## SUPPLEMENTARY INFORMATION:

*Experimental details for NEXAFS Measurements:* Carbon K-edge and Cu, Ni, and Co L-edge NEXAFS experiments were performed at National Institute of Standards and Technology (NIST) beamline U7A of the National Synchrotron Light Source at Brookhaven National Laboratory. A toroidal spherical grating monochromator with 600 lines/mm and 1200 lines/mm were used to acquire the C K-edge and transition-metal L-edge data, respectively, yielding an energy resolution of approximately 0.1 eV. The slits were set to 30  $\mu$ m by 30  $\mu$ m. The spectra were acquired in partial electron yield mode (PEY) with a channeltron electron multiplier detector with an entrance grid bias set to -150 V (carbon K-edge) and -250 V (metal L-edge) to enhance surface sensitivity and reduce lower energy edge noise. A charge compensating electron gun was used to remove the effects of charging, although this is negligible on conducting substrates. The PEY signals were normalized using the incident beam intensity obtained from the photoemission yield of a freshly evaporated Au grid with 90% transmittance places along the path of the incident X-rays. The C K-edge spectra were calibrated to an amorphous carbon mesh with a  $\pi^*$  transition at 285.1 eV. The C K-edge NEXAFS spectra are presented after pre- and post-edge normalization. In the case of transition-metal L-edge data, the spectra are only pre-edge normalized.



Figure S1:

Raman spectra of graphene grown on polycrystalline and single-crystal Cu and Ni substrates

Raman data acquired using 514.5 nm laser excitation. (a) and (b) are Raman spectra acquired for graphene grown on polycrystalline and single crystal Cu and Ni substrates, respectively. Spectra A-D correspond to the polycrystalline foil, [111], [110], and [100] substrates of both Cu and Ni.



Figure S2:

NEXAFS spectra of graphene synthesized on polycrystalline copper foil and single crystal copper substrates

NEXAFS spectra acquired at 25° incidence of the X-ray beam of SLG and FLG on Cu substrates prepared by CVD as discussed in the methods section. Here we explicitly show that the low-energy resonance in Figure 1 at normal incidence (85°) is not disenable at glancing incidence (25°).



## Figure S3:

Atomic Force Microscopy Images of Transition-Metal Contacts

Atomic force microscopy images (ÅFM) images of single layered graphene on  $SiO_2$  with and without transition-metal deposition. Image (a) corresponds to graphene transferred using thermal release tape (TRT) onto 300 nm  $SiO_2/Si$ . Images (b-d) are of single-layered graphene with deposited Cu, Ni, and Co, overlayers, respectively.



Figure S4: NEXAFS L-edge spectra of SLG/Transition-Metal Contacts

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Transition-metal L-edge NEXAFS spectra of Co, Ni and Cu 1 nm depositions on transferred SLG on SiO<sub>2</sub>. The spectra have only been preedge normalized enabling comparison of the edge jump intensities.



Figure S5:

Raman shifts of pinned (Cu/SLG) with Transition-Metal Contacts

Raman data acquired with 514.5 nm laser excitation. Spectra of metal-overlayer/SLG/Cu samples with 1 nm transition metal depositions for comparison to metal-overlayer/SLG/SiO<sub>2</sub> substrates shown in Figure 2b. Spectrum A is a reference sample with no metal deposition of SLG/Cu. Spectra B-C correspond to 1 nm deposition of Cu, Ni, and Co respectively. Note that a similar trend is observed but with a diminished amount of symmetry breaking, seen as a decrease in the *D*-band and preservation of 2D band as compared to Figure 2b.



Figure S6:

Band Structures of SLG/Cu Metal Contacts at varying  $d_z$ Varying the interfacial distance (Å) denoted upper right hand corner of each band structure, the reorganization and hybridization seen in Cu 2.1 and Cu 2.8 shifts to a rigid band shift at Cu 3.25 and decreases until no interactions between the SLG (Fig. 3) and Cu band structures can be seen.