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

Supplementary Figures

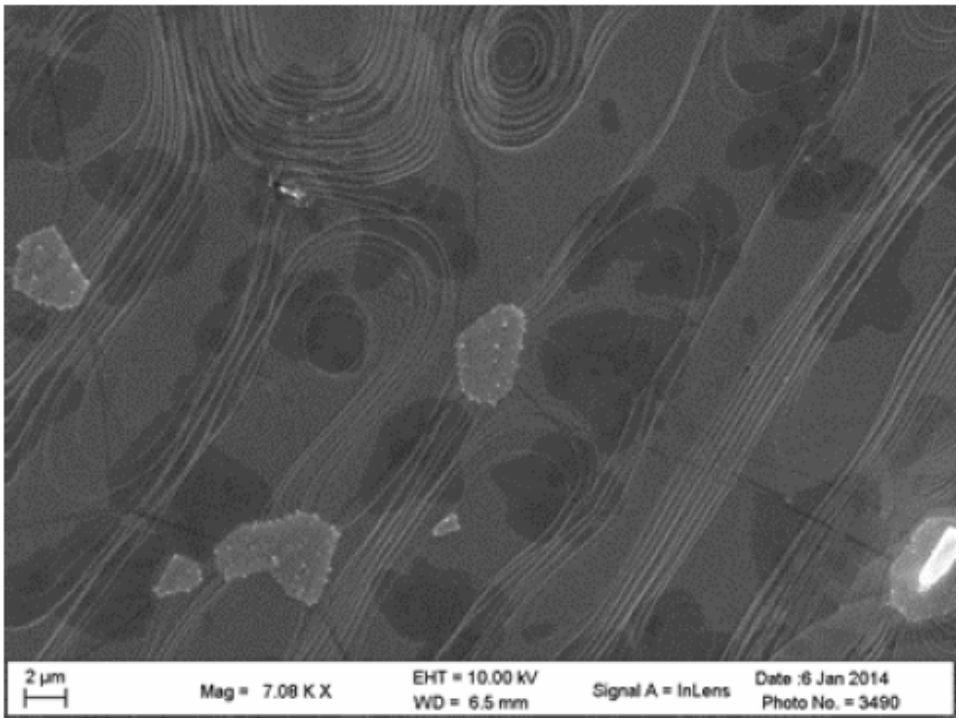

Fig. S1. SEM of sample. Ripple-like features are Cu surface steps. These steps would be covered by oxides and become invisible in bare Cu regions, but are visible since the Cu is protected by graphene from oxidation during the short air exposure between growth and SEM. This image indicates that the Cu surface is fully covered by graphene. The regions with a darker contrast than the surroundings are bilayer islands.

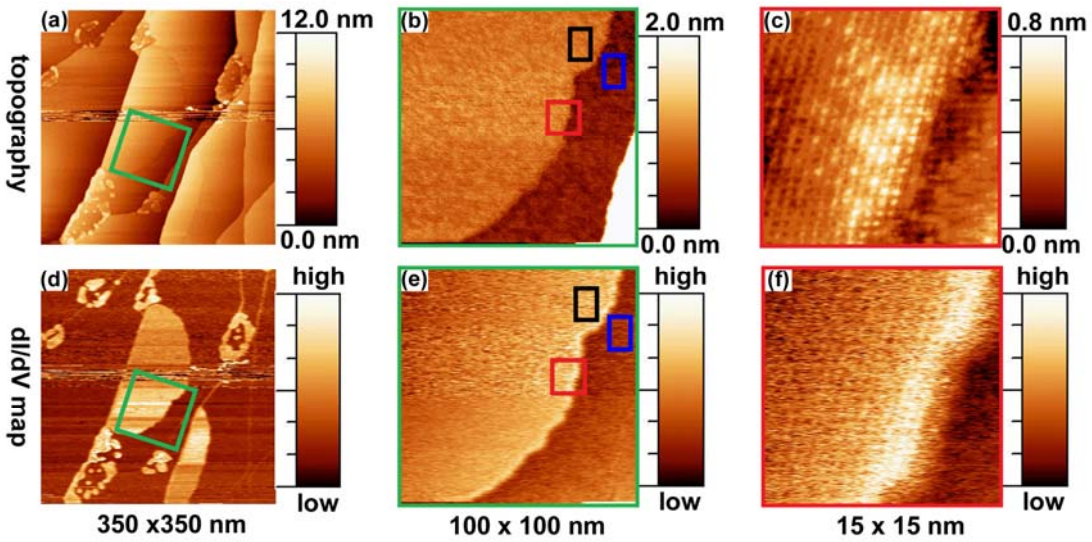

Fig. S2. STM images and simultaneously acquired STS maps taken after the 96 h, 430 °C annealing but before any higher temperature annealing. (b), (e) are the green boxed region in (a), (d). (c), (f) are the red boxed region in (b), (e). Square pattern in (c), (f) exhibits the same periodicity as in Fig. 2b in the main article. Blue and black rectangles in (b), (e) are areas in which the correspondingly colored STS curves in Fig. 3a of the main article are acquired. Set points: (a), (d): –0.8V, 0.4 nA; (b, (e) –0.7 V, 0.4 nA; (c), (f): –0.7 V, 0.4 nA.

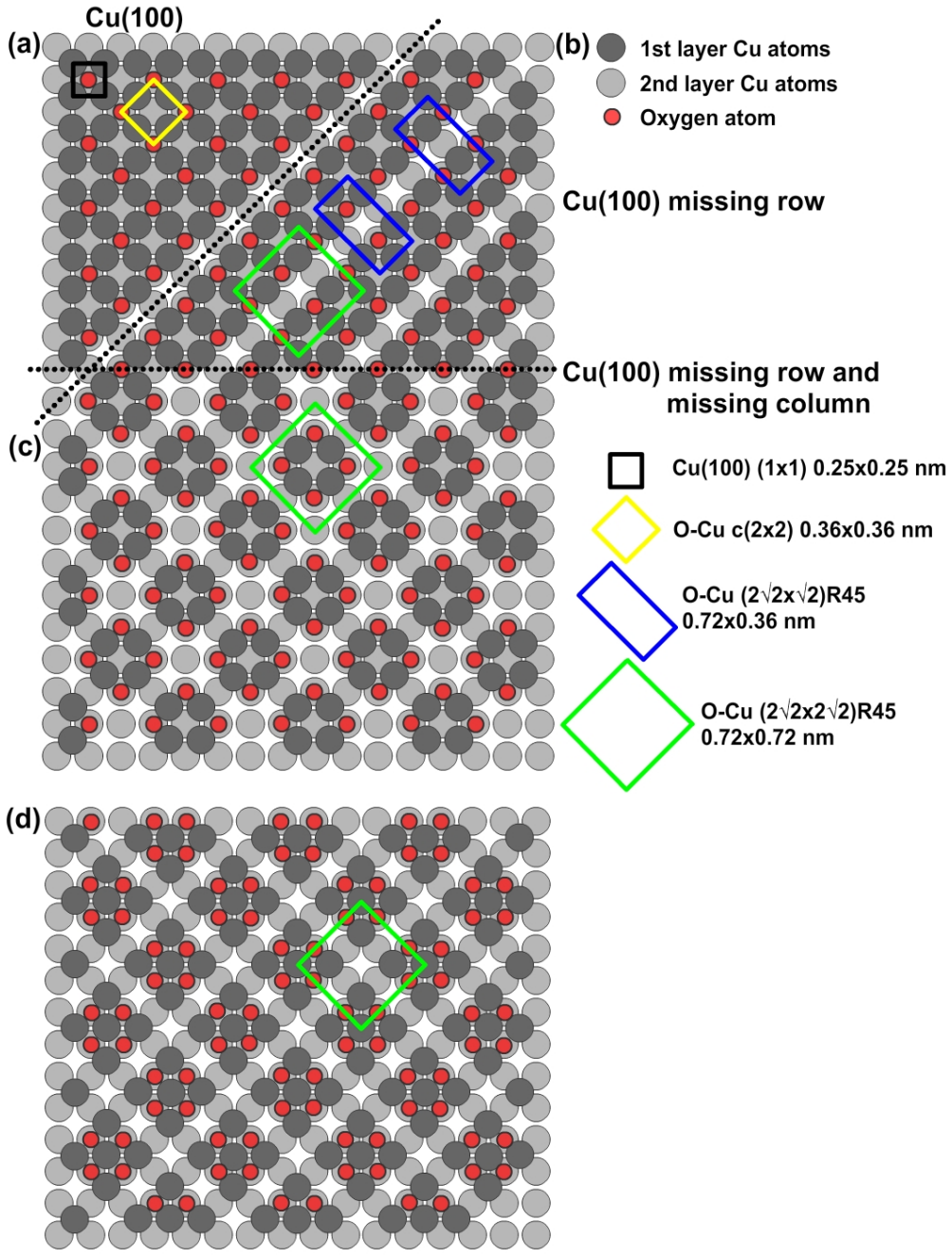

Fig. S3. Atomic models of O-Cu reconstructions. (a) c(2×2), (b) $(2\sqrt{2}\times\sqrt{2})$R45°, (c) $(2\sqrt{2}\times 2\sqrt{2})$R45° constructed by simply removing a column every four columns from $(2\sqrt{2}\times\sqrt{2})$R45° in (b). (d) An alternative $(2\sqrt{2}\times 2\sqrt{2})$R45° structure.

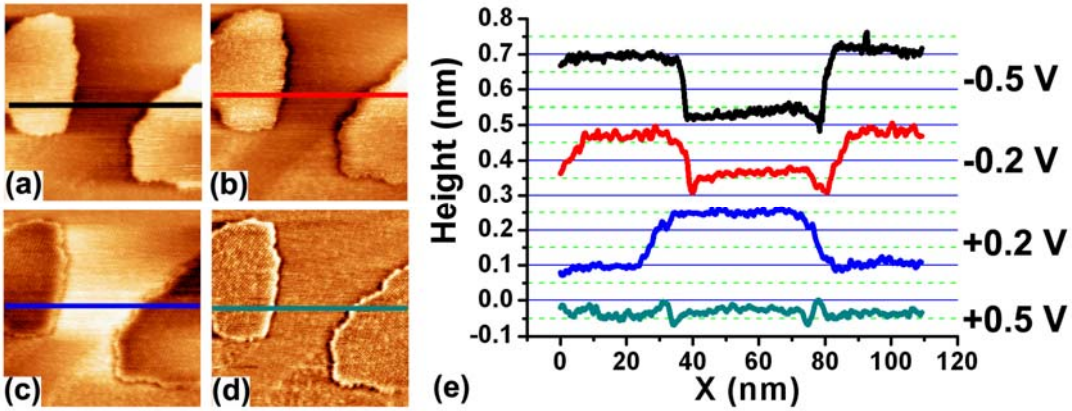

Fig. S4. STM images (a-d) and corresponding line profiles (e) acquired at different set points (0.2 nA tunneling current at sample biases labeled in (e)). Small differences in apparent height (even reversing sign at different biases) between patches and surrounding areas indicate that patches are not raised. See also Fig. S11 for three-dimensional model of intercalated oxygen.

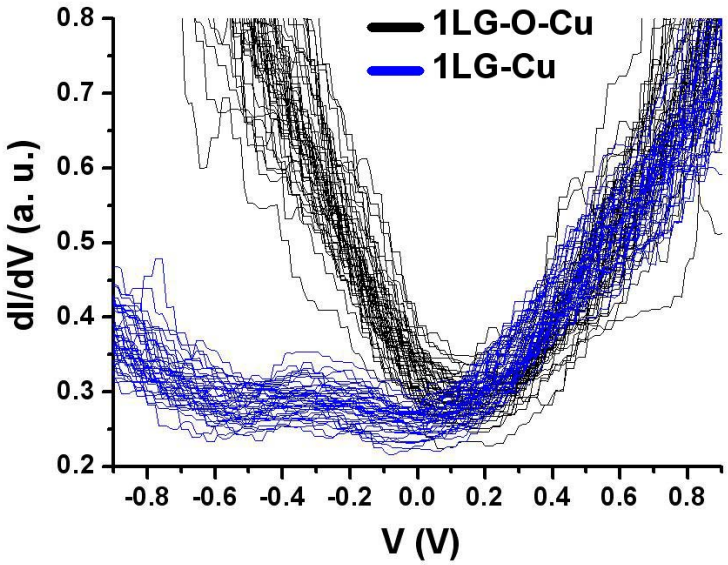

Fig. S5. Raw, individual *dI/dV* curves corresponding to the averaged curves in Fig. 3a. The black (patch) and blue (surrounding area) curves are acquired in boxes of corresponding colors in Fig. S2b,e.

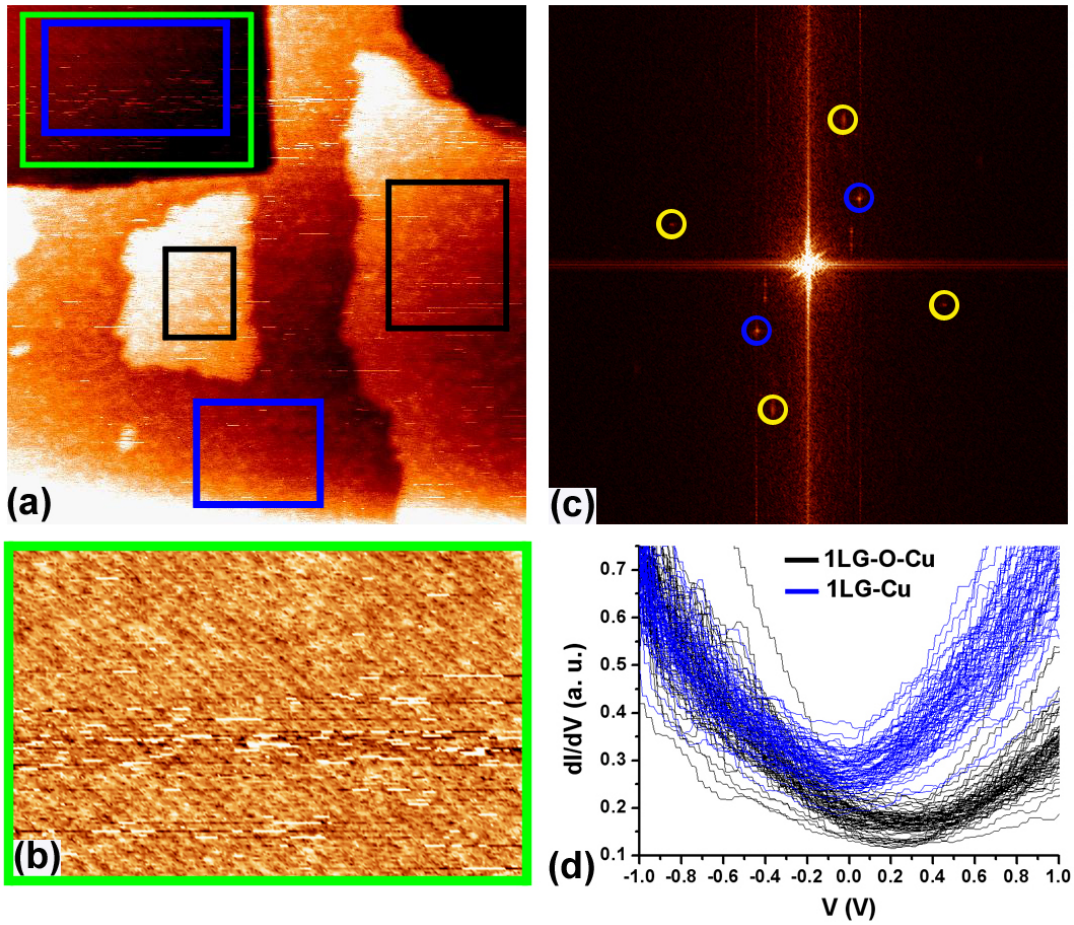

Fig. S6. (a) STM image of the area where the STS curves in Fig. 3b are obtained. (b) Zoomed-in image of the oxygen-free region in the green box in (a), showing the stripe moiré formed between 1LG and Cu(001). (c) FFT of (a), showing a pair of spots (in blue circles) corresponding to the stripe moiré in (b) and four spots (in yellow circles) attributed to the 0.72 nm × 0.72 nm periodicity of the $(2\sqrt{2}\times 2\sqrt{2})$ R45° O-Cu superstructure. (d) Individual STS curves. The curves in Fig. 3b are the averages of curves of corresponding colors, obtained in oxygen-free (blue boxes) and O-Cu (black boxes) regions, respectively.

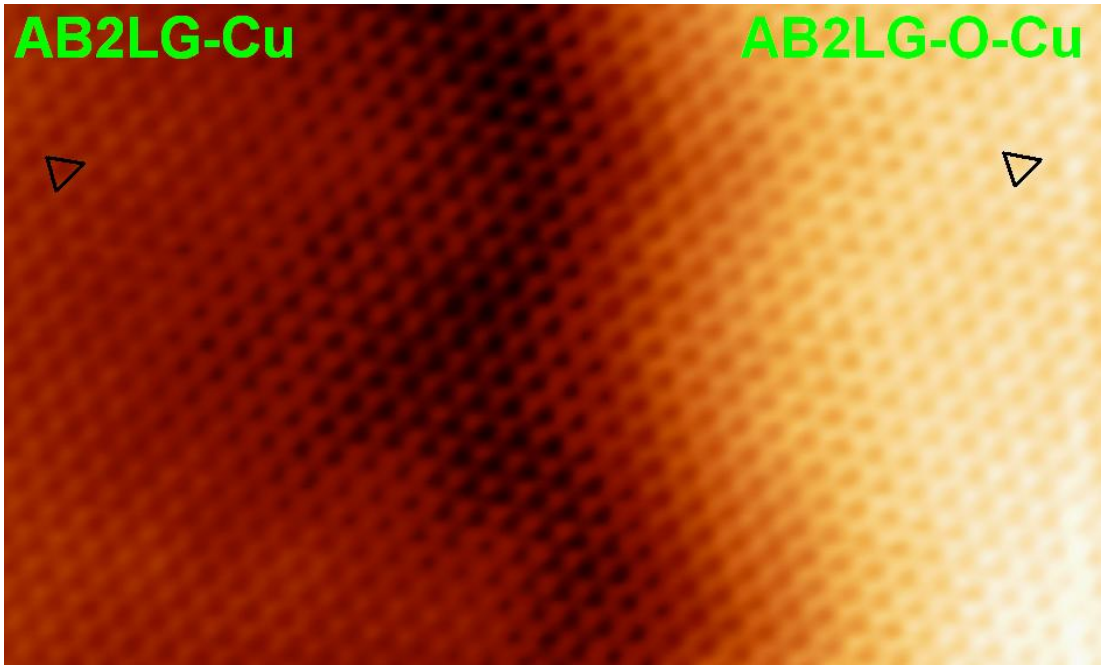

Fig. S7. Zoomed-in image (10 nm × 6 nm; –0.2 V, 0.3 nA) of the upper right corner of Fig. 4d. Three-fold symmetry indicates AB stacking.

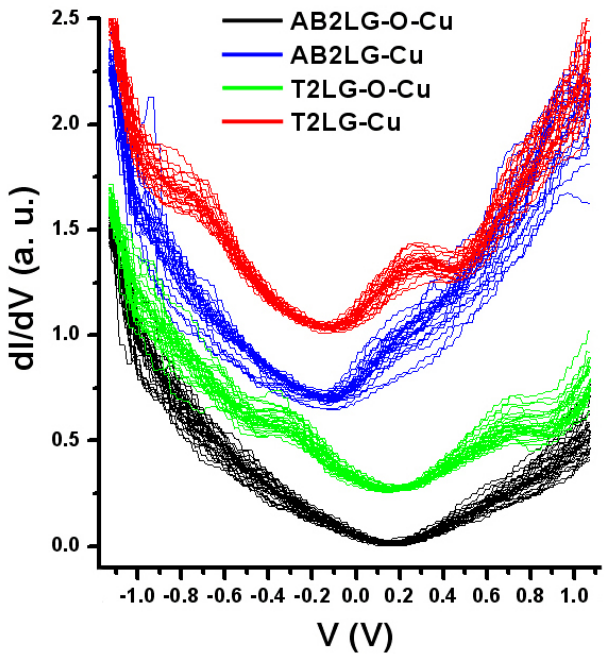

Fig. S8. Individual *dI/dV* curves corresponding to averaged curves of same colors in Fig. 4e of the main article. Curves are shifted vertically for clarity.

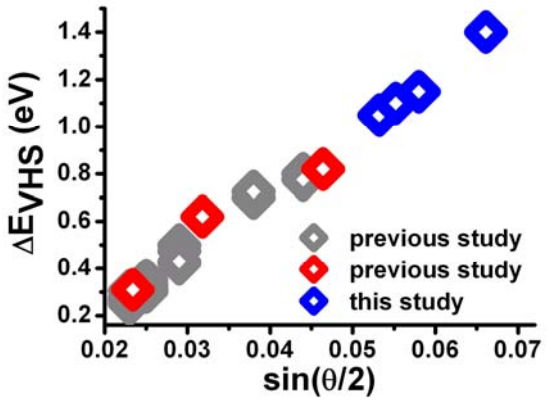

Fig. S9. Energy difference between two VHS peaks vs. sin(θ/2), where θ is the twist angle calculated from the moiré pattern. Gray and red data points are from Refs. 28 and 29 of the main article, respectively.

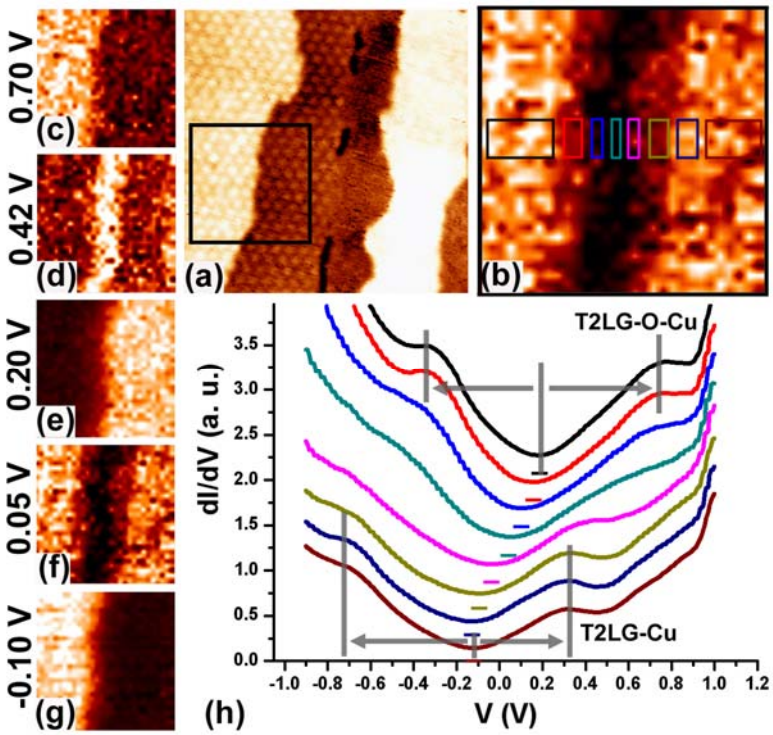

Fig. S10. Transition from p-doped T2LG-O-Cu to n-doped T2LG-Cu. (a) STM image, same as Fig. 4a in main article. (b) STS map of the boxed area in (a). (c-g) STS maps at various sample biases (labeled) of the boxed area in (a); (f) is same map as (b). (h) Averaged STS curves acquired in the boxes of corresponding colors in (b), showing the transition from p-doped T2LG-O-Cu to n-doped T2LG-Cu. Set point: 1.05 V, 1.2 nA. Curves are shifted vertically for clarity, each with a short line of corresponding color marking zero conductance.

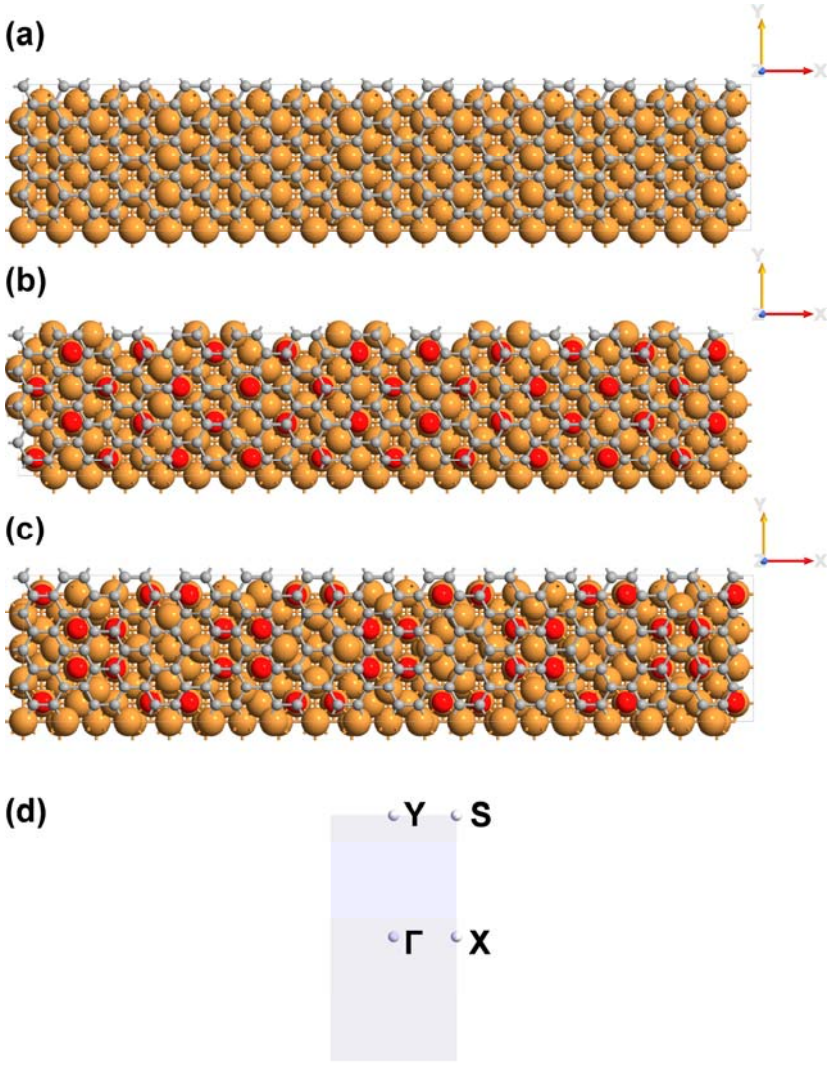

Fig. S11. Optimized geometry of monolayer graphene on Cu(001) (a) without oxygen intercalation (1LG-Cu) and (b,c) with oxygen intercalation (1LG-O-Cu). Panels (b) and (c) correspond to the O-Cu structures depicted in Fig. S3c,d, respectively. The x Cartesian axis is in the Cu[110] direction. (d) First Brillouin zone of the supercells in (a), (b), and (c).

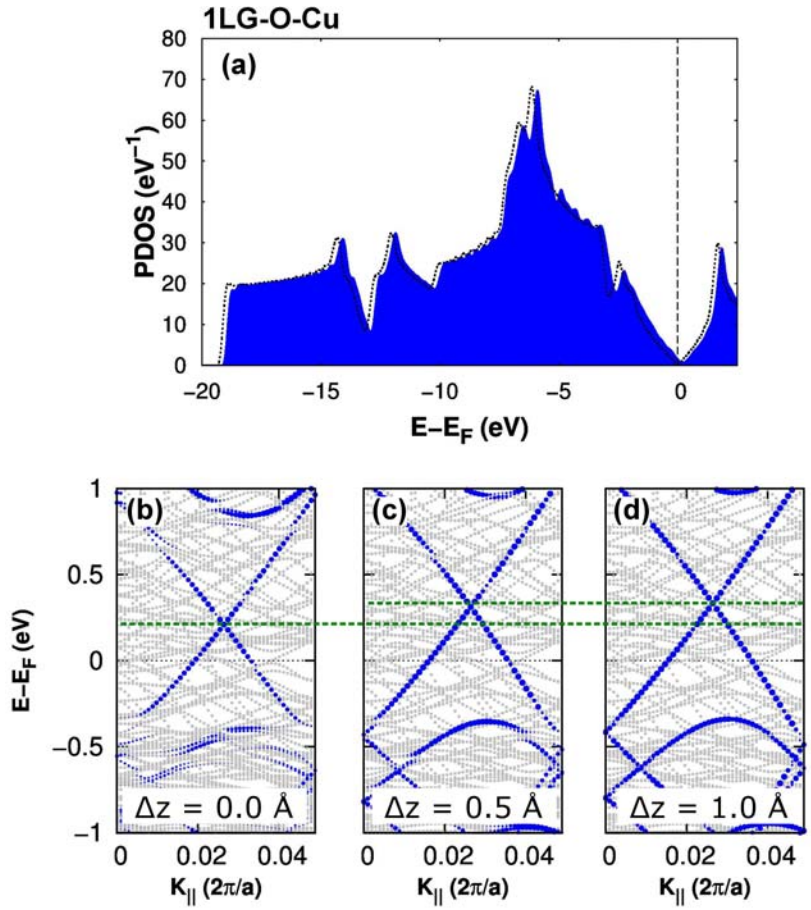

Fig. S12. Electronic structure of 1LG-O-Cu calculated by assuming the alternative $(2\sqrt{2}\times 2\sqrt{2})$R45° structure shown in Fig. S3d and Fig. S11c. (a) 1LG-O-Cu PDOS on C s and p orbitals (with blue shadow), in comparison with that of free-standing graphene (black dotted curve). (b,c,d) 1LG-Cu band structure in the YΓ direction at equilibrium distance, lifted by 0.5 Å, and by 1.0 Å, respectively. Here, $k_{//}$ denotes the wavevector in the YΓ direction with $k_{//} = 0$ at Y (see Fig. S11), and the unit of $k_{//}$ is $2\pi/a$, where a = 2.552 Å is the lattice constant of the Cu(001) surface lattice. Gray dots: folded bands. Blue dots: projections onto C s and p orbitals.

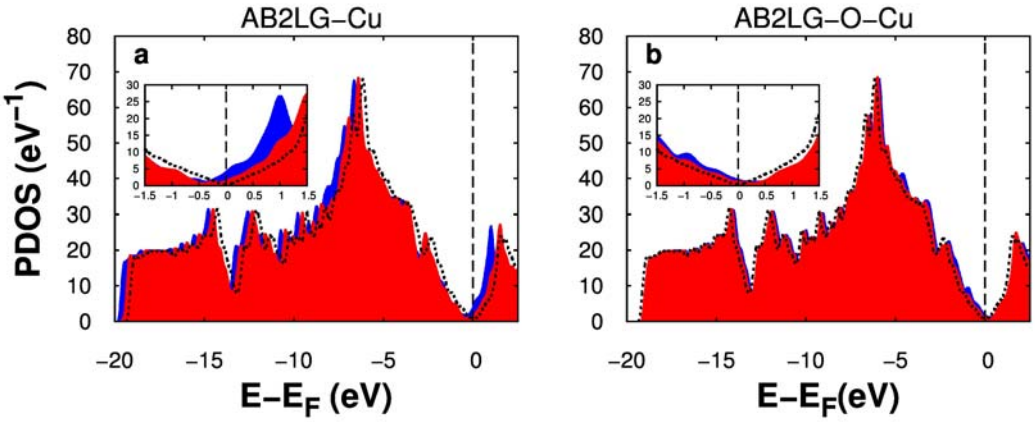

Fig. S13. PDOS of AB2LG-Cu (a) and AB2LG-O-Cu (b), with blue/red colors indicating bottom/top graphene sheets. Dotted curves are PDOS of free-standing 1LG for reference. Insets show details near E_F.

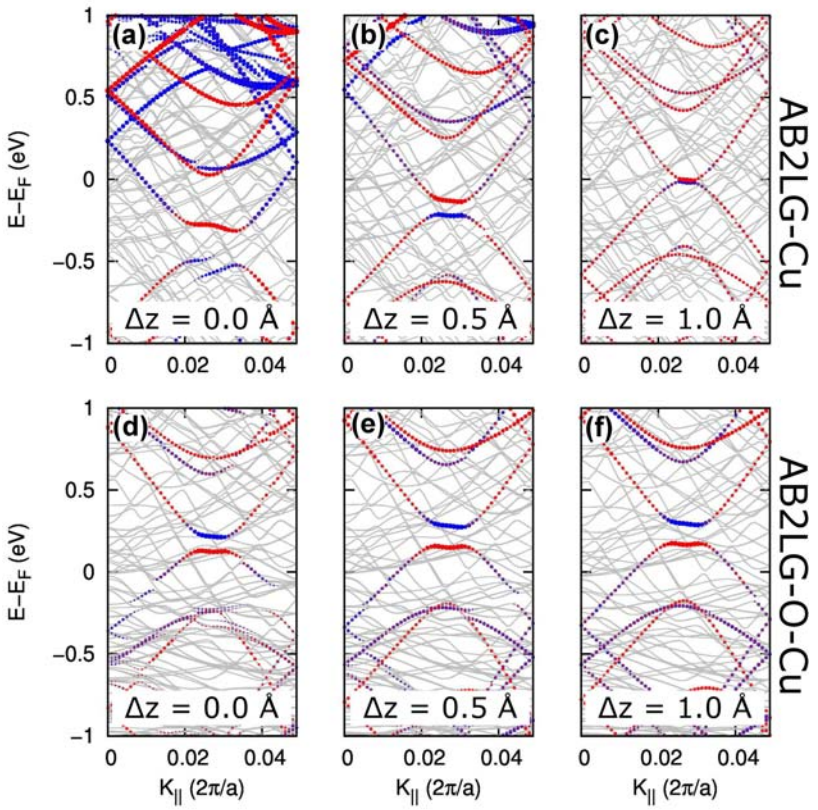

Fig. S14. Band structures of AB2LG-Cu (a-c) and AB2LG-O-Cu (d-f) lifted by Δz (labeled) from equilibrium position. Here, $k_{//}$ denotes the wavevector in the YΓ direction with $k_{//} = 0$ at Y (see Fig. S11), and the unit of $k_{//}$ is $2\pi/a$, where a = 2.552 Å is the lattice constant of the Cu(001) surface lattice.

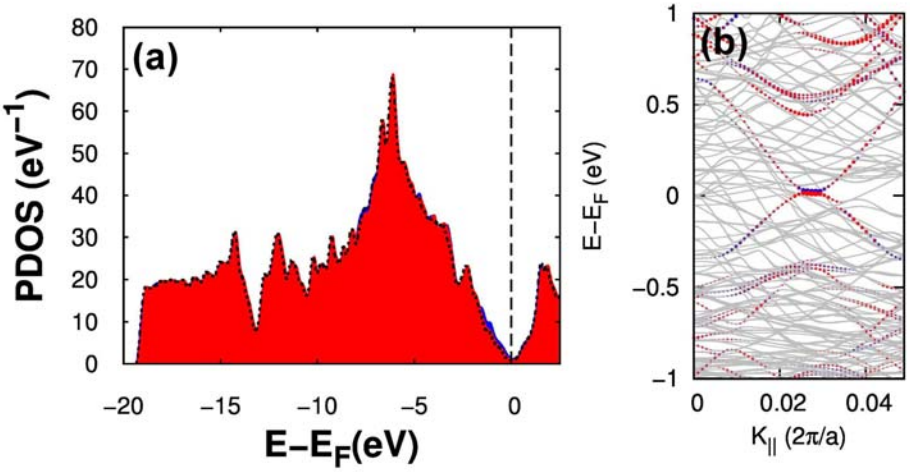

Fig. S15. PDOS and band structure of AB2LG-O-Cu calculated by assuming the alternative $(2\sqrt{2}\times 2\sqrt{2})$ R45° structure shown in Fig. S3d and Fig. S11c. Compared to Fig. S15d, the absence of a gap is due to minimal charge transfer (i.e. doping).

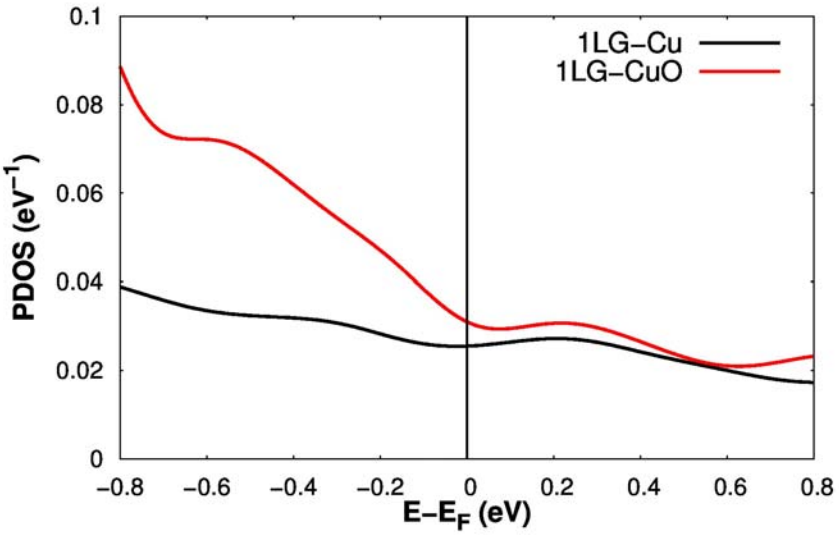

Fig. S16. PDOS onto Cu d_{z^2} for 1LG-Cu (black) and 1LG-O-Cu (red).

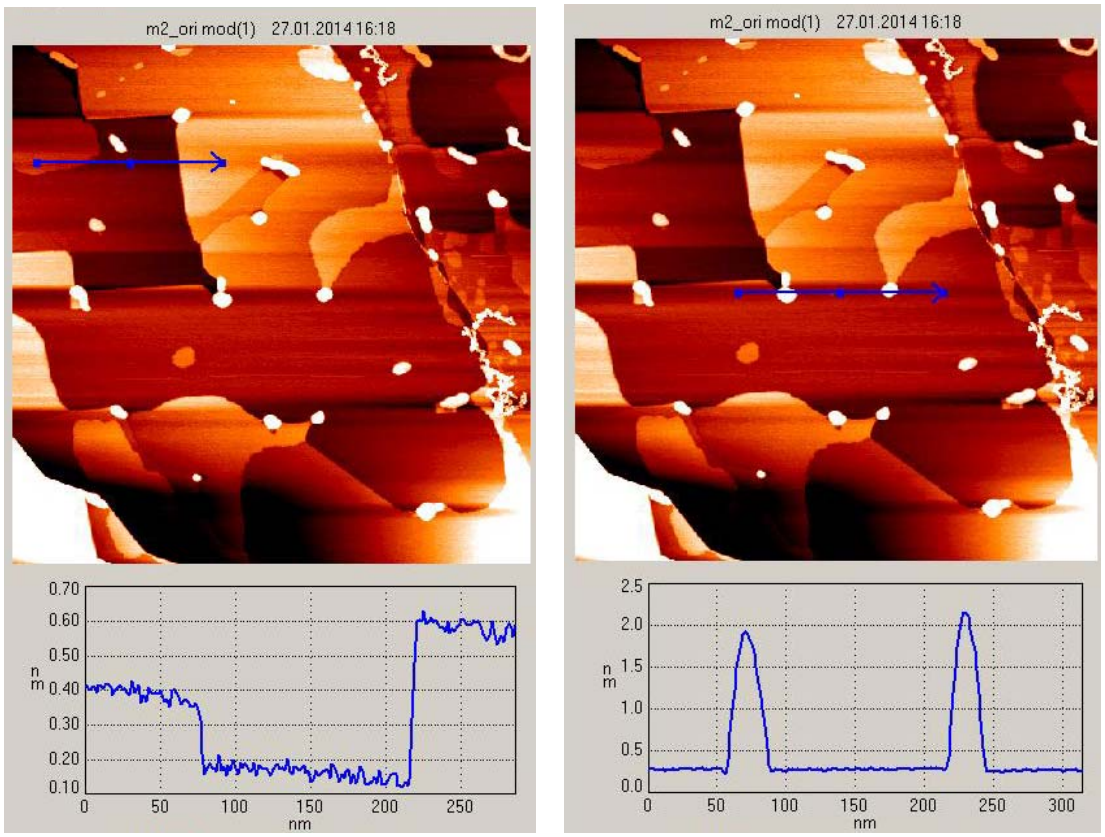

Fig. S17. Substrate morphology prevents graphene from relaxing to equilibrium distance above substrate surface after thermal cycles of large temperature change. Left: terrace height variation. Right: contaminations (particles), some of which may be between graphene and substrate surface. These undulations can support the graphene, preventing it from relaxing to equilibrium distance.

Supplementary Table S1

Regions	Thermal cycle stage	Experimental results	Theoretical results and explanations
1LG-Cu (oxygen-free)	96 hr at 430 °C only	**Fig. 3a** blue curve: E_D ~ –0.5 eV, another minimum at E_F.	**Fig. 5a,b**: E_D = –0.5 eV due to charge transfer at equilibrium separation (Δz = 0). Minimum at E_F due to inelastic tunneling gap with thermal broadening.
	After 20 min at 700 °C	**Fig. 3b** blue curve. E_D ~ –0.05 eV.	**Fig. 5c,d**: E_D = –0.2 eV when 1LG lifted by Δz = 0.5 Å; E_D = +0.1 eV when Δz = 1 Å. Actual Δz in between. As 1L-Cu distance increases, charge transfer approaches expectation from work function difference. Valleys at E_D and E_F merge.
1LG-O-Cu (oxygen-intercalated)	96 hr at 430 °C only	**Fig. 3a** black curve: E_D ~ +0.15 eV.	**Fig. 5e,f**: E_D = +0.39 eV at Δz = 0. **Fig. S12a,b**: E_D = +0.18 eV for alternative O-Cu structure. Oxygen alters graphene-Cu interaction.
	After 20 min at 700 °C	**Fig. 3b** black curve: E_D ~ +0.25 eV.	**Fig. 5g,h**: E_D = +0.42 eV for Δz = 0.5 Å and 1 Å. **Fig. S12c,d**: E_D = +0.3 eV for alternative O-Cu structure at both Δz.
AB2LG-Cu (oxygen-free)	96 hr at 430 °C only	-	**Fig. S13a**, **Fig. S14a**. E_D = –0.5 eV for equilibrium separation (Δz = 0).
	After 20 min at 700 °C	**Fig. 4e** blue curve. E_D ~ –0.13 eV.	**Fig. S14b,c**. E_D = –0.2 eV for Δz = 0.5 Å and E_D = 0.0 eV for Δz = 1 Å.
AB2LG-O-Cu (oxygen-intercalated)	96 hr at 430 °C only	-	**Fig. S13b**, **Fig. S14d**: E_D = +0.2 eV for equilibrium separation (Δz = 0). **Fig. S16**: E_D ~ 0 for Δz = 0 for the alternative structure.
	After 20 min at 700 °C	**Fig. 4e** black curve. E_D ~ +0.2 eV.	**Fig. S14e,f**: E_D = +0.25 eV for Δz = 0.5 Å and Δz = 1 Å.
T2LG-Cu (oxygen-free)	After 20 min at 700 °C	**Fig. 4e** red curve. E_D ~ –0.13 eV.	VHS peaks unambiguously confirm that the STS minimum between the two peaks corresponds to E_D.
T2LG-O-Cu (oxygen-intercalated)	After 20 min at 700 °C	**Fig. 4e** green curve. E_D ~ +0.2 eV.	