

Surface chemical reactions at epitaxial graphene and materials “beyond graphene”

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Graphene is a promising material in the fields of photonics, electronics, and plasmonics at the nanoscale. Such devices normally operate in air and, thus, it is crucial to establish whether their characteristics could be influenced by molecular species as O_2 and H_2O present in atmosphere. However, while the adsorption and the intercalation of metals have been widely studied, the chemical inertness of graphene toward ambient gases (not only under vacuum conditions, but also in atmosphere) has been claimed with a simplistic approach. On the other hand, some theoretical studies addressed the potential catalytic activity of graphene [1]. The knowledge of humidity-induced modification of graphene is fundamental for engineering devices which should work in ambient atmosphere. It has been reported that the charge carrier density of graphene can be modified by water or by environmental humidity and, moreover, that water molecules induce a band gap in graphene [2]. Furthermore, scanning tunneling microscopy studies on H_2O /graphene/Ru(0001) have shown that water can split graphene and intercalate [3]. Moreover, Geim and co-workers [4] have found that graphene allows unimpeded permeation of water while it is nearly impermeable to most vapors and gases, including He. Such strong water-graphene interaction is quite unexpected and still unclear.

High-resolution electron energy loss spectroscopy (HREELS) is an extremely versatile technique. Its high energy resolution (~ 0.5 meV) allows its application for studying vibrations of single atoms or molecules adsorbed onto the surface, phonons and plasmon modes [5]. By means of HREELS studies and complementary surface science-related techniques, we find that water molecules could dissociate at room temperature on epitaxial graphene (Figure 1). In both air-exposed graphene/Ru(0001) and graphene/Pt(111), C-H bending and stretching modes have been revealed at 180 and 360 meV, respectively, thus demonstrating water dissociation at room temperature on epitaxial graphene. The adsorption of water fragments induces a quenching in both the intraband and interband graphene plasmon modes (Figure 2).

The surface catalytic activity is also important for the prospect of electronic devices using ultrathin flakes of black phosphorus (few-layer phosphorene) [6, 7] or InSe [8, 9].

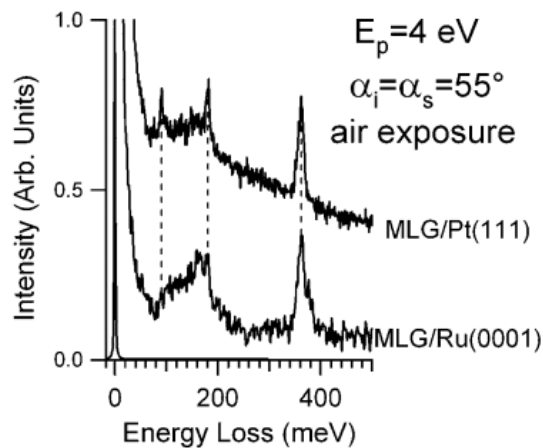


Figure 1: Vibrational spectra for monolayer graphene (MLG) grown on Pt(111) and Ru(0001) and successively exposed to ambient air humidity.

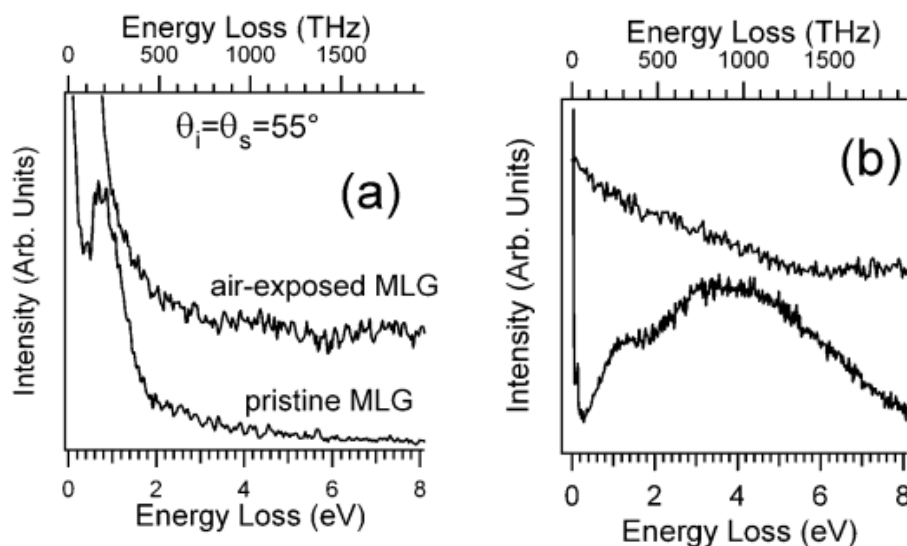


Figure 2: HREELS spectra, recorded in specular geometry and at room temperature for pristine MLG/ Ru(0001) (bottom spectrum) and the air-exposed sample (top spectrum); (b) HREELS spectra, acquired in off-specular geometry and at room temperature for pristine MLG (bottom spectrum) and the air-exposed sample (top spectrum). The two energy scales are reported in eV (bottom axis) and THz (top axis).

Many studies have reported the oxidation of black phosphorus and the formation of P_2O_5 upon air exposure [10]. However, the reactivity of phosphorene toward CO has been not studied yet. In phosphorene out-of-plane lone pairs exist. Doubly occupied sp^3 orbitals and energy levels lay below and this allows more overlap with CO orbitals. Vibrational spectra indicate that the CO adsorption on black phosphorus occurs via a weakening of the intramolecular C-O stretching frequency, which suggests that anti-bonding orbitals of CO are populated upon adsorption on phosphorene surface. Our data are supported by calculations.

In this talk, I will report on the study of surface chemical reactions with surface science techniques on epitaxial graphene, phosphorene, and InSe.

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