Supplementary Material to the article

"Adsorption of Na monolayer on graphene protected Pt(111) substrate"

1. Overlayer thickness calculation. To estimate how much Na was deposited on the surface we analyzed the Pt $4f$ spectra before and after adsorption of 2.6 ML (in terms of a graphene monolayer) of sodium shown in Fig. S1. The experimental intensity ratio I_0/I_d for Pt $4f$-states XPS spectra equals to 1.45, where I_0 is the intensity of the photoelectron signal before Na adsorption while I_d is the intensity of the signal after Na deposition. The equation for determining the thickness of the deposited sodium layer (Δd) using the photoelectron attenuation can be expressed as follows:

$$\Delta d = \lambda \cdot \ln\left(I_0/I_d\right), \tag{S1}$$

where λ is the electron inelastic mean free path, which can be determined in accordance with the universal curve [1] formally expressed as:

$$\lambda = 143/E^2 + 0.054\sqrt{E}, \tag{S2}$$

where E is the kinetic electron energy. Thus, the value for λ for the Pt $4f$ is ~ 4.3 Å and $\Delta d = 1.6$ Å.
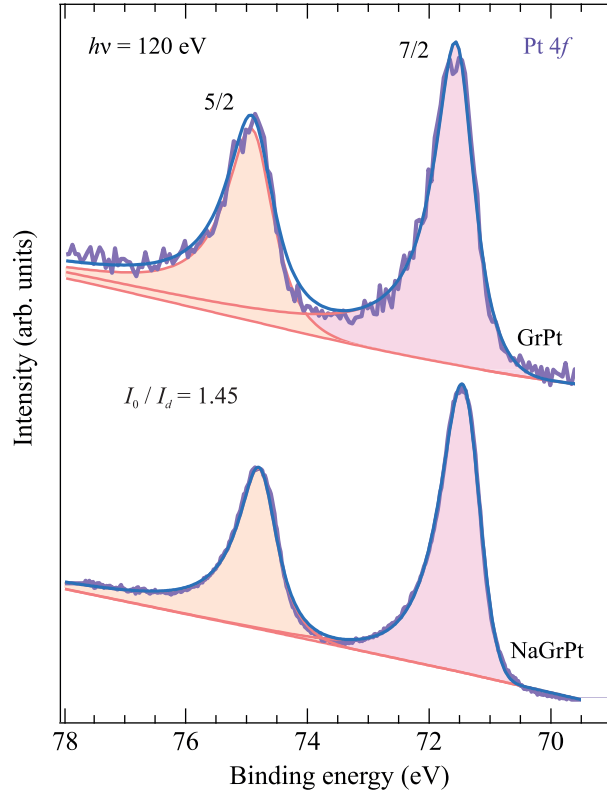

Fig. S1. XPS spectra of the core level Pt $4f$ for the GrPt system before and after Na adsorption at room temperature at various system formation stages: pristine GrPt sample and GrPt after Na deposition (2.6 ML). XPS data were measured at the photon energy of 120 eV

Considering the fact that the thickness of graphene monolayer is 3.4 Å [2], and the drop in the intensity of the photoelectron signal when passing through the atomic layer should be approximately proportional to the concentration of atoms in the layer, we can say that in our case $1\text{ML}_{\text{Na}} = 0.5\,\text{ML}_{\text{Gr}}$. This estimation corresponds to the *short* Na configurations in our DFT calculations, which are characterized by one Na atom per graphene unit cell.

Hence, we can conclude that through the synthesis, $\sim$1.6 Å of Na atoms was adsorbed on the Gr/Pt surface, which is close to the value of 1.7 Å provided by the DFT analysis in the current work.

2. The growth process of the sodium monolayer. The growth process of the Na monolayer is shown in ARPES data in Fig. S2. The spectrum in panel (b) shows two Dirac cones of graphene π states. The first one is denoted as (1) and is associated with clear surface regions of the Gr/Pt(111) sample with the characteristic p-doping as in panel (a). The second Dirac cone (denoted as (2)) position 1.2 eV, which is in agreement with the adsorbed *short bridge* overlayer of Na atoms. After prolonged deposition to 2.6 ML the whole graphene becomes covered by Na atoms, corresponds to the short bridge configuration (see Table 1 in the main paper) with only one Dirac cone in the ARPES dispersion (see panel (c)) and corresponding Dirac point position of 1.22 eV. When the dense layer is filled, there are no more stable adsorption sites and the excessive amount of sodium flies off.
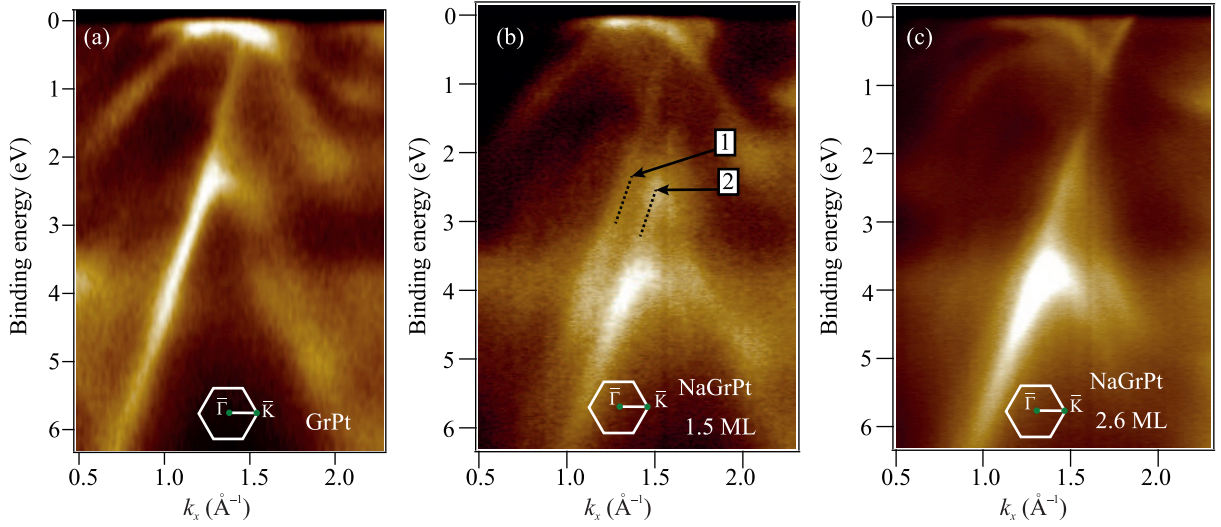

Fig. S2. Experimental ARPES maps in the $\bar{\Gamma}\bar{K}$ direction of graphene BZ: the Gr/Pt(111) system before (a), after depositions of 1.5 ML (b) and 2.6 ML (c) at RT. After Na deposition of 1.5 ML of Na with traces of two Dirac cones marked with dashed lines
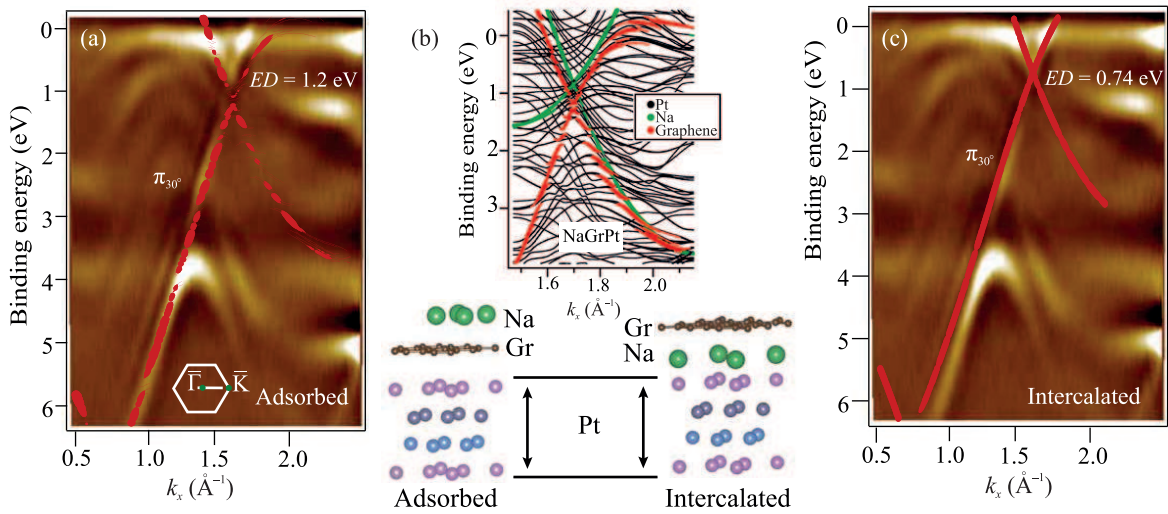

Fig. S3. Panels (a) and (c) show the same experimental dispersion map after taking the second derivatives of intensity with respect to energy after Na adsorption (2.6 ML), while the overlayed red lines are the calculated and (2×2) unfolded carbon bands for adsorbed (a) Na atoms in short bridge configuration and for the Na intercalated (c) case, respectively. Panel (b) demonstrates the calculation of sodium (green), carbon (red) and Pt (black) states near the $\bar{K}$-point for short bridge configuration as for the (a) panel

As noted in the Manuscript, we exclude the possibility of intercalation due to the absence in this case of visible hybridization of the graphene π states with the platinum d-states, which we clearly observe in the ARPES data. To demonstrate this in detail, we provide detailed comparison in Fig. S3, which represents the graphene π-bands obtained from the DFT calculations for adsorbed (a) and intercalated (c) configurations, where the former contains the avoided-crossing features, but the latter does not; the difference in graphene n-doping levels should be also noted. The overall DFT band structure is shown in Fig. S3b, where carbon and sodium states are highlighted in different colors so the π-d avoided-crossing features can be seen in more detail.

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1. M. Pl. Seah and W. A. Dench, Surf. Interface Anal. **1**, 2 (1979).
2. M. Dresselhaus, G. Dresselhaus, and R. Saito, Carbon **33**, 883 (1995).