

Supporting Information

Assessment and Control of the Impermeability of Graphene for Atomically Thin Membranes and Barriers

Piran R. Kidambi,¹* Rebekah A. Terry,¹ Luda Wang,¹ Michael S. H. Boutilier,¹ Doojoon Jang,¹ Jing Kong² and Rohit Karnik¹*

Dr. Piran R. Kidambi, Rebekah A. Terry, Doojoon Jang, Dr. Michael S. H. Boutilier, Dr. Luda Wang, Prof. Rohit Karnik

Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

E-mail: kpiran@mit.edu, karnik@mit.edu

Prof. Jing Kong

Department of Electrical Engineering and Computer Science and Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

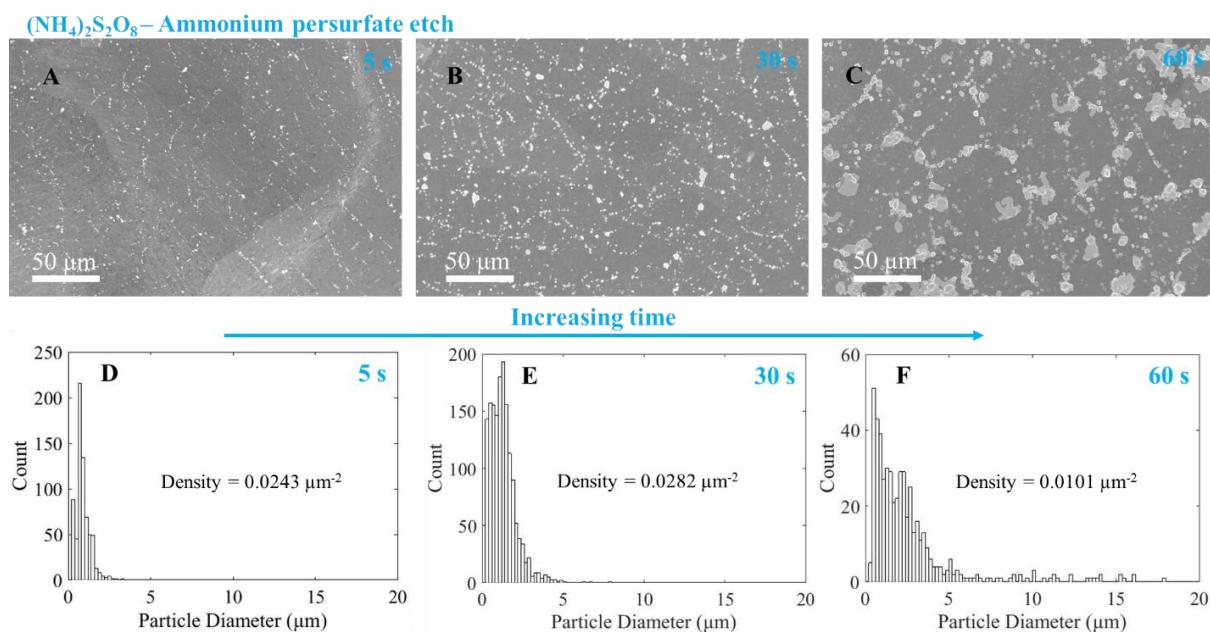


Figure S1. SEM images showing the etch pits formed after ammonium persulfate (APS, 0.1M in water) for A) 5s, B) 30s, C) 60s and corresponding size distributions D-F, respectively. The density values are averaged over several representative images. Note in figure S1 A,B) the etch pits line up along features similar to wrinkles seen on graphene on Cu foil.

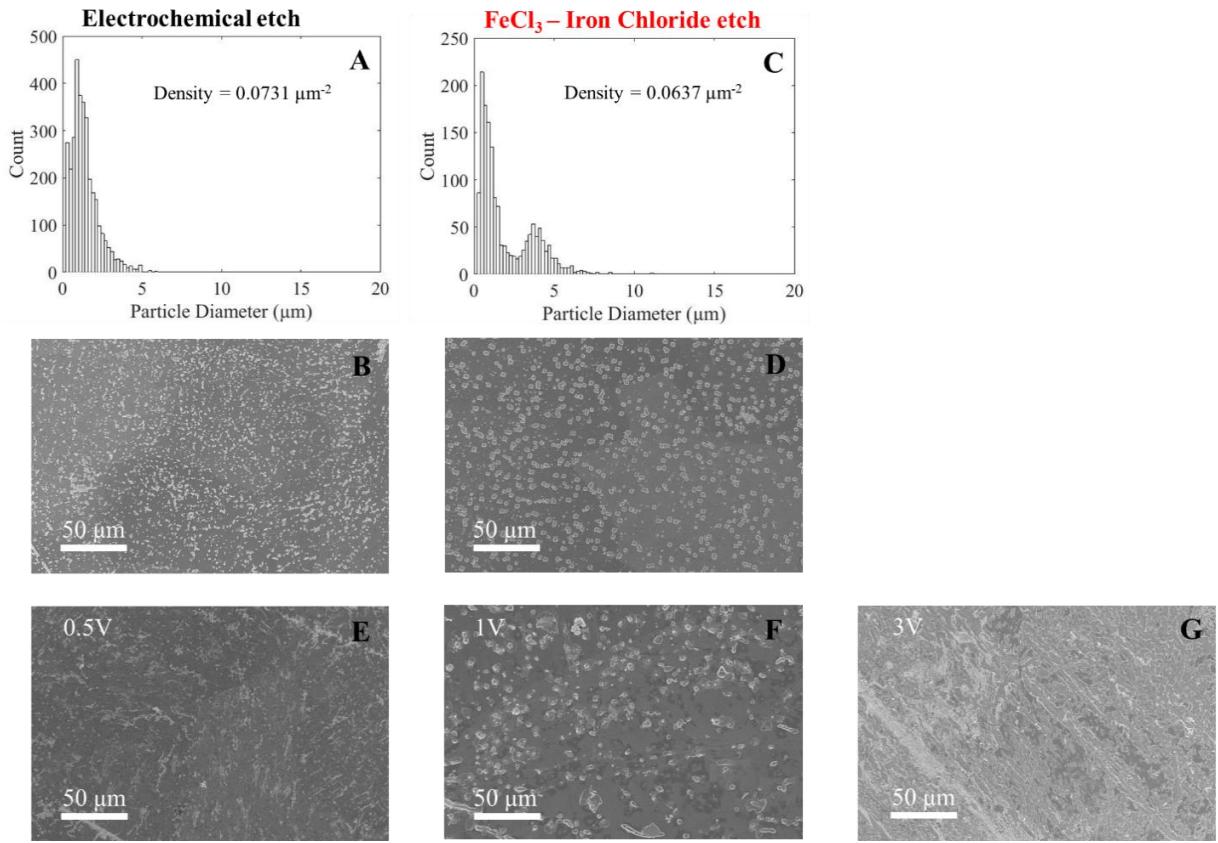


Figure S2. A reduction in crystalline quality of CVD graphene by lowering the synthesis temperature is clearly seen as an increase in etch pit density using electrochemical and FeCl₃ etch. A) Size distribution and B) SEM images for electrochemical etch 1V, t = 1s in 0.5M CuSO₄ solution compared with 30s 0.1M FeCl₃ etch (C,D) on graphene on Cu synthesized ~900 °C. Electrochemical etch with E) 0.5V, F) 1V and G) 3V for t = 1s on CVD graphene synthesized at ~1050 °C shows the optimum operation voltage ~1V for etch pit formation and complete removal of graphene at higher voltages.

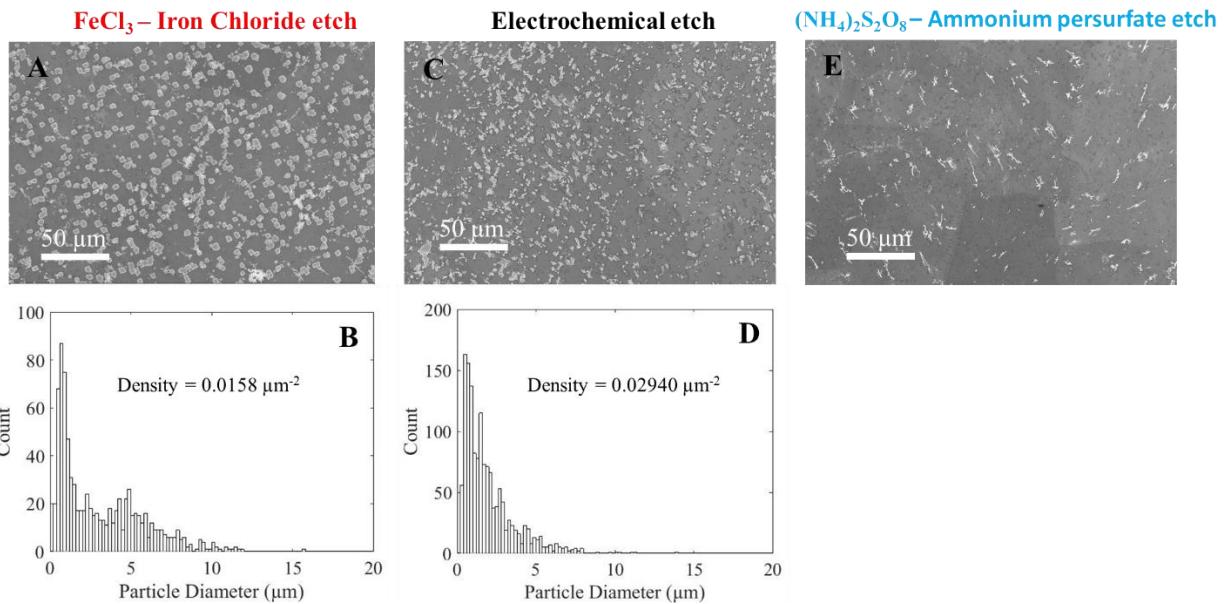


Figure S3. SEM images for A) Iron Chloride etch C) Electrochemical etch E) Ammonium persulfate etch and corresponding size distributions B,D) for CVD graphene on Cu that had been stored for 6 months after synthesis. The iron chloride and electrochemical etch do not significantly change after 6 months of storage that causes oxidation of Cu underneath graphene, while the ammonium persulfate etch is found to be unsuitable for oxidized samples.

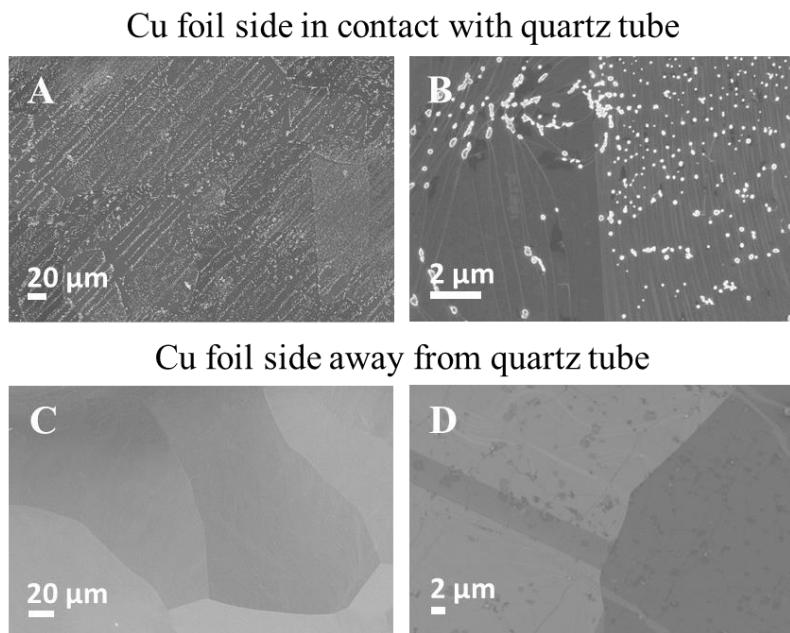


Figure S4. A,B) SEM images show bright particles on the side of Cu foil in contact with the quartz tube after graphene growth by CVD. These particles give rise to holes in the graphene. C,D) The side of the Cu foil facing away from the quartz tube does not show these particles.

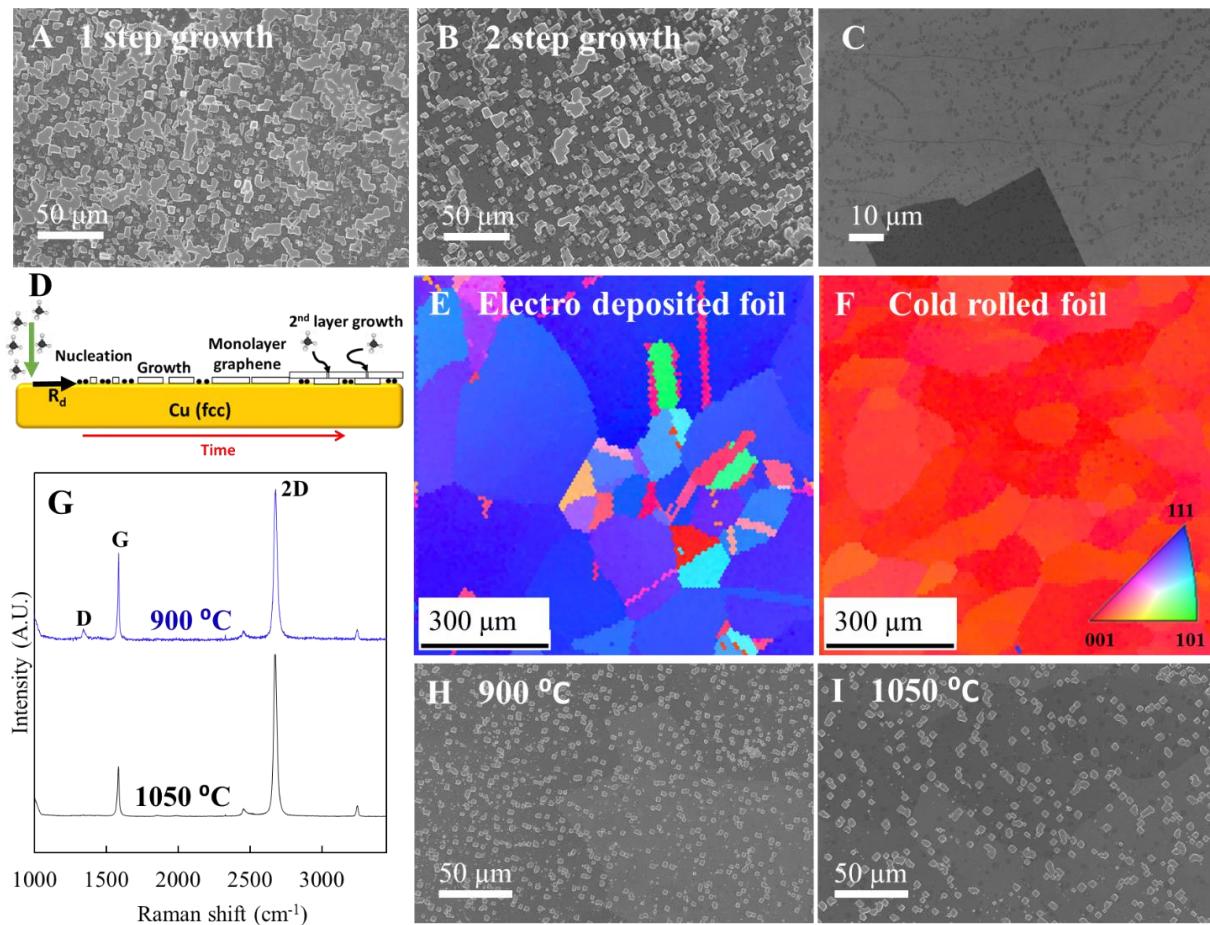


Figure S5. Identifying parameters affecting graphene quality of membrane applications. CVD graphene on Cu after acid etch with 0.1 M APS for 10 mins A) one-step growth (similar to commercial graphene see Figure S6) and B) two-step growth at 1000 $^{\circ}\text{C}$ on Alfa Aesar foil. C) Shows an SEM image of 2nd layer of graphene nuclei on Cu. D) Schematic showing transport through intrinsic defects and domain boundaries in the 1st layer enables growth of the 2nd layer underneath the 1st layer in contact with the Cu catalyst. EBSD maps for E) electrodeposited and F) cold rolled foils after graphene synthesis. Cold rolled foils show relatively more uniform grain orientations closer to Cu (100) over large area compared to electro-deposited foil (under the graphene synthesis conditions reported here), indicating their suitability for graphene synthesis for membrane applications. G) Raman spectra shows an increased D peak indicating more defects for graphene synthesized at 900 $^{\circ}\text{C}$. SEM images after acid etch with 0.1 M FeCl_3 for 30 s for graphene on Cu synthesized at H) 900 $^{\circ}\text{C}$ and I) 1050 $^{\circ}\text{C}$ using two-step growth.

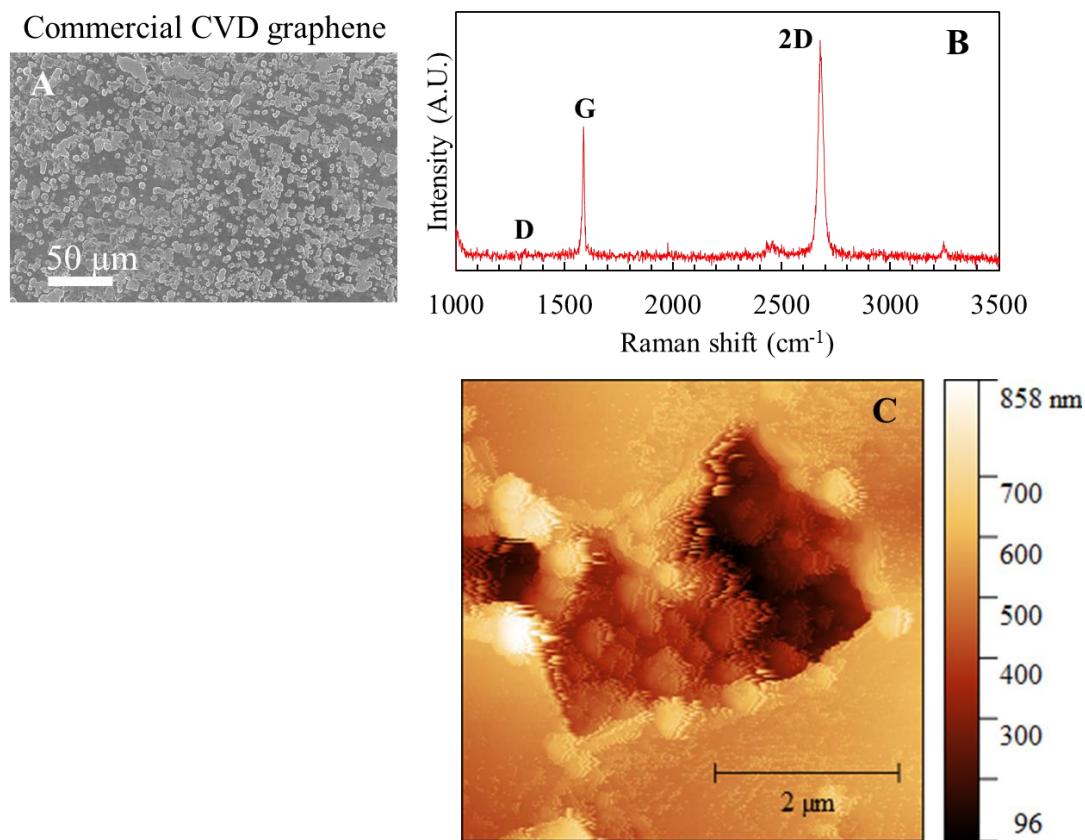


Figure S6. Commercially available graphene from Graphenea A) after etch test with 0.1M APS for 10 mins. B) Raman spectrum of graphene from Graphenea transferred to SiO_2 (300nm)/Si wafer. C) AFM image of an etch pit.

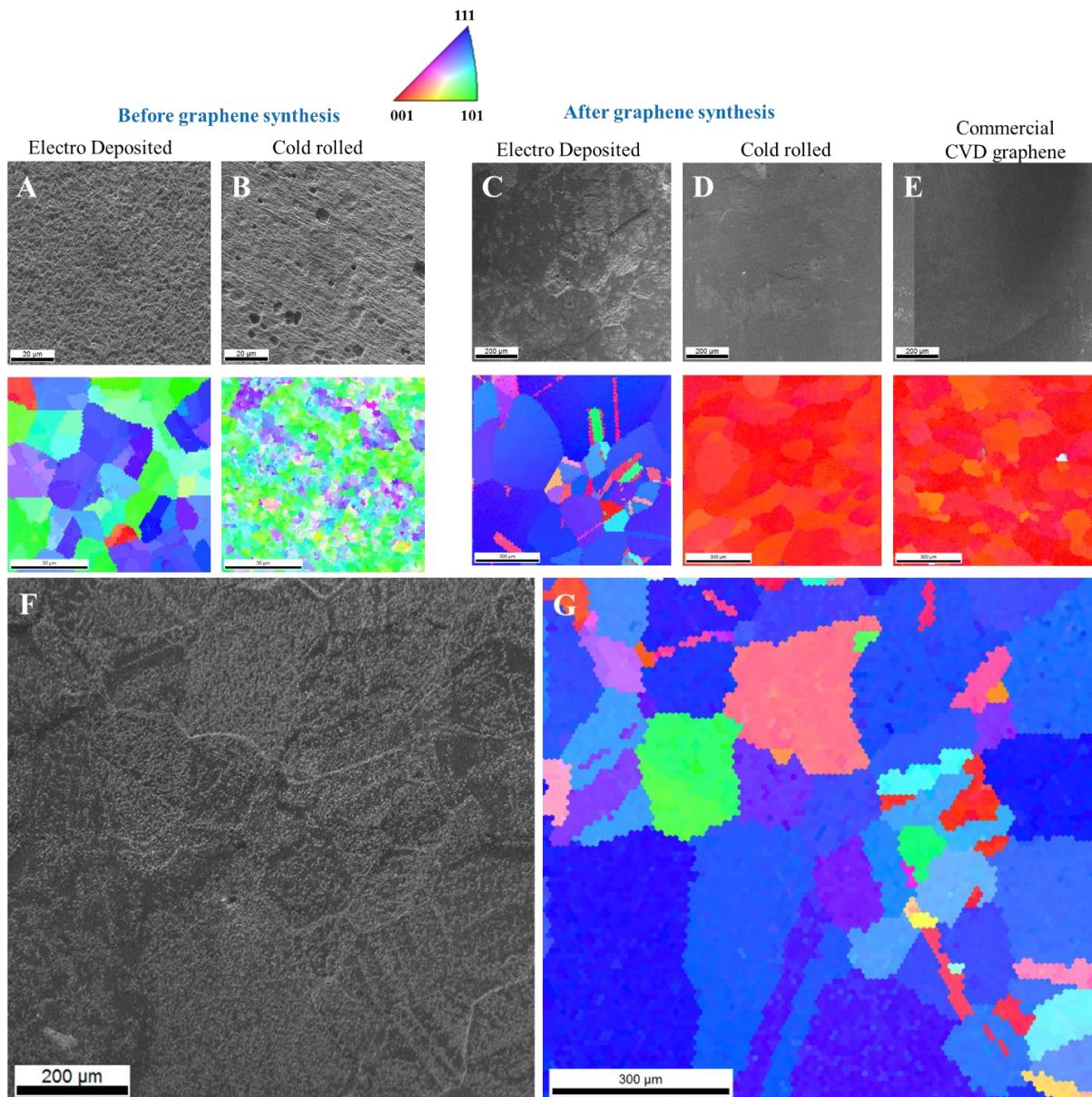


Figure S7. SEM images and corresponding EBSD maps for A,C) electrodeposited and B,D) cold rolled foils before and after graphene synthesis respectively along with E) commercially available CVD graphene from Graphenea. Cold rolled foils tend to give relatively more uniform grain orientations over large area (majority of Cu grains closer to 100 plane) compared to electrodeposited foils (large proportion closer 111 plane but several other orientations are also seen) and have hence been chosen for large area graphene synthesis for membrane applications. F,G) acid etch with 0.1M FeCl_3 for 60s on electrodeposited foil shows variations in graphene quality amongst different grains of Cu.