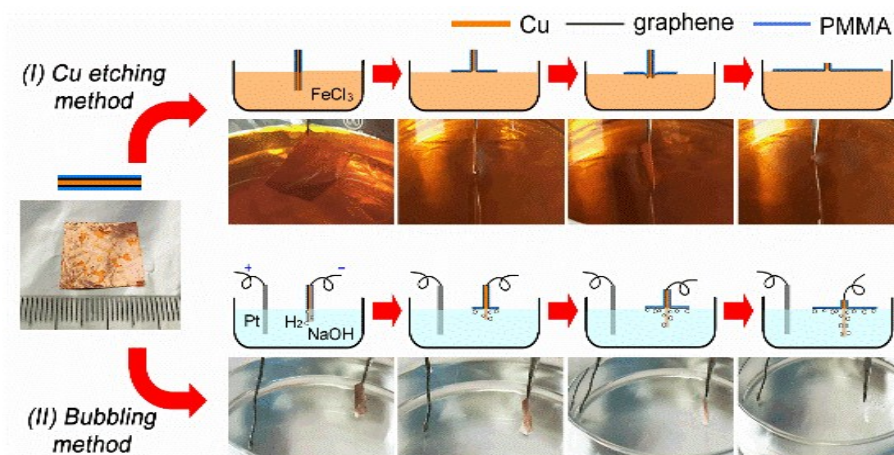


## Electronic Supplementary Information

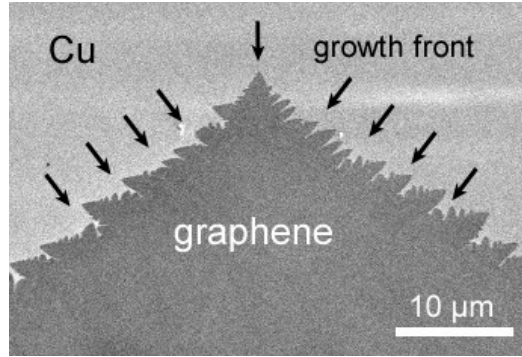
### Role of hydrogen in oxygen-assisted chemical vapor deposition growth of millimeter-sized graphene single crystals

Pei Zhao, Yu Cheng, Dongchen Zhao, Kun Yin, Xuwei Zhang, Shaoqian Yin, Yanan Song,

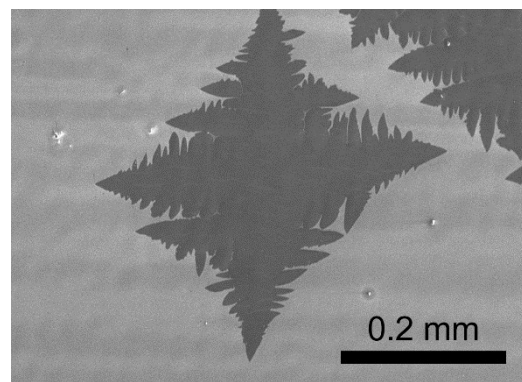
Peng Wang, Miao Wang, Yang Xia, Hongtao Wang



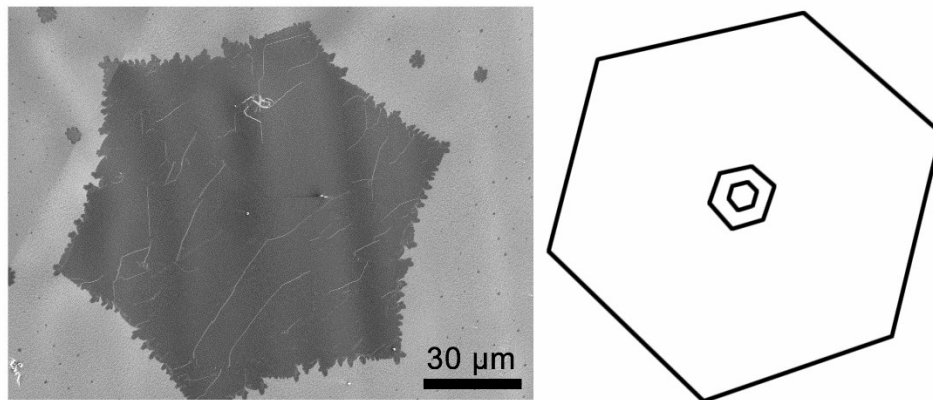
**Fig. S1** Simultaneous transfer of as-grown graphene single crystals (GSCs) from both Cu enclosure surfaces using a modified polymer-assisted liftoff technique. In method (I), the Cu foil was perpendicularly submerged into a FeCl<sub>3</sub> solution, and as the foil was continuously etched, two PMMA/GSC films were slowly isolated. In method (II), the Cu foil was submerged into a NaOH solution as the cathode for electrochemical bubbling, and a Pt wire was used as the anode. With a constant voltage supply, the PMMA/GSC films were detached very quickly by the generated H<sub>2</sub> bubbles at the film and metal interfaces.



**Fig. S2** Typical SEM image of the growth front of a GSC under low  $P_{H_2}$  partial pressure  $P_{H_2}$ .



**Fig. S3** GSCs grown under low  $P_{H_2}$  occasionally exhibit grain shapes with four-fold symmetry.



**Fig. S4** The adlayers exhibit a hexagonal shape as the first layer and with a Bernal-stacked configuration between the layers for GSCs grown under high  $P_{H_2}$ .