

Enhanced chemical reactivity of pristine graphene strongly interacting with a substrate: chemisorbed CO on graphene/Ni(111).

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Abstract: Graphene is usually considered a chemically inert material. Theoretical studies of CO adsorption on free standing graphene predict indeed quite low adsorption energies (< 0.1 eV). However, we show here by Vibrational Spectroscopy and Scanning Tunnelling Microscopy that non dissociative chemisorption of CO occurs at cold, pristine graphene grown on Ni(111). The CO adlayer remains stable up to 125 K, while some coverage survives flashes to 225 K. This unexpected result is qualitatively explained by the modification of the density of states close to the Fermi energy induced by the relatively strong graphene-substrate interaction. The value of the adsorption energy allows to estimate an equilibrium coverage of the order of 0.1 ML at 10 mbar pressure, thus paving the way to the use of graphene as a catalytically active support under realistic conditions.

Although graphene (G) is generally considered a chemically inert material, pioneering work has recently demonstrated that it can be effectively used in gas sensing applications^[1,2] while applications in chemistry have been envisaged, too.^[3-5] The CO adsorption energy was estimated theoretically to be ~0.11 eV^[6], a value suggesting that physical forces dominate the interaction. Much larger values are expected at G defects, such as the border of nanoribbons.^[7] In this case, values up to 1.3 eV, typical of chemisorptions, may be appropriate. Unfortunately, defects lower the quality of the layer, so that finding other means for enhancing the chemical bonds would be of pivotal importance. For catalytic applications, the adsorption energy of the reactant(s) must be, moreover, high enough to reach significant equilibrium coverage under reactive conditions but low enough to limit the overall reaction barrier.

It has been shown recently that the chemical reactivity of weakly interacting G on SiC can be modified by introducing mechanical strain in the layer^[8] and that the reactivity with

SiO₂ and Al₂O₃.^[9-10] In both cases the adsorbed species was an aryl radical. Thanks to the use of such reactive species, even graphite has been chemically functionalised.^[11] Interaction of G with alogenated compounds^[12] and with atomic hydrogen was also reported.^[13] When using less reactive environments/adsorbates only physisorption was detected^[14] at regular graphene sites.^[15]

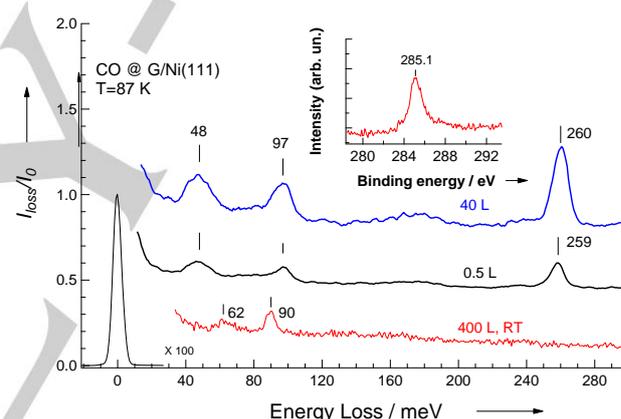


Figure 1. HREEL spectra normalised to the elastic peak intensity after CO exposure. The spectra are recorded at the dosing temperature. Note the absence of CO related intensity when the sample is exposed at RT (bottom spectrum) and the CO related losses at 48 and 259 meV when the exposure is performed at 87 K (2nd and 3rd spectrum). The spectra are vertically displaced with respect to the bottom one for sake of clarity. The feature at 90 meV already present before dosing is assigned to the ZO phonon mode of graphene.^[20] Such loss is excited by impact scattering being dipole-inactive. The loss at 62 meV is due to isolated carbon atoms adsorbed on Ni(111).^[21] The feature around 97 meV is associated to a slight water contamination.^[22] The inset shows the XPS spectrum of the C1s region of the clean G film.

We have thus investigated adsorption of CO, a simple molecule often used in model systems and having a bond dissociation energy significantly larger than the one of the CN bond in aryl diazonium salts. We show here that CO molecularly *chemisorbs* at regular sites on G in presence of a strongly interacting (and heavily *n* doped^[16]) substrate such as Ni(111). The minimal lattice mismatch between G and Ni(111) ensures that curvature effects^[8] are negligible. Moreover, the high substrate reactivity enables G production at relatively low surface temperature and at significantly lower pressure than needed for less reactive substrates such as Cu, thus allowing in situ growth under controlled ultra-high vacuum (UHV) conditions.^[17] The outcome of X-Ray Photoemission Spectroscopy (XPS) analysis upon G growth is shown in the inset of Fig. 1. The binding

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respect to covalent functionalization is enhanced in presence of large substrate induced electron-hole charge fluctuations for G on

energy of the main peak (binding energy, $E_b=285.1$ eV) agrees with the previously reported value for a single graphene layer, while residual traces of Ni_2C ^[18] contribute to the shoulder at lower E_b .

Such layer was eventually exposed to 400 L of CO at room temperature, RT, (red) and after 0.5 L and 40 L of CO at $T=87$ K (black and blue, respectively) and investigated by High Resolution Electron Energy Loss Spectroscopy (HREELS), see Fig. 1. As expected no adsorption is detected in the first case, while already a 0.5 L CO dose at $T=87$ K produces evident losses at 259 meV (internal CO stretch frequency, $\nu(\text{CO})$) and at 48 meV (CO-surface stretch).^[19] Upon further exposure, the CO-related losses increase and the CO-stretch mode frequency upshifts by 1 meV due to dipole-dipole interaction.^[19]

We firstly note that the CO stretch frequency is lower than the value of ~ 265 meV appropriate for gas phase^[23] and for physisorbed CO (e.g. on graphite^[23] or $\text{Ag}(111)$ ^[24]). Such lower value is indicative of weak CO chemisorption at on top sites.^[19] The presence of a loss at 48 meV, which is suitable for the adsorbate-substrate stretch of chemisorbed CO on a light substrate^[19] definitely proves our assignment. The possibility that adsorption occurs on residual bare Ni patches is ruled out by the absence of reactivity at room temperature (Fig. 1, bottom spectrum). Adsorption on Ni is indeed observed in the case of incomplete G/Ni(111) layers and occurs then also at RT (not shown), giving rise to two CO stretch losses at 229 (bridge) and 250 (on top) meV and to a metal-molecule stretch at 50 meV.^[25]

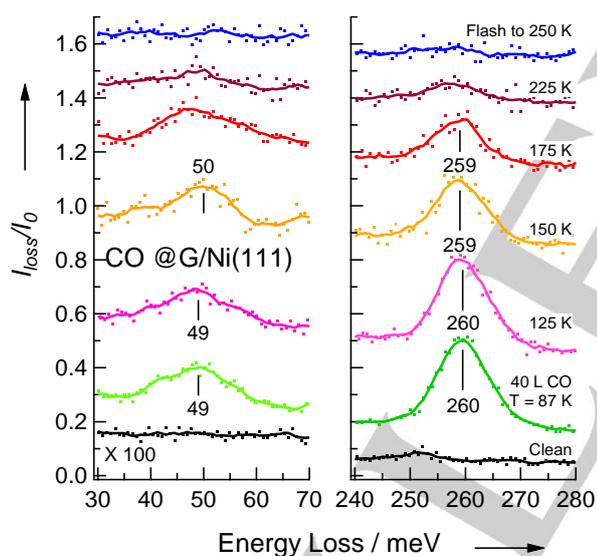


Figure 2. HREEL spectra showing the CO-substrate (left) and the $\nu(\text{CO})$ stretch (right) regions recorded after flashing the CO covered layer to the indicated temperatures and cooling back to 87 K. The attainable signal to noise ratio is limited by the need to keep the integration time short in order to avoid CO re-adsorption from the background.

After annealing the layer to increasingly higher T , the HREEL spectra evolve as shown in Fig. 2. It is apparent that the CO stretch mode intensity is stable up to 125 K, it is halved after flashing to 175 K and disappears definitively above 200 K. The observed thermal stability is also in accord with weak chemisorption since physisorbed CO does desorb at significantly lower T (e.g. 55 K on $\text{Ag}(111)$ ^[24]).

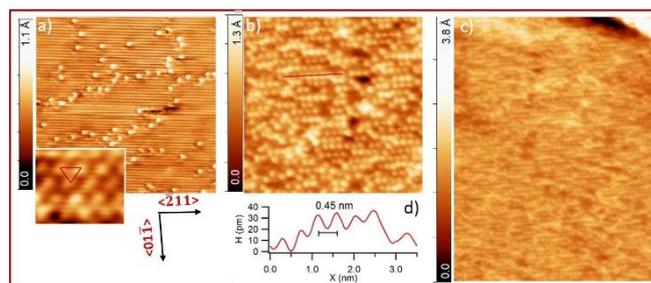


Figure 3. Panel a) STM image of the clean G/Ni(111) surface. Image size: $11.3 \times 11.3 \text{ nm}^2$, $V=0.19 \text{ V}$, $I=85 \text{ pA}$. The atomically resolved hexagonal lattice of the G layer is visible (see inset for an enlarged image; size: $10 \text{ \AA} \times 8.5 \text{ \AA}$, triangular unit cell marked). The brighter spots correspond to defects, as discussed in the text. The high symmetry directions of the Ni(111) substrate are reported below the image. b) G/Ni(111) after exposure to 1 L of CO dosed at 90 K. Image size: $11.3 \times 11.3 \text{ nm}^2$, $V=0.02 \text{ V}$, $I=0.55 \text{ nA}$. CO rows are mainly aligned along the $\langle -211 \rangle$ direction. c) Larger overview of the same area reported in b), showing that the CO ad molecules uniformly cover the whole graphene layer. Image size $21.2 \times 28.3 \text{ nm}^2$. d) Line profile of one CO row cut along the red line marked in b), i.e. along the $\langle -211 \rangle$ direction.

Fig. 3 reports the outcome of the corresponding CO adsorption experiment monitored by Low Temperature Scanning Tunneling Microscopy (LT-STM). Panel a) shows a typical area of Ni(111) covered with a monolayer of pristine G. The high symmetry directions are marked below the image and the inset shows an enlargement in which the triangular symmetry typical of top-fcc or top-hcp graphene^[16, 17] is evident. The Ni surface is not covered only by one type of G, since areas with top-bridge structure were also observed, as well as small regions in which Ni_2C has formed.^[26] The pristine surface shows a series of brighter spots forming sorts of irregular chains on the surface, which correspond most probably to Stone-Wales defects.^[27]

Being the defect site more reactive, their contamination by adsorption from the rest vacuum cannot be ruled out.

After 1 L CO exposure at $T=90$ K, the aspect of the surface changes dramatically (see Fig. 3b). Now it is fully covered by white dot features forming short chains mainly aligned along the $\langle -211 \rangle$ direction, see panel b). We identify them with CO molecules adsorbed at G domains. As evident from the large overview of panel c), CO is uniformly adsorbed on all the graphene film. The patches of Ni_2C are, on the contrary, still bare being unreactive even at low T (image not shown).

The average distance between CO molecules in the same row is $\sim 4.5 \text{ \AA}$ (see line scan in panel d). Although we are not able to determine the precise adsorption site of the molecule with respect to the graphene lattice underneath, this distance is well compatible with the adsorption of one CO molecule every second G unit cell. The packing in the perpendicular $\langle 01-1 \rangle$ direction is less regular. We observe, however, that the closest distance between adjacent CO rows is $\sim 3.8 \text{ \AA}$, which corresponds again to one CO unit every second G unit cell. We can therefore estimate a maximum local CO coverage of $1/6^{\text{th}}$ of monolayer (ML) in ML of G ($1/3$ in ML of Ni(111)). The global coverage is of course smaller, due to the irregular packing of the rows and to the presence of clean Ni_2C areas.

The outcome of our combined vibrational spectroscopy and STM experiments allows thus to conclude that:

- CO chemisorbs molecularly on G/Ni(111) at 87 K with a nearly unitary sticking probability.
- The adlayer is stable up to 125 K and desorbs gradually above this T .
- CO adsorption takes place at pristine graphene areas, not just at defects or at domain boundaries.

Assuming a pre-factor for desorption of 10^{13} Hz^[28-30] and using an Arrhenius like dependence for the desorption rate (see Supporting information), we estimate a desorption energy of ~ 0.35 eV/molecule (in ML of Ni(111)) and of ~ 0.58 eV/molecule in the low coverage limit. Since no adsorption barrier is present, this estimate equals the adsorption energy. The higher value in the low coverage limit (evidenced by the residual coverage after flashing at and above 150 K) can be due either to adsorption at defect sites^[31] or to repulsive interactions between admolecules at regular sites.^[32] Whatever the reason, the value of 0.35 eV/molecule is much higher than the one predicted for free-standing graphene.^[6] This allows to obtain a significant equilibrium coverage under realistic, catalytic conditions. Using a Langmuir isotherm, an equilibrium coverage of ~ 0.1 ML is attained at RT under a CO partial pressure of only 10 mbar.^[33] Occurrence of CO chemisorption, albeit weak, is an unexpected results which can only be accounted for by the presence of a reactive substrate such as Ni(111) below the G layer. Photoemission measurements^[34,35] show indeed that at the K point a substantial flattening of the π band occurs. Such strong perturbation of the ideal electronic structure of G is responsible for the opening of a gap^[34] and for the partial disruption of the Dirac cone. Band bending implies clearly a high DOS below the Fermi energy. This feature mimics the d band intensity of transition metals close to the Fermi level and is suggested therefore to account for the enhanced reactivity of Ni supported graphene with respect to a free-standing G film, although it is not yet clear whether the observed increase in the adsorption energy can be accounted for by intrinsic n doping alone.^[9] In conclusion we have demonstrated that Ni supported graphene enables CO chemisorption with relatively high adsorption energies, paving the way to its use in catalytic applications. The adsorption energy is thereby high enough to permit reaching an equilibrium coverage significantly higher than for un-supported graphene, but low enough to ensure that the removal of CO from graphene will not be the rate limiting step.^[36]

Experimental Section

The Ni(111) crystal is cleaned by repeated sputtering (with 3 keV Ne ions) and annealing ($T=1283$ K) cycles. G is grown in situ, by thermal dehydrogenation of ethene catalysed by the Ni surface exposing the substrate at $T_g=823$ K for 660 s. Such procedure produces single layer graphene domains up to a few tens of nm in size as verified by Low Temperature Scanning Tunnelling Microscopy (LT-STM). The cleanliness of the surface and the chemical nature of the carbon layer are checked by X-ray Photoelectron Spectroscopy (XPS). CO is dosed by backfilling the chamber. High Resolution Electron Energy Loss Spectroscopy (HREELS) is used to monitor CO adsorption while LT-STM allows the morphological characterisation of clean and adsorbate-covered G layers. HREEL spectra were recorded in-specular, with incidence angle $\theta_i=\theta_r=62^\circ$ with respect to the surface normal and with primary electron energy $E=4$ eV. STM images were acquired in constant current mode, with typical tunnelling currents of $85 \leq I \leq 600$ pA and bias voltages (of the sample with respect to the tip) of $-0.2 \leq V \leq 0.2$ V.

Acknowledgements

We thank for funding Compagnia San Paolo, MIUR (PRIN grant. N. 20105ZZTSE_003 and FIRB2012: Futuro in Ricerca Grant N.

RBFR128BEC_004) and Università di Genova (PRA 2013). We acknowledge P. Silvestrelli and A. Ambrosetti for scientific discussions.

Keywords: Graphene • Chemisorption • Surface • Vibrational spectroscopy • STM

- [1] F. Schedin, A.K. Geim, S. Morozov, E.W. Hill, P. Blake, M. I. Katsnelson, K. S. Novoselov *Nature Materials* **2007**, *6*, 652-655
- [2] T. O. Wehling, K. S. Novoselov, S. V. Morozov, E. E. Vdovin, M. I. Katsnelson, A. K. Geim, A. Lichtenstein *Nano Letters* **2008**, *8*, 173-177
- [3] L. Liao, H. Peng, Z. Liu *JACS* **2014**, *136*, 12194-12200
- [4] L. Ferrighi, M. Datteo, C. Di Valentin *JPCCC* **2014**, *118*, 223-230
- [5] L. Qu, Y. Liu, J. B. Baek, L. Dai *ACS Nano*, **2010**, *4*, 1321-1326.
- [6] X. Lin, J. Ni, C. Fang *Journ. Appl. Phys.* **2013**, *113*, 034306.
- [7] B. Huang, Z. Li, Z. Liu, G. Zhou, S. Hao, J. Wu, B. Gu, J. Duan *J. Phys. Chem. C* **2008**, *112*, 13442-1446
- [8] Q. Wu, Y. Wu, Y. Hao, J. Geng, M. Charlton, S. Chen, Y. Ren, H. Ji, H. Li, D. W. Boukhvalov, R. D. Piner, C. W. Bielawski, R. S. Ruoff *Chem Comm.* **2013**, *49*, 677-679
- [9] Q. H. Wang, Z. Jin, K. K. Kim, A. J. Hilmer, G. C. Paulus, C. Shih, M. Ham, J. D. Sanchez-Yamagishi, K. Watanabe, T. Taniguchi, J. K. P. Jarillo-Herrero, M. S. Strano *Nature Chemistry*, **2012**, *4*, 724-732;
- [10] L. Ferrighi, C. Di Valentin *Surf. Sci.* **2015**, *634*, 68-75
- [11] J. M. Eglert, C. Dotzer, g. Yang, M. Schmid, C. Papp, J. M. Gottfried, H. P. Steinrück, E. Spiecker, F. Hauke, A. Hirsch *Nature Chemistry*, **2011**, *3*, 279-286
- [12] C. Morchutt, J. Björk, S. Krotzky, R. Gutzler, K. Kern *Chem. Comm.* **2015**, *51*, 2440-2443
- [13] W. Zhao, J. Gebhardt, F. Spath, K. Gotterbarm, C. Gleichweit, H. P. Steinrück, A. Gorling, C. Papp *Chemistry A Europ. Journ.*, **2015**, *21*, 3347-3358
- [14] (a): S. Standop, T. Michely, C. Busse *JPCCC* **2015**, *119*, 1418-142. (b): P. Lazar, F. Karlicki, P. Jurecka, M. Kocman, K. Safarova, M. Otyepka *JACS* **2013**, *135*, 6372-6377
- [15] Reaction with O₂ has been indeed shown to occur only at defects and at high temperature: K. Gotterbarm, W. Zhao, O. Höfert, C. Gleichweit, C. Papp, H. P. Steinrück *PCCP* **2013**, *15*, 19625-19630. Also reaction with H₂O was shown to occur at defects: X. Feng, S. Maier, M. Salmeron *JACS* **2012**, *132*, 5662-5668
- [16] G. Gebhardt, F. Vines, A. Görling *Phys. Rev. B* **2012**, *86*, 195431
- [17] (a) W. Zhao, S. M. Kozlov, O. Höfert, K. Gotterbarm, M. P. A. Lorenz, F. Vines, C. Papp, A. Görling, H. P. Steinrück *J. Phys. Chem. Lett.* **2011**, *2*, 759-764; (b) F. Bianchini, L. L. Patera, M. Peressi, C. Africh, G. Comelli *J. Phys. Chem Lett.* **2014**, *5*, 467-473; (c) L. L. Patera, C. Africh, R. S. Weatherup, R. Blume, S. Bhardwaj, C. Castellarin-Cudia, A. Knop-Gericke, R. Schloegl, G. Comelli, S. Hofmann, C. Cepek *ACS Nano*, **2013**, *7*, 7901-7912
- [18] We note that the carbon atom density of Ni₂C is four times lower than the one of graphene.
- [19] H. Ibach, D.L. Mills in *Electron Energy Loss Spectroscopy and Surface Vibrations*, Academic Press, **1982**, pp 285-286
- [20] T. Aizawa, R. Souda, Y. Ishizawa, H. Hirano, T. Yamada, K. Tanaka, C. Oshima *Surf. Sci.* **1990**, *237*, 194-202
- [21] A. Cupolillo, G. Chiarello, F. Veltri, D. Pacilé, M. Papagno, V. Formoso, E. Colavita, L. Papagno *Chem. Phys. Lett.* **2004**, *398*, 118-122
- [22] D.V. Chakarov, L. Osterlund, B. Kasemo *Langmuir* **1995**, *11*, 1201-1214
- [23] D. Boyd, F. Hess, G. Hess *Surf. Sci.* **2002**, *519*, 125-138
- [24] W. Hansen, M. Bertolo, K. Jacobi *Surf. Sci.* **1991**, *253*, 1-12
- [25] S.L. Tang, M.B. Lee, Q.Y. Yang, J.D. Beckerle, S.T. Ceyer *J. Chem. Phys.* **1986**, *84*, 1876-1883
- [26] Since a very high resolution is required to distinguish among the three different G types, we do not have a rich enough statistics to determine their relative population. This information is, however, of little relevance with respect to the message of the present communication.
- [27] H. I. Rasool, C. Ophus, Z. Zhang, M. F. Crommie, B. i. Yakobson *Nanolett* **2014**, *14*, 7057-7063
- [28] K. Kolasinski in: *Surface Science: Foundation of Catalysis and Nanoscience*, Wiley, **2008**, pp 199
- [29] K. Liao, V. Fiorin, D. S. Gunn, J. S. Jenkins, D. A. King *Phys. Chem. Chem. Phys.* **2013**, *15*, 4059-4065
- [30] C. T. Campbell, L. Arnadottir, J. R. Sella *Phys. Chem* **2013**, *227*, 1435-1454
- [31] L. Vattuone, L. Savio, M. Rocca *Surf. Sci. Rep.* **2008**, *63*, 101-168

- [32] Y. Y. Yeo, L. Vattuone, D. A. King *J. Chem. Phys.* **1997**, *106*, 1990-1996
- [33] Due to the compensation effect in the Arrhenius analysis, assuming a 100 times lower (higher) value of the pre-factor affects the estimated adsorption energy by ~ 0.05 eV, but does not affect the order of magnitude of the attainable equilibrium coverage at given pressure and temperature.
- [34] (a) M. Batzill *Surf. Sci. Rep.* **2012**, *67*, 83-115; (b) A. Dahal, M. Batzill *Nanoscale* **2014**, *6*, 2548-2562
- [35] A. Varykhalov, J. Sanchez-Barriga, A. M. Shikin, C. Biswas, E. Vescovo, A. Rybkin, D. Marchenko, O. Rader *Phys. Rev. Lett.*, **2008**, *101*, 157601.
- [36] Notably the adsorption energy found here is comparable with the one found on alumina in A. Zecchina, E. Escalona Platero, C. O. Areal *J. Catal.* **1987**, *107*, 244-247

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Graphene is considered chemically inert. We find out experimentally that CO chemisorption does occur at single layer graphene grown on Ni(111).

