Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Charge Doping in Graphene on Thermodynamically Preferred $BiFeO_3$ (0001) Polar Surfaces

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Table S1. Atomic relaxations of the BFO (0001) surfaces due to adsorption of graphene. The larger the layer number becomes, the further away the atomic layer from the surface is. Δd_{xy} indicates the displacements within the *xy*-plane, while Δd_z the relaxation along the *z*-axis. For Δd_z, the positive (negative) value refers to displacements in direction outwards (inwards) of the BFO (0001) surface. As regard for the BFO Z– surface, the oxygen atoms of the -Bi-O_2 termination have splitted into two layers due to surface reconstruction (see Ref. [38]), and we denote the outmost and the second O atomic layer as $O_{I'}$ and O_I, respectively.

Layer No.	G@BFO Z+	Δd_{xy} (Å)	Δd_z (Å)	Layer No.	G@BFO Z–	Δd_{xy} (Å)	Δd_z (Å)
1	Bi	0.00	-0.07	1	$O_{I'}$	0.49	-0.22
2	O_3	0.02	-0.04	2	O_I	0.11	-0.05
3	Fe	0.00	-0.02	3	Bi	0.17	-0.15
4	Bi	0.00	-0.05	4	Fe	0.04	-0.11
5	O_3	0.01	-0.02	5	O_3	0.09	-0.11
6	Fe	0.00	-0.01	6	Bi	0.04	-0.09

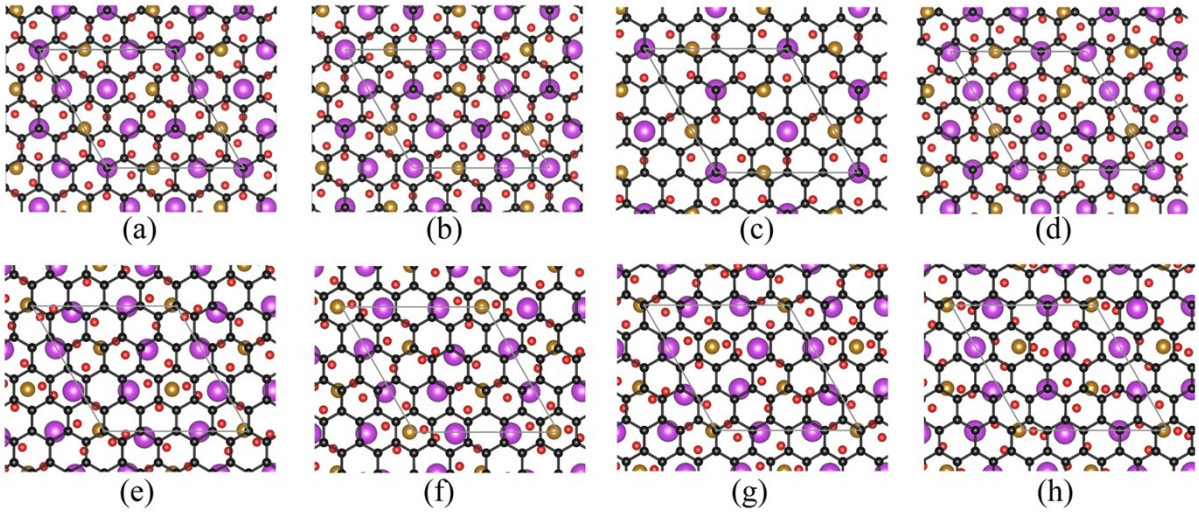

Fig. S1 Different atomic configurations of the graphene/BFO (0001) interfaces. Only graphene and the outmost Fe-O_x-Bi trilayer are shown for clarity. (a-d) graphene@BFO Z+ surface and (e-f) graphene@BFO Z– surface. The symbols of Bi, Fe, O, and C atoms are shown in Fig. 1.

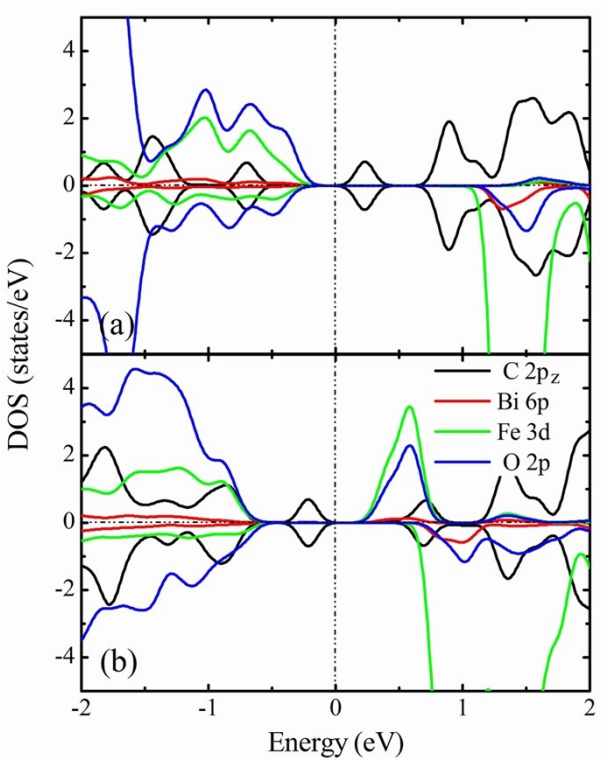

Fig. S2 Projected DOS on C-2p_z Bi-6p, Fe-3d, and O-2p orbitals of the graphene and the outmost Fe-O_x-Bi (x = 2 and 3 for the Z– and Z+ surface, respectively) trilayer. (a) graphene@BFO Z+ surface and (b) graphene@BFO Z– surface.

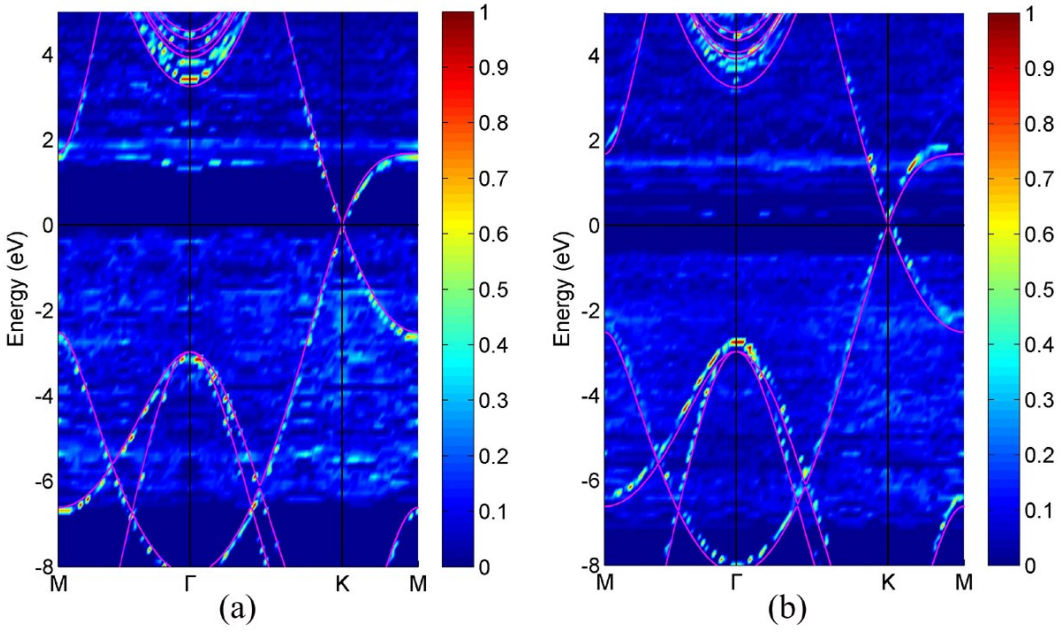

Fig. S3 Effective band structure of the down-spin electrons unfolded along the high-symmetry directions of graphene's primitive-cell Brillouin zone. (a) graphene@BFO Z+ surface and (b) graphene@BFO Z– surface. The color scale represents the number of unfolded primitive-cell bands, while the purple curve denotes the band structure of pristine graphene.

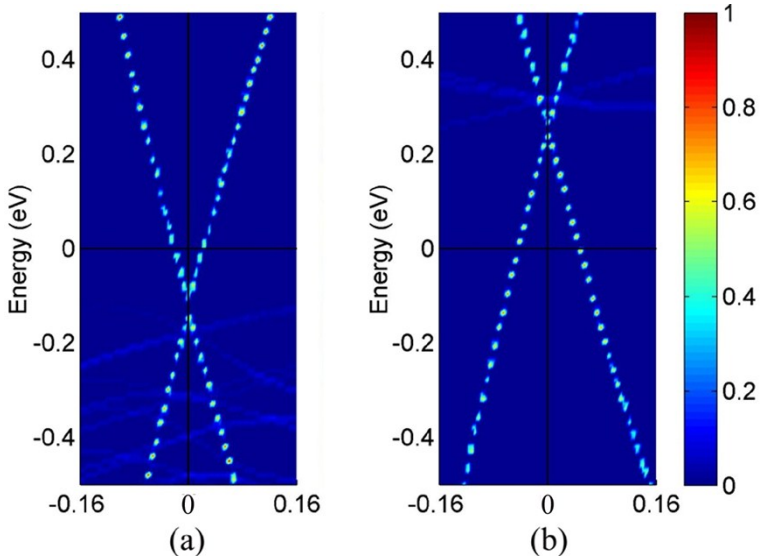

Fig. S4 Asymmetric doping of the down-spin band of graphene adsorbed on the (a) BFO Z+ and (b) Z– surface. The point *K* is at $k = 0$. The positive (negative) k value denotes the direction along *K*–*M* (*K*–Γ) direction and the unit of k is $Å^{-1}$. The color scale represents the number of unfolded primitive-cell bands.

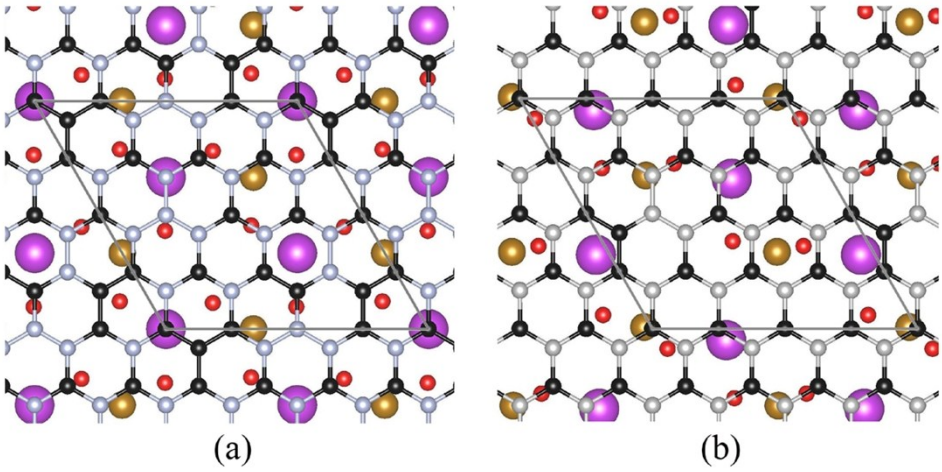

Fig. S5 Space distribution of doped carriers in graphene adsorbed on the (a) BFO Z+ surface and (b) BFO Z– surface through the Bader's charge analysis. The black and gray symbols represent the carbon atoms with electron and hole carriers, respectively. For graphene on the BFO Z+ surface, the average value for the obtained and lost electrons is -0.031 $|e|$ and +0.025 $|e|$, respectively. As regard to the graphene on the BFO Z– surface, the obtained and lost electrons are characterized by -0.047 $|e|$ and +0.060 $|e|$, respectively.