

Supporting Information

Growth of large single-crystalline two-dimensional boron nitride hexagons on electropolished copper

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Methods

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Electropolishing of Cu foil. Copper foils were purchased from Alfa Aesar (25 μm , 99.8%) and degreased with acetone, IPA, and milli-Q water sequential rinsing prior to use. Copper foil surface tailoring was performed on a Struers Lectropol 5 automatic electropolishing unit utilizing an electrolyte composed of 330 mL dI H_2O , 167 mL ortho-phosphoric acid, 167 mL ethanol, 33 mL isopropyl alcohol, and 3.3 g urea. Copper foil sample areas of 5 cm^2 were electropolished at 8 V under constant flow for the designated polishing time.

Synthesis of h-BN by APCVD. Prior to deposition, the unpolish/polished Cu foil was dipped in dilute nitric acid for a few seconds to remove the native oxide and rinsed in DI water. 5 mg of Ammonia borane ($\text{NH}_3\text{-BH}_3$) was used as a precursor and placed in a ceramic boat, away from the heating source. The Cu foil was positioned towards the rear end of the quartz tube $\sim 30\text{ cm}$ away from the ceramic boat. Under the protection of 425 sccm of Ar and 75 sccm of H_2 , the Cu foil was annealed at $800\text{ }^\circ\text{C}$ for 20 min and then raised up to $1050\text{ }^\circ\text{C}$ in 40 min. During growth, the temperature was kept at $1050\text{ }^\circ\text{C}$ for 10 - 30 min and ammonia borane was heated up by a flexible heating belt at $60 - 65\text{ }^\circ\text{C}$. At the same time, the gas flow of Ar and H_2 was reduced to 170 sccm and 30 sccm, respectively. At the end of the growth, the gas flow of Ar and H_2 were set back to 425 sccm and 75 sccm, respectively, and the lid of the furnace was lifted for fast cooling.

Transfer process. poly(methyl methacrylate) (PMMA) was spin coated on the as-grown h-BN on Cu foil at 3000 rpm for 30 s and baked at 105°C for 2 min. The PMMA coated Cu foil was then placed into a Cu etchant, $\text{Fe}(\text{NO}_3)_3$ for several hours until the Cu was completely etched. The PMMA/h-BN was then rinsed in DI water for a few times before it was extracted onto $285\text{ nm SiO}_2/\text{Si}$ or quartz substrates. The transferred PMMA/h-BN film was left to dry and subsequently PMMA was removed by submerging the substrate into acetone.

Characterization. Scanning electron microscope (SEM) images were taken on as-grown h-BN on Cu using LEO 1550 Gemini. Atomic force microscope (AFM), Cypher scanning probe microscopy and Asylum Research MFP-3D, were done using tapping mode to characterize the morphology of the polished and unpolished Cu foil as well as the transferred h-BN films. WITec Raman spectroscopy with laser excitation wavelength of 532nm was used to determine the quality of the h-BN film and map the hexagonal-shape BN domain at room temperature. Transmission electron microscope (TEM) was carried on JEOL 2100 and 2010, operated with an acceleration voltage of 200 kV, to determine the atomic arrangement and thickness. X-ray photoelectron spectroscopy (XPS) was used to characterize the elemental composition of boron and nitrogen constituents of h-BN, and surface oxidation of the Cu foils. Ultraviolet-visible (UV-vis) spectroscopy (Shimadzu UV-2450) was used to measure the OBG of h-BN film. X-ray diffraction (XRD) was used to determine the Cu orientation.

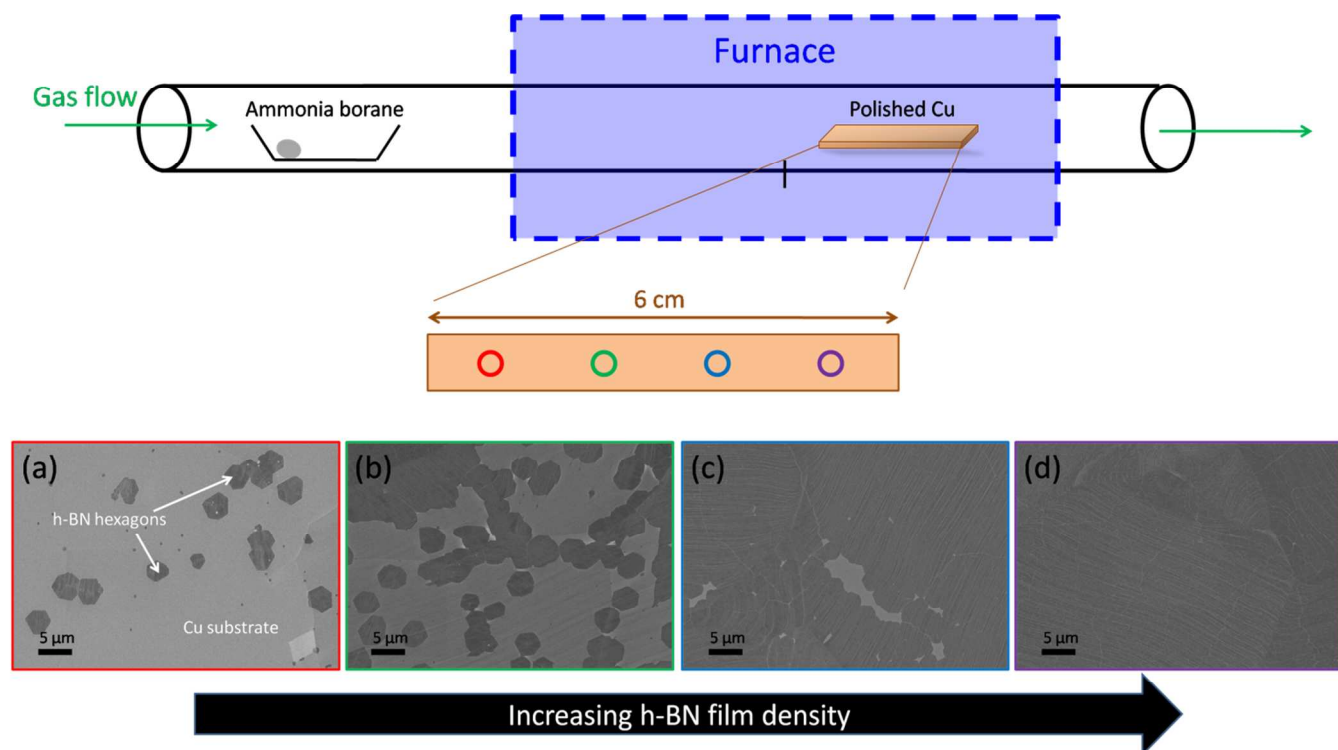


Figure S1. Variable h-BN film density at different regions on the polished Cu. Schematic illustration of CVD setup and placement of Cu substrate. The Cu substrate is placed ~30 cm away from the precursor (ammonia borane). The polished Cu is cut into half, and placed sequentially in the quartz tube to achieve an effective length of ~6 cm. SEM images are taken ~1 cm apart at different regions indicated by (a) red, (b) green, (c) blue, (d) violet circles, respectively.

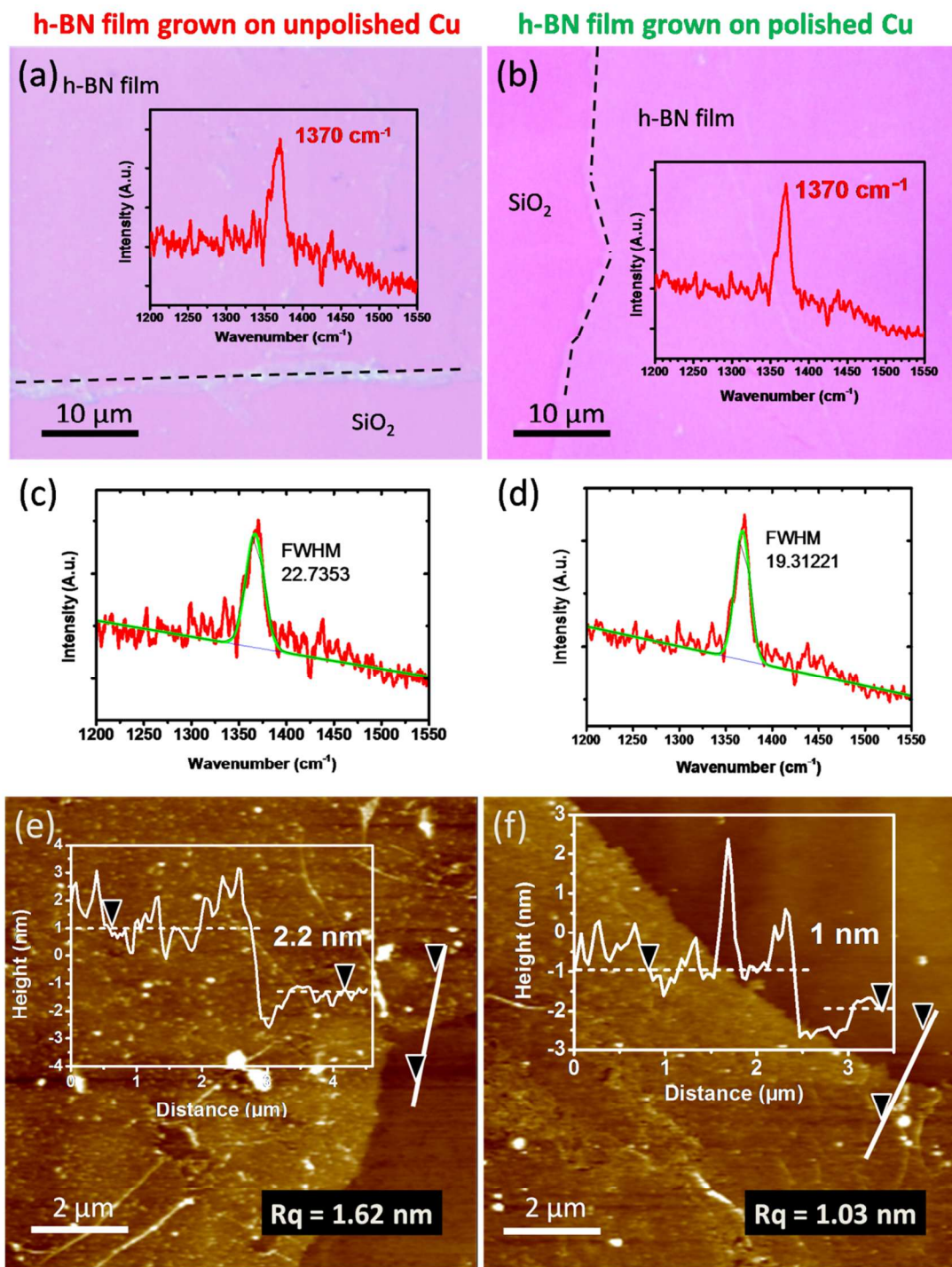


Figure S2. Comparison between of h-BN films grown on unpolished and polished Cu. (a,b) Optical images of transferred large-area continuous h-BN film growth by using unpolished and polished Cu, respectively. The insets show the corresponding Raman spectrum with peaks at 1370 cm⁻¹, attributing to

the presence of h-BN. (c,d) Full width of half maximum (FWHM) calculation for Raman spectrum in (a) and (b), respectively. (e,f) AFM images with scanned line over the films' edges. The insets show the corresponding height profile of the scanned line with thickness of 2.2 nm and 1 nm, and RMS surface roughness of 1.62 and 1.03 nm for h-BN films grown on unpolished Cu and polished Cu, respectively.

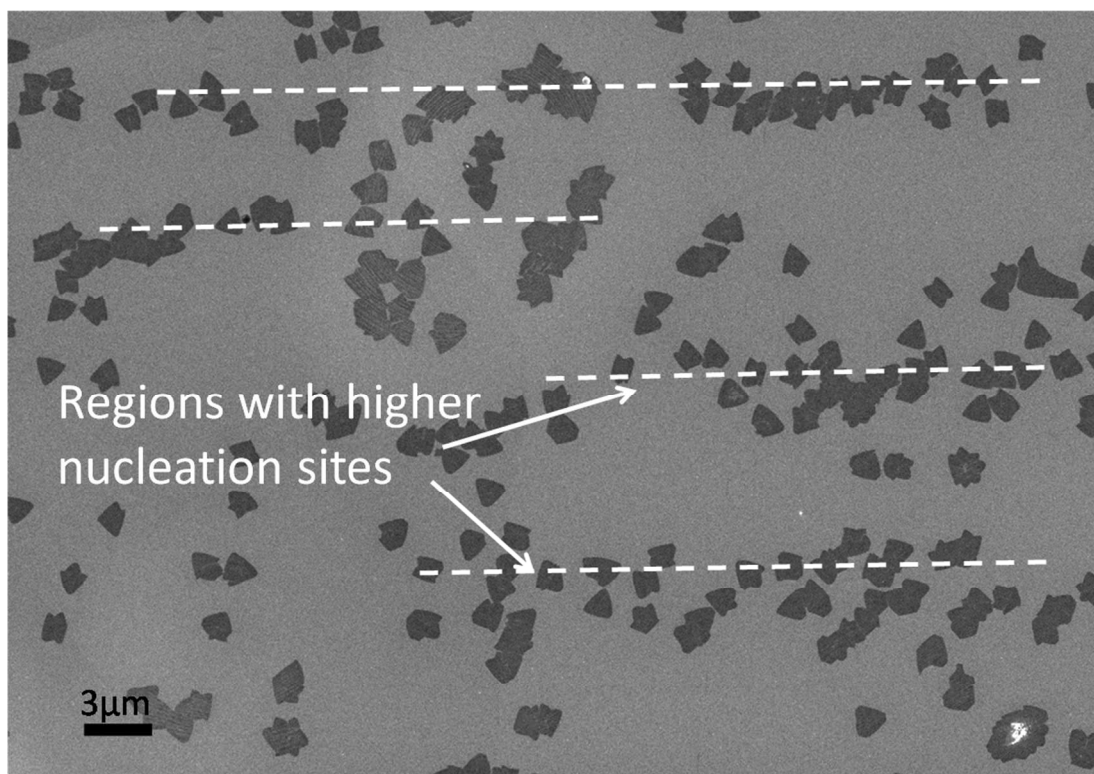


Figure S3. Influence of Cu surface morphology of nucleation sites and multilayer regions of h-BN. During the initial stages of growth, h-BN tends to nucleate along the uneven parallel strips on the Cu foil, the h-BN domains continue to grow to coalesce to form a continuous film after prolong period of growth time.

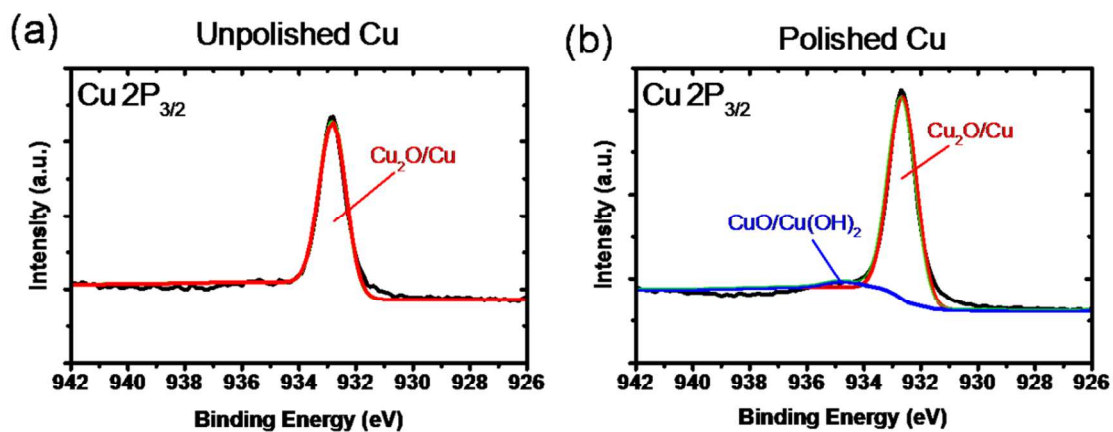


Figure S4. Cu oxidation due to electropolishing process. Cu 2P_{3/2} XPS spectra of (a) unpolished and (b) polished Cu substrates. Presence of higher content of Cu oxide is evident due to the increased in intensity of Cu₂O, CuO and Cu(OH)₂ peaks respectively. During electropolishing, surface oxidation occurs as Cu ions react with phosphoric acid (H₃PO₄) causing the formation of Cu₂O, CuO and Cu(OH)₂.

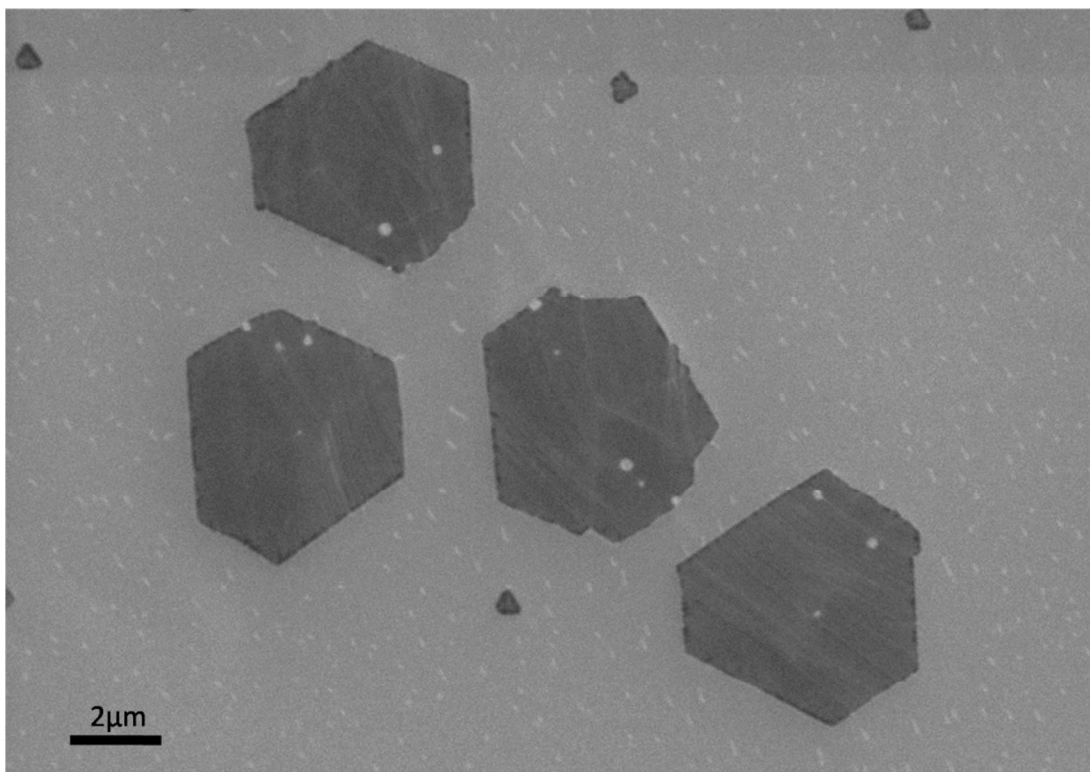


Figure S5. Elongated hexagonal-shape h-BN domains. SEM image of irregular shaped h-BN hexagons. Large hexagonal h-BN flakes are not always in perfect symmetry, some are elongated in shape due to its asymmetric nature of N and B-terminated edges and other CVD process factors.

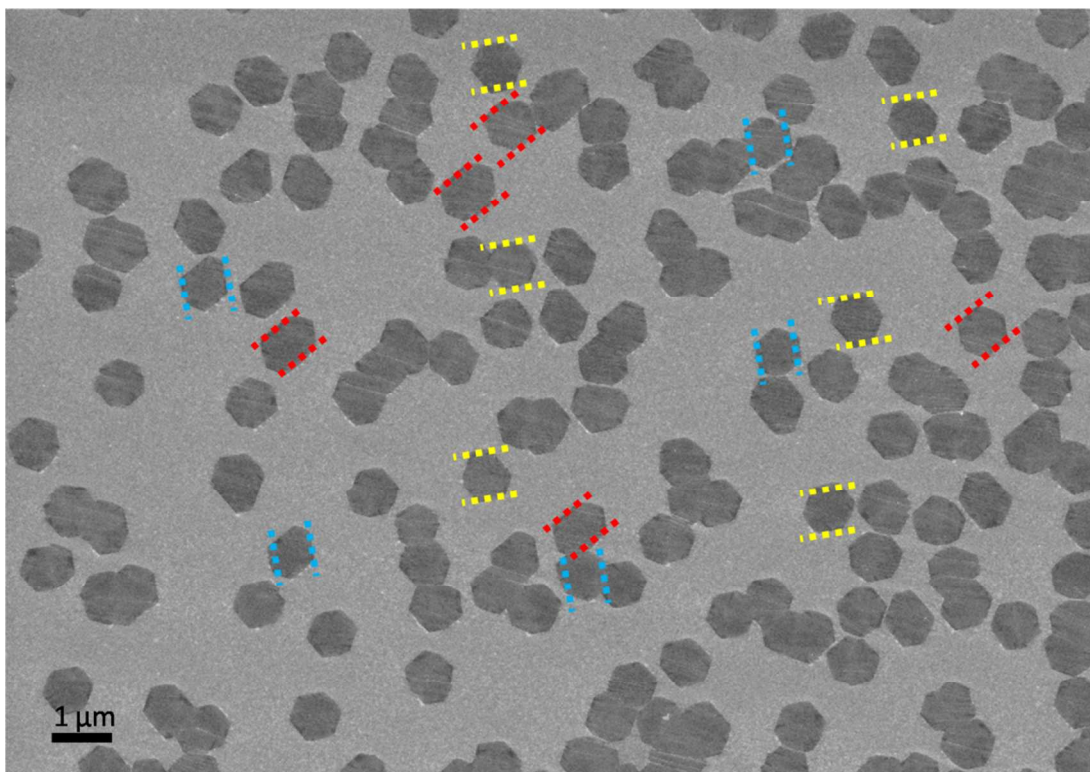


Figure S6. Orientation of hexagonal-shape h-BN domains. SEM image of h-BN hexagons which are randomly ordered indicated by the dotted blue, red and yellow lines, respectively. Similarly, triangular-shape h-BN are also randomly orientated due to the mismatch of the (100) Cu surface (4-fold symmetry) and the hexagonal structure of h-BN (6-fold symmetry).

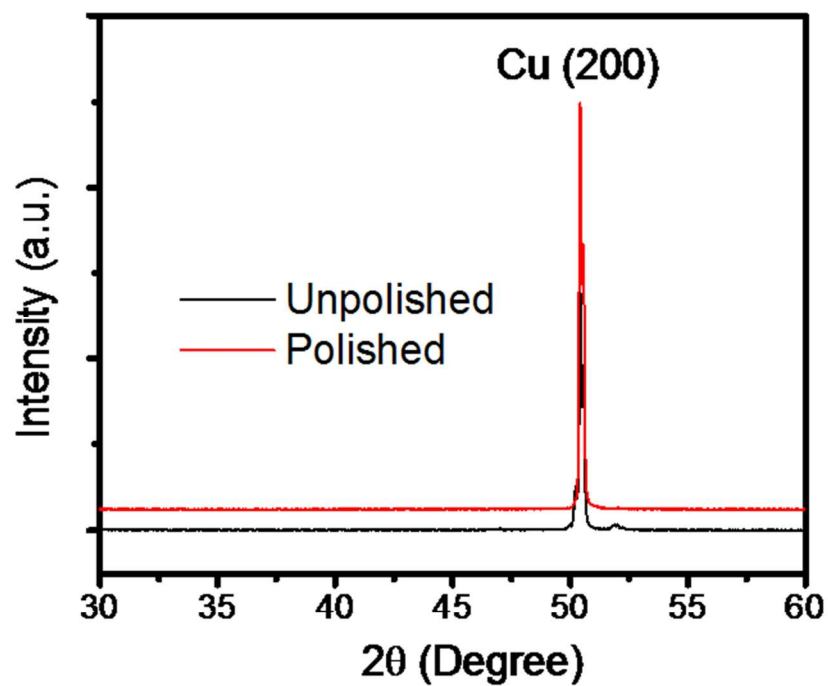


Figure S7. Comparison of Cu orientation after h-BN growth. XRD measurements show a sharp diffraction peak at $\sim 50.42^\circ$ for both Cu foils, which is assigned to Cu (200) diffraction. This indicates that both Cu foils, regardless of polished or unpolished, have a Cu (100) surface orientation.