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# Adsorption of Na monolayer on graphene covered Pt(111) substrate[1)]

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Currently graphene continues to attract significant research interest due to its great potential for practical application in electronics and spintronics [1–4] due to the linear dispersion of electronic $\pi$ states near the $\bar{K}$-point of the Brillouin zone (BZ), the so-called Dirac cone [5, 6]. This feature is responsible for a number of unique phenomena, for example, non-dissipative electronic transport [5]. Furthermore, modification of graphene electronic properties via contact with atoms of different kind allows for designing a number of functional post-silicon electronic devices. Specifically, 2D metallic layer formation over graphene is a promising approach to improving the electronic properties of graphene-based systems.

Here we study the electronic structure of "sandwich" system Na/graphene/Pt(111) experimentally by means of angle-resolved photoemission spectroscopy and theoretically via *ab initio* calculations. As we expected, adsorption of the sodium layer leads to a charge transfer from Na both to graphene atoms and to atoms of the first Pt layer which causes a *n*-doping graphene. Since the prime problem of the *p*-doped graphene on Pt has been solved it is possible to experimentally observe the graphene gap-like feature, that is most probably related to hybridization with Pt states, required for spin-dependent effects. On the other hand, experimental data show the appearance of new additional Dirac cone-like state in the band structure of the system related with sodium monolayer formation. The ARPES band maps of the Na/Gr/Pt(111) system after Na adsorption in the direction orthogonal to $\bar{\Gamma}\bar{K}$ are shown in Fig. 1a, where Pt 5*d* states and the graphene Dirac cone can be observed. In Figure 1a the lower part of the Dirac cone is seen, but at higher binding energies, the strong hybridization with Pt states results in a complicated picture. One can resolve $\pi^*$ state dispersing from the Fermi level to $\sim$ 0.9 eV; note the absence of the visible intersection of the upper and the lower parts of the cone, so there may be a Dirac gap in the range 0.9–1.6 eV. Two new branches with less intensity appear inside the region enclosed by the $\pi^*$ branches just below the Fermi level, see Fig. 1a, b (new branches are marked with green dashed lines). Two weak peaks related to graphene Dirac cone (2) and new Na-related (1) branches can be seen in the energy distribution curves (EDC) spectrum in Fig. 1c taken along the momentum cut indicated in Fig. 1b by the dashed line. To explain this experimental feature of the Na/Gr/Pt(111) electronic structure, we show the calculation results in Fig. 1d overlayed onto the dispersion map of this system after taking second derivative of intensity with respect to energy. Here red markers correspond to unfolded graphene states and green markers correspond to folded sodium states which resemble the Kanji symbol 因.

Careful theoretical analysis demonstrate that the Na/Gr/Pt system is characterized by the strong coupling between Na and spin-polarized Pt 5*d* states. Such a graphene-mediated interaction results in formation of partially spin-polarized Dirac-like state that consists of Na bands, folded into the 2 supercell, which can also participate in electronic transport. The emergence of such extremely rare superstructure effect in Na/Gr/Pt bands is explained exactly by the graphene supporting role which provides formation of the Na monolayer.

We present a combined study of the effects of Na adsorption on the electronic properties of Gr/Pt(111) by

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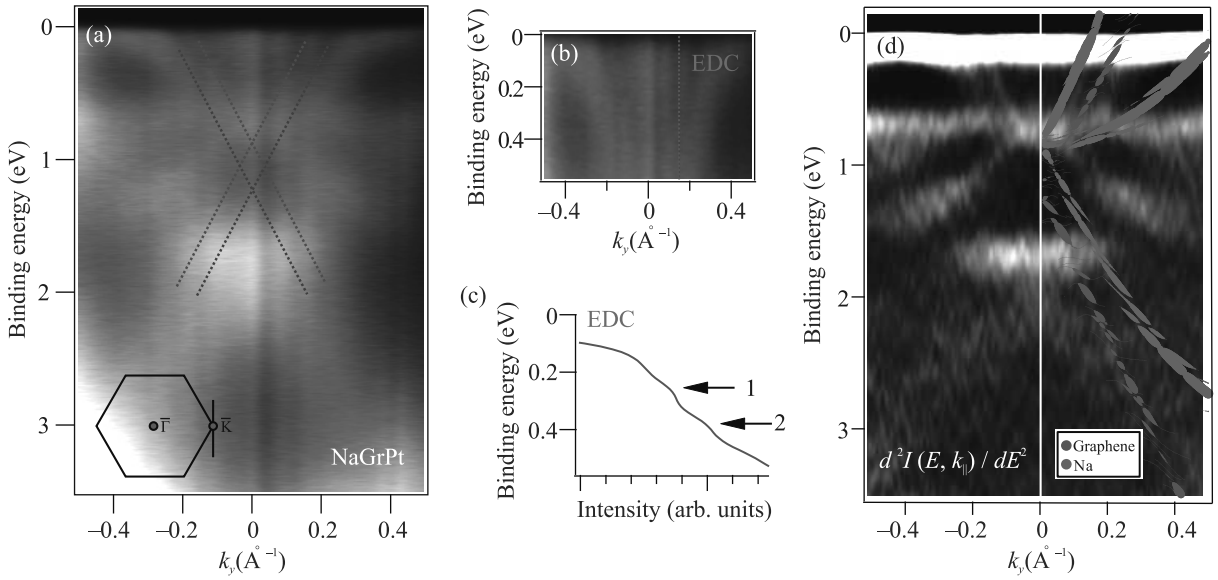


Fig. 1. (Color online) (a) – Experimental ARPES dispersion maps of Gr/Pt(111) electronic states after Na deposition (2.6 ML). The red dashed lines are a schematic representation of the graphene Dirac cone and the green dashed lines are that of sodium states. Panel (b) presents the expanded region of the dispersion map from (a). Panel (c) shows the energy distribution curves (EDC) for the $k_y$ momentum value along the cut indicated in (b). In panel (c) two peaks with numbers (1) and (2) indicate states related to graphene Dirac cone and new Na-related branches, respectively. Panel (d) shows the dispersion map from (a) after taking second derivative of intensity with respect to energy with superimposed unfolded carbon (red) and Kanji symbol-like $(2 \times 2)$ folded sodium (green) calculated bands for *short bridge* configuration. All dispersion maps are taken along the direction orthogonal to $\bar{\Gamma}\bar{K}$

ARPES and *ab initio* DFT (density functional theory) calculations. The results obtained allows us to state that adsorbing sodium atoms forms the dense short bridge configuration on top of the Gr/Pt(111) system due to the supporting interaction with the substrate. Adsorption of the dense sodium layer leads to a charge transfer from Na both to graphene atoms and atoms of the first Pt layer which causes a shift of the graphene Dirac point to the binding energy of 1.2 eV, rendering $n$-doped graphene. Hence, this allowed us to experimentally observe the gap-like feature in the Dirac point.

The system with adsorbed Na can be characterized by the strong coupling between Na and spin-polarized Pt 5$d$ states. The ARPES map demonstrates the emergence of the Kanji symbol-like states with two additional graphene-like branches just below the Fermi level. This feature is explained within the DFT framework by the formation of the Na layer $2 \times 2$ superstructure that leads to emergence of the partially spin-polarized Na folded bands in the electronic structure of Na/Gr/Pt(111). This superstructure effect takes place thanks to the graphene supporting role, which via the charge transfer with the platinum substrate, facilitates the *short bridge* structure for the sodium layer.

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