

# High-quality N doped graphene layers: “inside out” growth and reactivity

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The 2D honeycomb structure of graphene (Gr) is responsible for its fascinating and peculiar properties, which turn out to be relevant in several research fields, such as energy storage, high-frequency electronics, photodetectors, as well as gas reactors and gas sensors. Nevertheless, pristine Gr suffers from serious limitations in some applications and, nowadays, doping of Gr is claimed to be a promising approach in order to tune its properties. In particular, nitrogen doped Gr (N-Gr) is predicted to have strong potential as a 2D material for new devices, including, for example, usage for gas sensing and storage [1,2]. To this purpose, a high-quality N-Gr layer is mandatory.

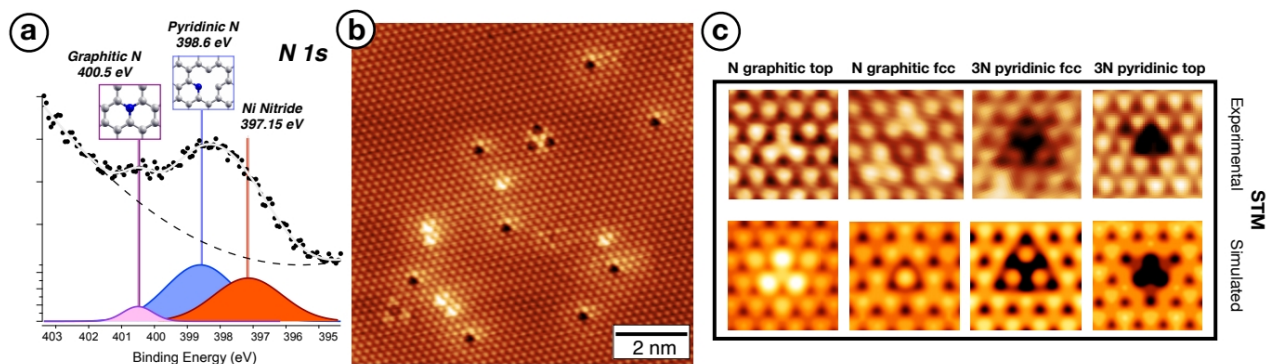
We prepared high-quality N-Gr on nickel (Ni) with an “inside out” approach, by exploiting both the catalytic properties of Ni and the solubility of N atoms into its bulk: following the standard chemical vapor deposition procedure in ultra high vacuum (UHV), a previously N-doped Ni substrate was exposed to a commonly used precursor (ethylene) so that N atoms, segregating to the surface, remained trapped in the growing Gr network. The produced N-Gr layers were thoroughly characterized at the atomic level by Scanning Tunneling Microscopy (STM) and X-ray Photoelectron Spectroscopy (XPS) in synergy with Density Functional Theory simulations. This approach yields very homogeneous and flat layers, with a well-defined set of N defects in the Gr mesh that we have identified and fully characterized (see Figure 1). Our approach ensures the formation of reproducible high-quality layers and is potentially easily scalable, from small samples prepared under UHV conditions to large foils in industrial production.

Finally, preliminary studies on its interaction with near ambient pressure of CO at room temperature demonstrates an enhanced reactivity of N-Gr with respect to the pristine Gr case, confirming what already reported in literature [3] and opening the way to a potentially scalable production of high-performance devices in the field of catalysis, gas sensing and storage.

## References

- [1] Inagaki, M., et al. Carbon 132 (2018): 104-140
- [2] Celasco, E., et al. Physical Chemistry Chemical Physics 18.28 (2016): 18692-18696
- [3] Carraro, G., et al. Applied Surface Science 428 (2018): 775-780

## Figures



**Figure 1:** (a) XPS spectrum of N1s core level. Nitrogen is present in three forms: (i) Ni nitride (N atoms in the very first layers of the Ni substrates), (ii) pyridinic N and (iii) graphitic N. (b) STM image (8x8 nm<sup>2</sup>) of N-Gr on Ni(111) taken at 77 K. Imperfections are related to N defects. Image parameters: I= 500 pA, V<sub>bias</sub>= -0.2 V. (c) STM experimental images (top) and corresponding theoretical simulations (bottom) of N graphitic and pyridinic defects in the graphene layer.