

Enhanced Chemical Reactivity of Pristine and Doped Graphene Strongly Interacting with a Substrate: Chemisorbed CO on Graphene/Ni(111).

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Graphene (G) 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). In spite of that, pioneering work has recently demonstrated that it can be effectively used in gas sensing [1,2] with possible applications also in chemistry [3]. However, to the best of our knowledge, functionalization of G layers was achieved so far only using reactive species, as aryl radicals or atomic hydrogen, or by adsorption at defect sites. When using less reactive environments/adsorbates only physisorption [4] was detected at regular graphene sites. On the other side, the introduction of dopant atoms like B, N and S was proved to enhance the chemical activity of the G layer with respect to some selected reactions like ORR or methanol oxidation [5].

Here we summarize our results on the reactivity of pristine and n-doped G films grown on Ni(111) with respect to CO adsorption. G films were grown on Ni(111) single crystal by CVD under UHV conditions. We show by Vibrational Spectroscopy and Scanning Tunnelling Microscopy that non dissociative chemisorption of CO occurs at cold, pristine graphene samples [6]. For pristine graphene only on top bonded CO is present and characterised by a stretching mode at 260 meV (see Figure). Spectra recorded after annealing to different temperatures show that the CO adlayer remains stable up to 125 K, while some coverage survives flashes to 225 K. An adsorption energy of 0.35 eV/molecule at a CO coverage of 1/6 ML of G is then estimated yielding 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.

References

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The value of the adsorption energy, the frequency of the internal CO stretch and of the substrate-molecules stretch demonstrates that chemisorption has occurred.

STM images [6] clearly demonstrate that adsorption occurs at pristine G sites (and not only at defects or at domain boundaries) and that a coverage of 1/6 of ML of G is present. 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.

We performed similar experiments on n-doped graphene obtained by sputtering the pristine G grown on Ni(111) with low energy N₂ ions. Vibrational spectra indicate that a second CO moiety with a vibrational frequency characteristic of bridge-bonded CO is now present. Such moiety is characterized by an adsorption energy higher than the one observed in absence of extrinsic doping and is thus potentially even more promising for catalytic applications [7].

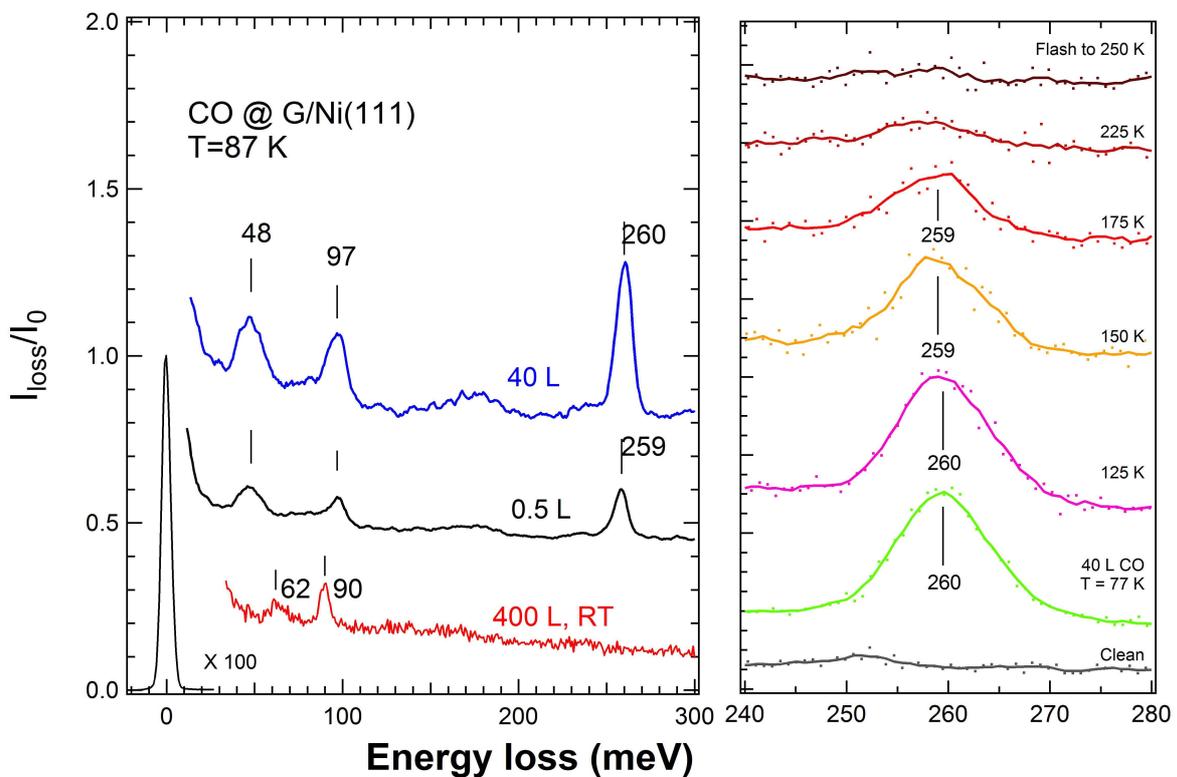


Figure 1: Left: Vibrational spectra recorded after dosing CO on pristine G/Ni(111) under different conditions. Upon 400 L exposure at room temperature (RT, red trace) no signature of CO adsorption is present. Upon exposure of only 0.5 L both the CO stretch mode (259 meV) and the G-CO stretch (48 meV) are present (black trace). The intensity of the vibrational features increases further when increasing the exposure to 40 L (blue trace). Right: Evolution of the vibrational spectrum in the region of the CO stretch mode upon annealing the layer: it is apparent that the loss starts to decrease above 125 K and disappears completely at 250 K. The initial coverage of CO, as determined by STM [6] is 1/6 ML of graphene. The adsorption energy decreases with decreasing CO coverage and reaches 0.58 eV/molecule in the low coverage limit.