational C-O bands on Ir clusters after dosing CO at low temperatures. We argue that these bands are correlated with the presence of one and two atomic layers high Ir clusters. In contrast, CO does not adsorb on bare graphene/Ir(111) at 190 K. The assignment of the components is further confirmed by temperature dependent FT-IR measurements and rationalized by DFT calculations.

EXPERIMENTAL AND COMPUTATIONAL METHODS

All experiments were performed in the UHV cluster of the DESY NanoLab²⁶. The sample surface preparation took place in a UHV chamber (base pressure $3 \cdot 10^{-11}$ mbar) equipped with

electron beam assisted sample heating, gas inlets, sputter gun and commercial e-beam evaporator. Iridium was evaporated from a rod with 99.9% purity. Prior to CO adsorption and graphene growth, a clean Ir(111) surface was prepared by cycles of Ar ion sputtering and annealing up to 1450 K under ultra-high vacuum conditions. High structural perfection graphene was grown using ethylene as a carbon source²⁷. The sample was additionally heated to 1250 K under UHV, before growing clusters. Ir clusters are grown on graphene at 300 K by Ir deposition of 0.05, 0.1, 0.15 and 0.2 ML Ir. The Ir deposition was calibrated using X-ray reflectivity with $\pm 10\%$ reproducibility. The nominal amount of a deposition is then verified by STM. The samples were transferred to the UHV-infrared chamber or to the STM chamber right after growth to avoid residual gas adsorption through an interconnecting transfer tunnel with base pressure $< 5 \cdot 10^{-11}$ mbar.

IRRAS measurements were performed in a UHV-system equipped with an IR spectrometer coupled to the UHV chamber via differentially pumped KBr-windows to avoid atmospheric moisture adsorption, thus resulting in a superior sensitivity and stability of the system. Each IR spectrum was accumulated in 1024 Scans with a resolution of 2 cm^{-1} and was taken with the unpolarized beam at an incidence angle of 80° with respect to the surface normal at a base pressure of 4×10^{-10} mbar. The reflected signal was detected by a liquid nitrogen cooled mercury cadmium telluride (MCT) detector.

The STM measurements were carried out at a base pressure better than 5×10^{-11} mbar. All images were recorded in constant current mode at room temperature. The STM images were post processed by linear background subtraction.

The DFT calculations were performed with the Vienna Ab-initio Simulations Package (VASP)^{28,29}, using PAW potentials with a cutoff energy of 400 eV^{30,31} and the van-der-Waals corrected optB86 exchange-correlation functional^{32,33}. It should be noted that common GGA functionals tend to predict the wrong adsorption site for the adsorption of CO on several

transition metal surfaces^{34,35}, but the correct top site is predicted for CO/Ir(111)¹⁷. For the adsorption of CO on bare Ir(111), the surface was modelled by adsorbing 0.33 and 0.58 ML CO on a 5 layer slab in a $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ supercell. The structures were fully relaxed with the three lowest substrate layers fixed. A $5\times 5\times 1$ k-point grid was used for the integration of the Brillouin cell. For the graphene-supported clusters, the substrate was modelled by a (10×10) graphene mesh supported on a (9×9) three-layer Ir(111) slab, using a single k-point. A detailed description of the setup can be found in ref. 36. The vibrational spectra were evaluated in a harmonic approach without additional scaling of the frequencies.

RESULTS

1. STM images of Ir clusters on Graphene/Ir(111): 0.05 and 0.15 ML

To check **if** our procedure of cluster growth and transfer resulted in the desired well-ordered cluster arrays we performed STM measurements on two cluster sizes. STM topographs in Fig. 1 (a) and (b) show the cluster lattices after deposition of 0.05 and 0.15 ML of Ir, respectively. Generally, the clusters form arrays following the graphene moiré domains with 38 % of the 2035 measured moiré cells being filled for 0.05 ML and 91 % of 1789 of the moiré cells for 0.15 ML Ir clusters. The height distribution of the clusters, as seen in Fig. 1 (c), shows that for 0.05 ML Ir the majority of the clusters (74 %) are a single atomic layer high, while 26 % are two atomic layers high. At 0.15 ML the height distribution is instead peaked around two atomic layers, with 28% being single layer, 66 % double layer, and 6 % three layers high. Earlier studies of 0.05 ML Ir on graphene flakes on Ir(111)^{5,37}, showed almost exclusively single layer high clusters and a higher occupancy of the moiré cells. Such small clusters are known to be sensitive even to very low doses residual gas and one possible explanation for the discrepancies could be sintering of the clusters due to the slightly elevated pressure during deposition ($8\text{-}9\times 10^{-10}$ mbar in the present work compared to low 10^{-10} mbar in ref. 5) ³⁷.

Another possibility lies in the graphene coverages; while the previous STM study³⁷ was performed on graphene flakes the present study uses a fully covering graphene layer, which may lead to a locally different strain state in the graphene layer which may affect the cluster growth.

Figure 1: Representative images for 0.05 ML and 0.15 ML coverage are shown in (a) and (b), respectively. [$U_t = -3.75$ V, $I_t = 35$ pA]. (c) Histogram of cluster heights. The number of atomic layers in the clusters is indicated by the boxes labeled I-III. The blue profile corresponds to 0.05 ML Ir clusters and the red one to 0.15 ML Ir clusters on graphene/Ir(111).

A schematic view of the surface is represented in Fig. 2 for 0.05 ML and 0.15 ML Ir deposit and the experimental distribution found for one and two layer high clusters (neglecting the small amount of three layer high clusters): one layer high clusters consist of 7 atoms, whereas

two layer high clusters exhibit a 12 atom base in the first layer and 7 atoms in the second layer. Both clusters are found to be stable in DFT calculations³⁹. For the deposition of 0.05 ML Ir this scenario is equivalent with 74% 7 atom, one layer high clusters and 26%, 19 atom, 2 layer high clusters occupying the 38% filled cells.

Figure 2 Respective view of the graphene moiré unit cell with (a) 0.05 ML and (b) 0.15 ML Ir clusters on graphene/Ir(111). The Ir surface is depicted in red, the graphene layer in black.

2. IRRAS studies of CO adsorption

2.1 CO adsorption on clean Ir(111) surface

To have an accurate infra-red band assignment of the IR studies on Ir clusters and single crystal surface, we performed IRRAS measurements after CO adsorption on a Ir(111) single crystal surface, clean graphene/Ir(111) and Ir clusters. The IRRAS spectra recorded after CO adsorption on the clean Ir(111) single crystal surface at 195 K are presented in Fig. 3. A small amount of CO molecules was likely adsorbed on the Ir(111) single crystal surface during sample transfer which is visible in the spectrum of the nominally clean sample before CO

dosing (Fig. 3 a). After exposing the pure Ir(111) single crystal to CO at 195 K, one C-O vibrational band appeared at 2043 cm^{-1} and shifted to higher frequencies and reached its maximum intensity at 2082 cm^{-1} at higher CO coverage in agreement with the DFT calculations. We therefore suggest that the IR mode at 2082 cm^{-1} is due to the adsorption of CO in the experimentally observed $(3\sqrt{3}\times 3\sqrt{3})R30^\circ$ superstructure with a coverage of 0.7 ML^{40} , but did not explicitly include the phase in our simulations. The IR bands at 2090, 2030 and 2060 cm^{-1} were reported for CO adsorbed in on top configuration^{24,17,23} at room temperature. The continuous shift with coverage suggests that for all coverages CO occupies the same on-top sites. The blue shift of the IR band is due to the dipole-dipole interactions between adjacent CO molecules at higher CO coverages.

Figure 3. Adsorption of CO on clean Ir(111) surface. IRRAS spectra obtained after exposing the clean sample to CO at 195 K. (A) Clean sample with back pressure of CO; and dosing CO: (B) 0.05 L, (C) 0.1 L, (D) 0.5 L, (E) 1 L, (F) 3 L, (G) 6 L, (H) 10 L, (I) 50 L, (J) 100 L, (K) 500 L, (L) 1000 L.

2.2. CO adsorption on clean Graphene/Ir(111)

To distinguish the interaction of CO with Ir clusters from the CO interaction with graphene, IR spectra were recorded after exposing the bare graphene/Ir(111) to CO molecules. No IR band was observed after dosing CO on graphene/Ir(111) at 195 K, indicating that CO does not adsorb on graphene and in addition that the graphene layer is fully covering the Ir(111) surface. Intercalation of CO under sub monolayer graphene was shown to occur at CO pressures above 0.1 mbar above room temperature⁴⁰. Based on the IRRAS spectra in Fig. 4, we exclude both CO adsorption on the surface and CO intercalation at lower pressures for a full monolayer of graphene on Ir(111).

Figure 4. Adsorption of CO on bare graphene/Ir(111). IRRAS spectra obtained after exposing graphene/Ir(111) to CO at 195 K. (A) clean graphene/Ir(111); and dosing CO: (B) 0.5 L, (C) 5 L, (D) 10 L, (E) 100 L.

2.3. Adsorption of CO on Ir clusters: 0.05-0.2 ML Ir/graphene/Ir(111)

We carried out IRRAS experiments of CO adsorption after deposition of 0.05 ML Ir, resulting in the predominant formation of one layer high, 7 atom Ir clusters on graphene/Ir(111) as discussed in section 1. Due to low amount of Ir clusters, we decided to cool the sample to 135 K to be able to record the trace amount of adsorbed CO. A reference spectrum of the sample was recorded before CO exposure. After dosing CO on the 0.05 ML Ir covered graphene/Ir(111) at 135 K, one IR band appeared at 2050 cm^{-1} at low CO exposure (0.1 L). At higher CO coverage a new superimposed IR band rose at higher frequency at 2088 cm^{-1} and the blue shifted initial C-O band at 2050 cm^{-1} remained visible as a shoulder in the right side of the spectra (Fig. 5).

Figure 5. Adsorption of CO on Ir/graphene/Ir(111) after deposition of 0.05 ML Ir. IRRAS spectra obtained after exposing the clean nanoparticles to CO at 135 K. (A) before CO dosing; and dosing CO: (B) 0.05 L, (C) 0.1 L, (D) 0.5 L, (E) 0.8 L, (F) 1 L, (G) 6 L, (H) 10 L.

Furthermore, the IRRAS experiments of CO adsorption on the Ir clusters obtained after deposition of 0.1 ML Ir on graphene/Ir(111) was carried out at 195 K. After dosing CO on 0.1 ML Ir/graphene/Ir(111), one IR band appeared at 2050 cm^{-1} at low CO coverage (0.1 L) and shifted to 2054 cm^{-1} at higher coverages. In addition, a new IR band rose at 2062 cm^{-1} and shifted to 2070 cm^{-1} at higher CO coverage and both IR bands at 2054 cm^{-1} and 2070 cm^{-1} remained stable and dominant up to higher CO dosage at 195 K (Fig. 6). Annealing the sample to elevated temperatures showed a decrease of the IR band at 2054 cm^{-1} , while the IR band at 2070 cm^{-1} increased in intensity. Both IR bands were stable up to 353 K. We know that the Ir clusters are stable on graphene at this temperature; however adsorbed CO and consequent annealing can increase the mobility of one layer high clusters, which were present according to our STM measurements. A larger decrease in IR intensity band for the CO stretching mode at 2050 cm^{-1} compared to the CO stretching mode at 2070 cm^{-1} may be related to the sintering of one layer high clusters to several layers high, larger clusters. Although CO is expected to be mobile under annealing conditions, we exclude CO transfer from 2 layers high to one layer high clusters, as this would lead to an increase of IR band at 2050 cm^{-1} . Our observations are in-line with a rearrangement of the CO molecules after sintering of the nanoparticles, resulting in an increase of the IR band at 2070 cm^{-1} . Furthermore, the IR bands become significantly narrower in widths suggesting that annealing leads to more ordered CO structures on larger clusters. The adsorbate-induced sintering in metal particles is known and was recently reported in several studies^{38,41}. Gerber et al. reported a CO-induced Smoluchowski ripening of Pt clusters on graphene/Ir(111), where the clusters became more three-dimensional. The CO molecules do not desorb in the annealing process and stay on the clusters³⁸.

Figure 6. (a) Adsorption of CO on clean 0.1 ML Ir /graphene/Ir(111). IRRAS spectra obtained after exposing the clean sample to CO at 195 K. (A) before CO dosing; and dosing CO: (B) 0.05 L, (C) 0.1 L, (D) 0.5 L, (E) 3 L, (F) 10 L, (G) 50 L, (H) 60 L and (b) Annealing the sample after dosing 60 L CO. (A) 60 L CO at 195 K; (B) 313 K, (C) 323 K, (D) 333 K, (E) 343 K, (F) 353 K.

The IRRAS experiments of CO adsorption on 0.15 ML Ir clusters on graphene/Ir(111) were also performed at 195 K, see Fig. 7. After dosing CO on 0.15 ML Ir/graphene/Ir(111), one broad IR band was observed centered at 2048 cm⁻¹. At higher coverages this band shifted to 2056 cm⁻¹ and a new IR band appeared at 2070 cm⁻¹. Annealing the sample to elevated temperatures showed again a decrease of the IR band at 2054 cm⁻¹ and a red shift of the whole spectrum; both species are stable up to about 350 K. As for the 0.1 ML Ir deposition, the intensity of the CO band at 2048 cm⁻¹ decreased more quickly than the IR band at higher frequencies (Fig. 7 (b)).

Figure 7. (a) Adsorption of CO on the clean 0.15 ML Ir/graphene/Ir(111). IRRAS spectra obtained after exposing the clean sample to CO at 195 K. (A) Clean sample; and dosing CO: (B) 0.05 L, (C) 0.1 L, (D) 1 L, (E) 3 L, (F) 10 L, (G) 50 L, (H) 60 L and (b) Annealing the sample after CO dosing. (A) 60 L CO at 195 K, (B) 253 K, (C) 313 K, (D) 323 K, (E) 333 K (L), (F) 343 K, (G) 353 K.

Finally, we carried out IRRAS experiments of CO adsorption at 195 K for the 0.2 ML Ir deposit on graphene/Ir(111). After dosing 0.1 L CO (5×10^{-9} mbar, 30 sec) on 0.2 ML Ir/graphene/Ir(111) at 195 K, one IR band was observed at 2052 cm^{-1} . This band increased in intensity and shifted to 2070 cm^{-1} at higher CO exposure, while a less pronounced shoulder remained at lower wave numbers. The sample was annealed to elevated temperatures after exposure to CO. The dominant IR band at 2070 cm^{-1} shifted to lower wavenumbers at 343 K but it did not change much in intensity, demonstrating strong CO adsorption and enhanced stability of CO molecules on the predominantly 2 atomic layers high Ir clusters (Fig. 8).

Figure 8. (a) Adsorption of CO on clean 0.2 ML Ir/graphene/Ir(111). IRRAS spectra obtained after exposing the clean sample to CO at 195 K. (A) Clean sample; and dosing CO: (B) 0.05 L, (C) 0.1 L, (D) 1 L, (E) 3 L, (F) 10 L, (G) 50 L, (H) 60 L and (b) Annealing the sample after CO dosing. (A) 60 L CO at 195 K, (B) 313 K, (C) 323 K, (D) 333 K, (E) 343 K .

3. DFT calculations for single crystal Ir(111) surface and one layer cluster

The DFT calculations allow tracing the origin of the modes resulting from CO adsorption and more information about the binding energy of adsorbates. For the lowest investigated CO coverage (0.33 ML), the adsorbates form a $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure (Fig. 9 a), where the CO molecules are adsorbed at the top sites of the substrate Ir atoms with an adsorption energy of 2.24 eV per CO molecule. The charge transfer leads to a reduction of the internal CO stretching mode to a theoretical value of 2046 cm⁻¹, compared to an experimental low-coverage value of 2043 cm⁻¹. Considering the difference between the experimental gas phase

stretching frequency of CO (2143 cm^{-1})⁴² and the theoretical value (2130 cm^{-1}), it is evident that this level of agreement is fortuitous, but nevertheless the values are significantly smaller than the value of 2114 cm^{-1} found in ref. 17. In addition, the calculations predict a frequency of 525 cm^{-1} for the CO-Ir vibration.

When the CO coverage is increased, a $(2\sqrt{3}\times 2\sqrt{3})\text{R}30^\circ$ superstructure is formed with a coverage of $7/12$ ($= 0.58$) ML²². Again all CO molecules are predicted to adsorb at on top sites (see Fig. 9 b). This in turn leads to a weaker binding to the surface ($E_{\text{ads}} = 2.10\text{ eV}$), which is also reflected in the vibrational spectra: The highest – symmetric – vibrational mode is increasing to a value of 2064 cm^{-1} , while additional asymmetric modes appear in a range of $1984 - 1996\text{ cm}^{-1}$. Due to the anti-symmetry of the neighboring CO molecules we expect a strongly quenched IR intensity for these additional modes. In addition, the CO-Ir mode is slightly reduced to a value of 516 cm^{-1} . Our calculations data show that the stress induced by these higher coverages can be partially released by a tilting of the CO molecules at the rim of these patches, explaining the decrease of the IR band intensity as it is observed in Fig. 3.

Summarizing, the calculations for the Ir(111) surface predict an increase in the internal CO vibrational mode frequency of about 20 cm^{-1} between increasing the coverage from $1/3\text{ ML}$ to 0.58 ML , in agreement with predictions from models based on a dipole coupling between the adsorbates¹⁹.

Figure 9. Structural models for the adsorption of CO on Ir(111). The substrate Ir atoms are shown in green, C in black and O in red. The $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ supercell is drawn in black. (a) $(\sqrt{3}\times \sqrt{3})R30^\circ$ with a coverage of 0.33 ML, (b) $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ -7 CO structure with a coverage of 0.58 ML.

We investigated the adsorption of various amounts of CO on the graphene-supported Ir₇ clusters (see Fig. 2), including 1, 3, 6 and 7 CO molecules using the DFT calculations. In the limit of a single CO molecule, we find a clear preference for the adsorption in on top site at the edge of the cluster ($E_{\text{ads}} = 2.0$ eV), compared to the central (terrace-like) Ir atom ($\Delta E = -0.23$ eV). At CO higher coverages of up to 7 CO molecules per cluster the adsorption energy is only slightly decreased by about 20 meV, suggesting a fully covered Ir cluster at our experimental conditions. The reason for this weak effective repulsion is a complex adsorption mechanism: The adsorption of the CO molecules weakens the binding of the Ir cluster to the graphene sheet, which in turn enhances the reactivity of the cluster.

The vibrational spectrum of the fully covered Ir cluster (Ir₇(CO)₇) on the graphene support has the highest (symmetric) mode at a value of 2031 cm^{-1} , followed by the asymmetric modes ranging from $1956 - 1986\text{ cm}^{-1}$. Therefore, the calculations predict a red shift of the stretching frequency for a fully covered one-layer high clusters by 34 cm^{-1} , as compared to the $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ CO/Ir (111) surface. As the local geometric structure of the CO molecules adsorbed on the fully covered cluster is similar to the patches formed in the latter phase, an estimate for the contribution of the missing long-range dipole-dipole interactions can be

derived from a simple dipole-interaction based model¹⁹. Even although this model is only valid for similar electronic properties of the adsorbed molecules, the small elongation of the CO bond length of about 0.01 Å compared to the 0.58 ML phase indicates only a minor charge transfer. Indeed, this simple model already predicts a shift of about 40 cm⁻¹ for the fully covered clusters, suggesting an important contribution from the missing dipole-dipole interactions at the boundaries of the cluster.

4. DISCUSSION

The growth of Ir clusters investigated by STM shows the arrays following the graphene moiré domains with 38 % of the 2035 measured moiré cells being filled for 0.05 ML and 91 % of 1789 for 0.15 ML Ir clusters. The height distribution was mostly single layer for 0.05 ML Ir and two layers high for the 0.15 ML Ir clusters.

Furthermore, DFT calculations provided information about the CO adsorption on Ir single crystal surface and clusters. Our results show that CO adsorbs only in on top sites with an adsorption energy of 2.24 eV per CO molecule with the stretching mode at 2046 cm⁻¹. The adsorbates form a ($\sqrt{3}\times\sqrt{3}$)R30° superstructure for the lowest CO coverage (0.33 ML), while for the higher CO coverage a ($2\sqrt{3}\times2\sqrt{3}$)R30° superstructure is formed with a coverage of 7/12 (= 0.58) ML with all CO molecules adsorbed at on top sites with a higher stretching mode at 2064 cm⁻¹.

The IRRAS spectra after CO adsorption on the Ir(111) single crystal surface at 195 K shows only one dominant CO band at 2043 cm⁻¹ very close to the DFT calculated value at 2046 cm⁻¹ that shifts to higher frequencies and reaches its maximum intensity at 2082 cm⁻¹ at higher CO coverage. The frequency blue shift (2043 to 2082 cm⁻¹) from lower to higher CO coverages can be explained by the dipole-dipole interactions. As it was expected from DFT calculations, our results demonstrate CO adsorption only on top Ir atoms on Ir(111) surface and no bridge features were observed. DFT calculations for the adsorption of CO on the Ir₇ cluster show

that the increased charge transfer at the cluster leads to a reduction of the frequencies of ~ 30 cm^{-1} compared to the Ir(111) high-coverage phase. A summary of IR spectra after highest exposure of CO on different Ir clusters (0.05-0.2 ML) is shown in Fig. 10. Indeed, for the smallest clusters, 0.05 ML, two IR bands are observed at 2060 cm^{-1} and 2088 cm^{-1} . The IR band at 2050 cm^{-1} rises first but it slowly overlaps with a second strong and dominant band at 2088 cm^{-1} , growing in intensity at higher CO exposure so that the band at 2050 cm^{-1} could be observed only as a shoulder in the right hand of it. Therefore, we assign the lower band to the adsorption of CO on the initial 7-atom Ir cluster, while the second band, which is close to the value for the bare Ir(111) surface is attributed to the CO adsorption on larger clusters.

The structural model for 0.05 ML and 0.15 ML Ir clusters on the graphene moiré unit cell shown in Fig. 2 demonstrates a possibility for both one layer (7 atoms) and two layers high clusters (19 atoms). Based on the STM data discussed in section 1, for the 0.05 ML Ir deposition the one layer high clusters are dominant (74%), while 26% of cluster grows two layers high and 62% of the moiré cells are empty. This is consistent with our IR data showing the C-O stretching frequency at 2050 cm^{-1} for the CO adsorption on single layer clusters, and 2088 cm^{-1} for the adsorption of CO on mostly two layers high clusters. The blue shift from 2050 cm^{-1} to 2088 cm^{-1} for the 1st layer to 2nd layer adsorption can be explained by the interaction between CO and Ir cluster originating from the stronger donation from CO 5σ orbital and π -back donation from the 5d orbital of Ir and was observed previously on Pt/graphene/Ir(111) as well²⁵.

The intercalation of CO in graphene is excluded in this work as a full monolayer graphene is grown on Ir(111).

Figure 10. IRRAS spectra obtained after exposing Ir clusters to highest CO exposure (60 L) at 195 K. (A) 0.05 ML Ir/graphene/Ir(111) (B) 0.1 ML Ir/graphene/Ir(111) (C) 0.15 ML Ir/graphene/Ir(111) and (D) 0.2 ML Ir/graphene/Ir(111).

For the 0.1 and 0.15 ML Ir clusters, the ratio of 2 layers high clusters to 1 layer high clusters increases dramatically. The histogram of cluster height in Fig. 2 shows a contribution of 1 layer, 2 layers and three layers height clusters for the 0.15 ML clusters. The IRRAS data of the highest exposure of CO on the 0.1 and 0.15 ML clusters demonstrate two dominant C-O stretching vibrations bands at 2050 and 2070 cm^{-1} and 2048 and 2070 cm^{-1} , respectively. Both IR bands shift to higher frequency at higher CO exposure. Annealing the samples after CO exposure reveals a large decrease in the intensity of the IR band at 2050 and 2048 cm^{-1} , while the C-O stretching mode at 2070 cm^{-1} becomes stronger. The IR band at 2048 and 2050 cm^{-1} are assigned to the CO adsorption on the 1 layer high clusters and undercoordinated atoms at the cluster corners, while the IR band at 2070 cm^{-1} is attributed to the CO adsorption on 2 or

more layers high clusters. The decrease of the IR band intensity at 2048 and 2050 cm^{-1} during thermal treatments can be explained by sintering of the small clusters and consequently formation of larger clusters.

IRRAS spectra of the CO exposure on the 0.2 ML cluster demonstrate one dominant band at 2053 cm^{-1} at low CO coverage at 195 K. At higher CO exposure another IR band appears at 2070 cm^{-1} , but the C-O stretching mode at 2053 cm^{-1} is present only at the right shoulder of the new band, giving an asymmetry shape to the IR band. After annealing, the shoulder at 2053 cm^{-1} becomes weaker and only the dominant band at 2070 cm^{-1} remains stable up to 343 K. As expected from the STM topograph in this work for the 0.15 ML clusters, the growth procedure leads to the formation of two or more layers high cluster for larger Ir deposition. Based on the IR data we can expect 2 layers (or more) height for the 0.2 ML Ir clusters and consequently more CO molecules are adsorbed on the clusters of this size, while the CO band on one layer high clusters (2053 cm^{-1}) is small and nearly disappears after annealing due to sintering, forming larger clusters. Therefore, only one IR band is present at 2070 cm^{-1} on 0.2 ML Ir clusters. This feature was also reported by Podda et al.²⁵ by observing CO adsorption only in on top of one layer and two layers Pt clusters. In addition, the red shifted shoulder compared to the single crystal metal surface was assigned to more CO adsorption on undercoordinated metal atoms in cluster.

CONCLUSIONS

The interaction of carbon monoxide (CO) with clean Ir(111) single crystal surface and different sized Ir clusters on graphene/Ir(111) was studied in detail by employing IRRAS. The growth of Ir cluster monitored by STM shows the formation of both one layer and two layers high clusters even for small clusters such as 0.05 ML Ir under our experimental conditions.

The ratio of one layer and two layers high clusters changed from 0.05 ML to 0.15 ML deposited Ir from about 3:1 to 1:3.

At 195 K, CO adsorbs at low coverage only on top Ir atoms on Ir(111) surface with a vibrational frequency at 2043 cm^{-1} , in agreement with the DFT calculations. Increasing CO exposure leads to a blue shift of the C-O stretching vibrations to higher frequencies at 2082 cm^{-1} , in line with CO adsorption only on Ir top sites. The adsorption of CO on different Ir clusters shows adsorption on both one layer and two layers high clusters as both are present in our sample based on the STM images. Our IR results provide direct spectroscopic evidence that CO adsorbs on clusters with different heights by presenting two different IR bands. DFT calculations prove that the adsorption of the CO molecules weakens the binding of the Ir cluster to the graphene sheet, which actually leads to a slight reduction of the effective adsorption energy compared to Ir(111) single crystal surface.

Furthermore, annealing the samples after CO adsorption shows a large decrease in the IR band assigned to the CO adsorbed on one layer high clusters, while the other CO band from two layers high cluster grows in intensity, verifying sintering and formation of larger clusters. Finally, based on IRRAS spectra we exclude CO intercalation under a full monolayer graphene on Ir(111).

ACKNOWLEDGMENT

Thomas Michely is acknowledged for fruitful discussions. The Vienna Scientific Cluster (VSC) is acknowledged for CPU time.

Figure capture

Figure 1 Representative images for 0.05 ML and 0.15 ML coverage are shown in (a) and (b), respectively. [$U_t = -3.75$ V, $I_t = 35$ pA]. (c) Histogram of cluster heights. The number of atomic layers in the clusters is indicated by the boxes labeled I-III. The blue profile corresponds to 0.05 ML Ir clusters and the red to 0.15 ML Ir clusters on graphene/Ir(111).

Figure 2. Respective view of the graphene moiré unit cell with a) 0.05 ML and b) 0.15 ML Ir clusters on the graphene/Ir(111). The Ir layer is depicted in red, the graphene layer in black.

Figure 3. Adsorption of CO on clean Ir(111) surface. IRRAS spectra obtained after exposing the clean sample to CO at 195 K. (A) Clean sample with back pressure of CO; and dosing CO: (B) 0.05 L, (C) 0.1 L, (D) 0.5 L, (E) 1 L, (F) 3 L, (G) 6 L, (H) 10 L, (I) 50 L, (J) 100 L, (K) 500 L, (L) 1000 L.

Figure 4. Adsorption of CO on clean graphene/Ir(111). IRRAS spectra obtained after exposing the clean graphene/Ir(111) to CO at 195 K. (A) clean graphene/Ir(111); and dosing CO: (B) 0.5 L, (C) 5 L, (D) 10 L, (E) 100 L.

Figure 5. Adsorption of CO on clean 0.05 ML Ir/graphene/Ir(111). IRRAS spectra obtained after exposing the clean nanoparticles to CO at 135 K. (A) before CO dosing; and dosing CO: (B) 0.05 L, (C) 0.1 L, (D) 0.5 L, (E) 0.8 L, (F) 1 L, (G) 6 L, (H) 10 L.

Figure 6. (a) Adsorption of CO on clean 0.1 ML Ir/graphene/Ir(111). IRRAS spectra obtained after exposing the clean sample to CO at 195 K. (A) before CO dosing; and dosing CO: (B) 0.05 L, (C) 0.1 L, (D) 0.5 L, (E) 3 L, (F) 10 L, (G) 50 L, (H) 60 L and (b) Annealing the sample after dosing 60 L CO. (A) 60 L CO at 195 K; (B) 313 K, (C) 323 K, (D) 333 K, (E) 343 K, (F) 353 K.

Figure 7. (a) Adsorption of CO on the clean 0.15 ML Ir/graphene/Ir(111). IRRAS spectra obtained after exposing the clean sample to CO at 195 K. (A) Clean sample; and dosing CO: (B) 0.05 L, (C) 0.1 L, (D) 1 L, (E) 3 L, (F) 10 L, (G) 50 L, (H) 60 L and (b) Annealing the sample after CO dosing. (A) 60 L CO at 195 K, (B) 253 K, (C) 313 K, (D) 323 K, (E) 333 K (L), (F) 343 K, (G) 353 K.

Figure 8. (a) Adsorption of CO on clean 0.2 ML Ir/graphene/Ir(111). IRRAS spectra obtained after exposing the clean sample to CO at 195 K. (A) Clean sample; and dosing CO: (B) 0.05 L, (C) 0.1 L, (D) 1 L, (E) 3 L, (F) 10 L, (G) 50 L, (H) 60 L and (b) Annealing the sample after CO dosing. (A) 60 L CO at 195 K, (B) 313 K, (C) 323 K, (D) 333 K, (E) 343 K.

Figure 9. Structural models for the adsorption of CO on Ir(111). The substrate Ir atoms are shown in green, C in black and O in red. The $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ supercell is drawn in black. (a) $(\sqrt{3}\times \sqrt{3})R30^\circ$ with a coverage of 0.33 ML, (b) $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ -7 CO structure with a coverage of 0.58 ML.

Figure 10. IRRAS spectra obtained after exposing Ir clusters to highest CO exposure (60 L) at 195 K. (A) 0.05 ML Ir/graphene/Ir(111) (B) 0.1 ML Ir/graphene/Ir(111) (C) 0.15 ML Ir/graphene/Ir(111) and (D) 0.2 ML Ir/graphene/Ir(111).

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