Electronic Interaction between Nitrogen-Doped Graphene and Porphyrin Molecules

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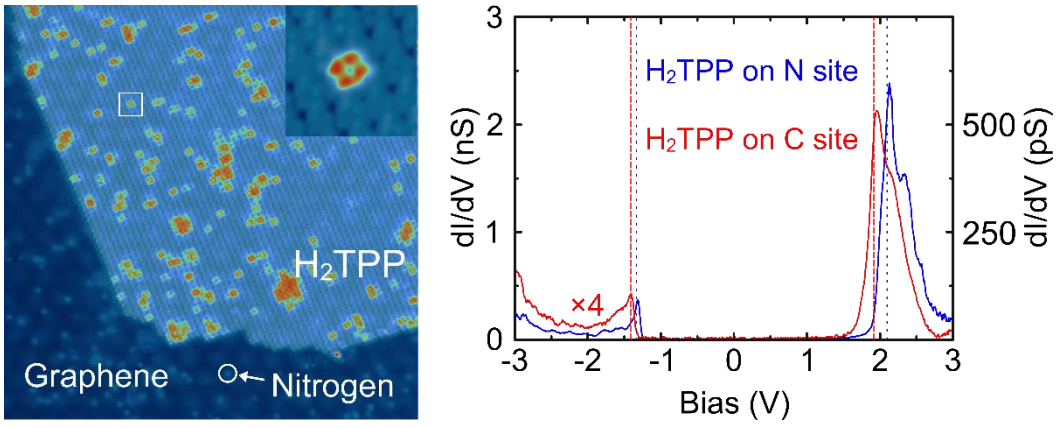
Abstract

Controlling the properties of graphene and mastering its interaction with molecules is a cornerstone for the realization of graphene-based devices. One of the promising routes explored to tune the properties of graphene is the doping by nitrogen atoms inserted in the carbon lattice.
Here, we present an extensive study of the interaction of porphyrin molecules (H_2TPP) with nitrogen doped graphene. Using scanning tunneling microscopy and spectroscopy (STM and STS) we evidenced the decoupling effect by the opening of the HOMO-LUMO gap of the porphyrin molecules adsorbed on graphene (3.3 eV) as compared to Au (111) (2.4 eV). The comparison of the spectroscopy of molecules on carbon and nitrogen sites reveals a downshift of the molecular levels typical of a charge transfer towards the molecule at the nitrogen sites. This shift induces a clear topographic contrast in the STM images that allows us to discriminate the molecules above the nitrogen sites (that appear bright) compared to those on the carbon sites at +2V (see Figure), which is attributed to the purely electronic effect.
These results show a fascinating understanding at the atomic scale of the porphyrin molecules on graphene, in which the electronic interaction of molecules with graphene, particularly, on doped graphene, the sensitive charge transfer at nitrogen sites provide new strategic study for the further investigation of graphene as well as graphene-based devices.

References

[1] Georgiou et al., Nature Nanotechnology, **8** (2013), 100.
[2] F. Schedin et al., Nature Materials **6** (2007), 652.
[3] Bruno F. Machado et al., Catal. Sci. Technol. **2** (2012) 54.
[4] Yan et al., ACS Nano, **8** (2014) 4720.

Figures



Topography image reveals the molecule island on N doped graphene in which the red molecules correspond to those adsorbed on N sites. Comparative dI/dV spectra recorded on H_2TPP molecules on carbon (blue) and nitrogen (red) sites showing the energy shifts of the HOMO and LUMO states measured on the molecular island.