

## Supporting Information

### **Graphene/Graphite Sheets Assisted Growth of High-Areal-Density Horizontally Aligned Carbon Nanotubes**

Huanhuan Xie,<sup>ab</sup> Rufan Zhang,<sup>b</sup> Yingying Zhang,<sup>\*a</sup> Wenlin Zhang,<sup>a</sup> Muqiang Jian,<sup>ab</sup>  
Chunya Wang,<sup>ab</sup> Qi Wang<sup>ab</sup> and Fei Wei<sup>\*b</sup>

<sup>a</sup> Center for Nano and Micro Mechanics, School of Aerospace Engineering, Tsinghua University,  
Beijing 100084, China

<sup>b</sup> Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department  
of Chemical Engineering, Tsinghua University, Beijing 100084, China

\*Address correspondence to [yingyingzhang@tsinghua.edu.cn](mailto:yingyingzhang@tsinghua.edu.cn) (Y. Y. Zhang), [wfdce@tsinghua.edu.cn](mailto:wfdce@tsinghua.edu.cn) (F. Wei).

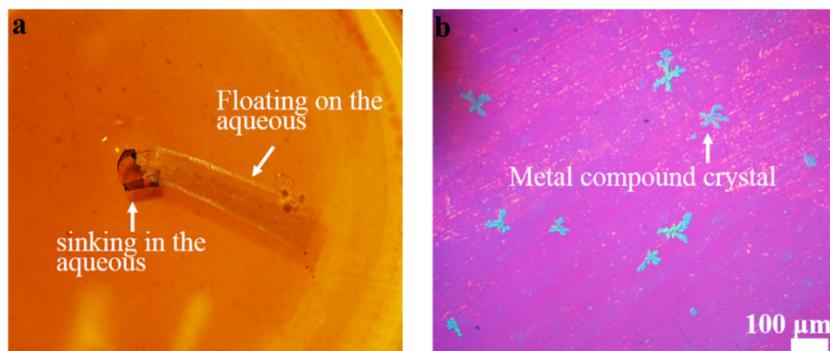
## EXPERIMENTAL SECTION

**Synthesis and Transfer of GP Sheets.** The synthesis process was performed in an atmospheric pressure CVD system equipped with a quartz tube (inner diameter: 31 mm). Prior to the synthesis of GP sheets, Cu foil (25  $\mu\text{m}$  thick, Alfa Aesar) was cleaned by ultrasonic in diluted hydrochloric acid, ethanol and deionized water sequentially. Then Cu foil was dried with pure  $\text{N}_2$ . The Cu foil was put into the center of the quartz tube in the CVD system supported with a quartz boat. Firstly, Cu foil was reduced in  $\text{H}_2/\text{Ar}$  (100/50 sccm). Then, deposition of GP sheets was carried out in  $\text{H}_2/\text{Ar}/\text{CH}_4$  (60/110/10 sccm) at 1000  $^\circ\text{C}$  for 5 min. Lastly, the sample was cooled to room temperature by directly opening the cover of the furnace in  $\text{H}_2/\text{Ar}$  (100/50 sccm). The GP sheet were released by etching Cu in  $\text{FeCl}_3$  aqueous, leaving the GP sheet on the top surface of the foil floating on the solution while the GP sheet on the other side sinking in the solution. There were some metal ions in the etchant solution, such as  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Fe}^{2+}$ , left on the GP sheets (Figure S1b). We usually washed the GP sheets with deionized water (DI water) for several times before transferring the GP sheets. Finally, a silicon substrate with a certain thickness of oxide layer was used to fish up the GP sheet. In order to provide a better adhesion between GP sheet and substrate, GP sheet/silicon substrate was dried for a day at room temperature.

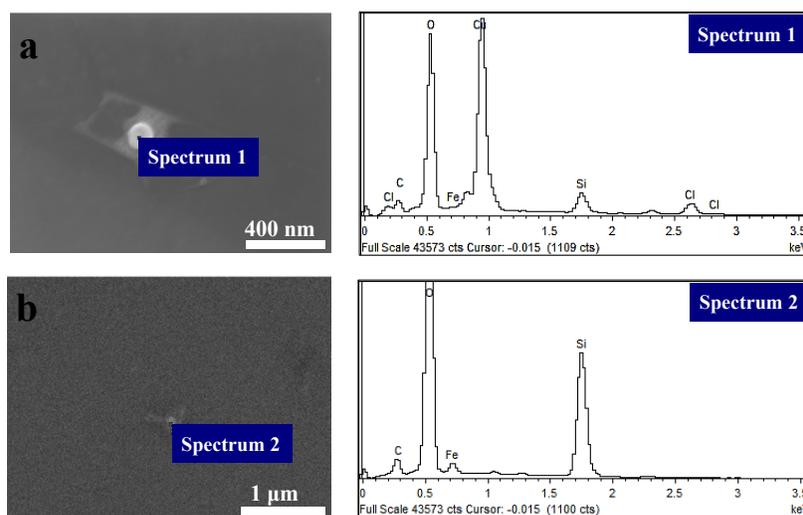
**Synthesis of Ultralong HACNTs.** The synthesis process was performed in the same CVD system used for the growth of GP sheets. Silicon wafer with 800-nm-thick oxide layer was used as the substrate. The substrate was cleaned with same procedure as the above. 0.03 mol/L  $\text{FeCl}_3$  ethanol solution was used as the catalyst precursor and loaded onto one end of substrate by microcontact printing method. Then, the substrate was put into the center of the quartz tube supported with a quartz boat. Catalysts were reduced in  $\text{H}_2/\text{Ar}$  (110/63 sccm) flow at 910  $^\circ\text{C}$  for 30 min. The synthesis of ultralong HACNTs was carried out in  $\text{H}_2/\text{CH}_4$  (50/25 sccm) with a trace of water vapor at 1010  $^\circ\text{C}$  for 20 min. The reaction was terminated by turning off the  $\text{CH}_4$ . Finally, the furnace was cooled down to room temperature with flow of  $\text{Ar}/\text{H}_2$ .

**Synthesis of Ultralong HACNTs Assisted with GP Sheets.** Silicon substrates with GP sheets on one end were used to grow ultralong HACNTs, with the same growth parameters as the above. The end of the substrate with GP sheets was put in the upstream. In order to understand the status of catalyst NPs during the CVD process in detail, GP sheets, which were treated with the process of catalyst reduction in flow at 910 °C for 30 min and the process of HACNTs growth without adding carbon source (CH<sub>4</sub>), respectively, were also prepared.

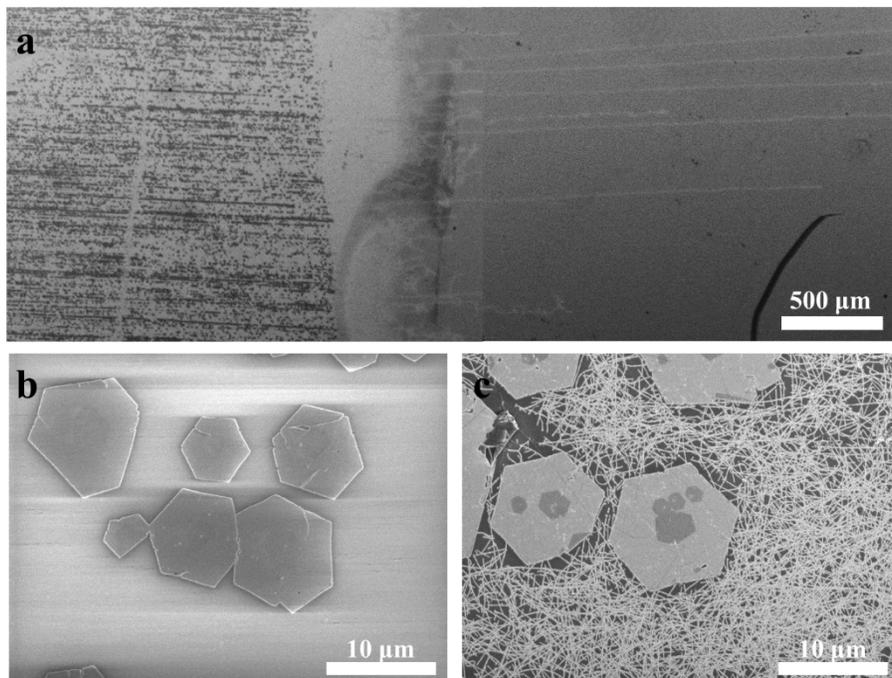
**Characterization.** The morphology of GP sheets and CNTs were characterized with SEM (JSM 7401F). High-resolution TEM (JEM 2010) was used to characterize the number of layers in GP sheets. Besides, the GP sheet treated only with the catalyst reduction process was also characterized with AFM (NanoScope V, Veeco). A Raman spectroscope (HORIBA HR800) equipped with a 633 nm laser was used to characterize the structure of HACNTs and GP sheets.



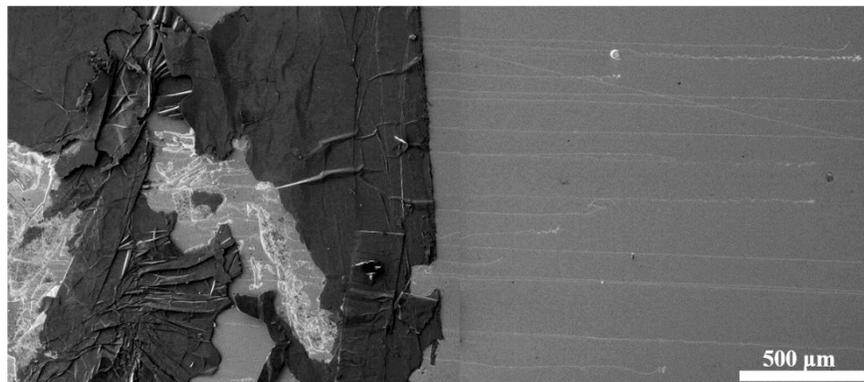
**Fig. S1. Transfer process of GP sheets.** **a.** An optical image of GP sheet in the  $\text{FeCl}_3$  aqueous after etching copper foil. The GP sheet on the top of the copper foil floated on the solution while the GP sheet on the other side sank in the solution. **b.** An optical microscope image of a GP sheet transferred onto a silicon substrate (with 285 nm thick oxide layer) without washed in DI water. Some metal compound crystals formed on the GP sheet.



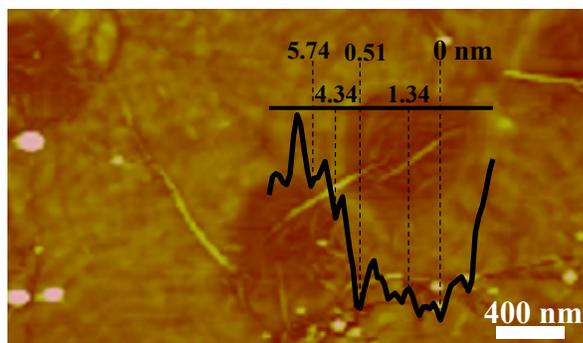
**Fig. S2. SEM images and corresponding energy dispersive X-ray (EDX) spectra of metal nanoparticles on the GP sheets.** The EDX spectra show there are some metal residues on the GP sheet, such as Fe and Cu. The element of C should come from the GP sheet, elements of Si and O should come from the silicon substrate, and element of Cl should come from the etchant solution.



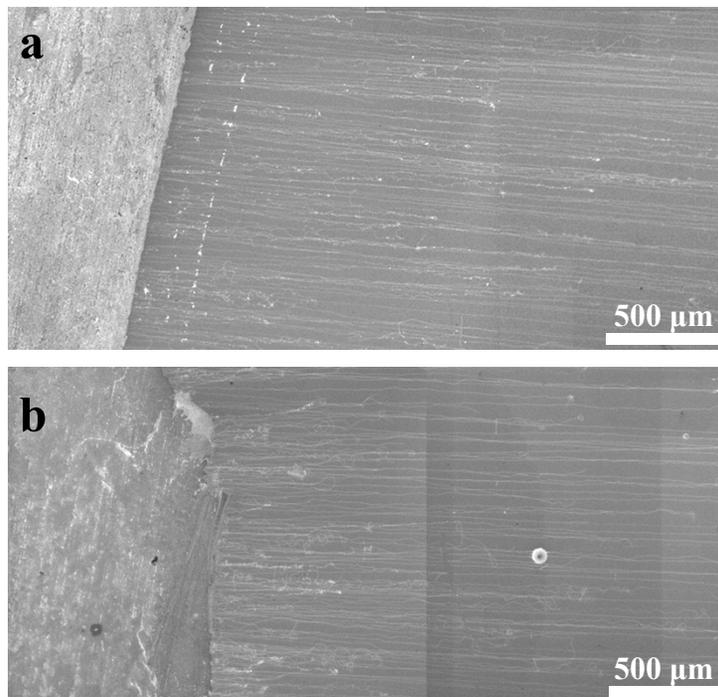
**Fig. S3. HACNTs grown from single-layer graphene flake transferred with polymer support.** Hexagonal single-layer graphene flakes were grown on the copper foil by CVD and transferred onto silicon substrate supported with PMMA film (polymethyl methacrylate). The PMMA was removed by acetone vapor. **a** shows the HACNTs grown from the part of silicon covered with single-layer graphene flakes (Left part) . The gas flow was from the left to the right. **b** and **c** shows the hexagonal single-layer graphene flakes before and after growing CNTs. There are few HACNTs grown from the zone covered with graphene while there are many short CNTs around graphene flakes. The reason is that the polymer film would cover and protect graphene flakes from contacting with etchant solution, and less metal ions (such as  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ) would be left onto the surface of graphene flake to sever as catalyst. In contrast, the catalyst precursor may be deposited on the substrate from the etchant solution.



**Fig. S4. HACNTs directly grown from a thick graphite film peeled from HOPG.** The left dark zones were the graphite film after the growth of CNTs. Obviously, the graphite film were damaged and some part of them detached from the substrate after the CVD process.



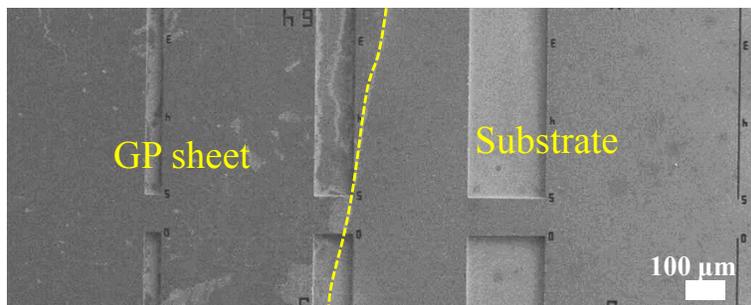
**Fig. S5. AFM image of the GP sheet on a silicon substrate.** The obvious height contrast indicates that GP sheet has graphene flakes with different layers, consistent with the SEM and TEM characterizations in Figure 2. The numerical values in the image are the relative height, which takes the rock-bottom marked “0 nm” as the horizontal plane. The unit is nm. The maximum of height difference in the GP sheet is over 5.74 nm, which indicates that the thick flake is graphene with more than 17 layers.



**Fig. S6. SEM images of HACNTs directly grown from GP sheet.** GP sheet is in the left and the gas flow direction is from the left to the right.



**Fig. S7. The controlled experiment to grow HACNTs with Cu ions on the GP sheets.** The etchant solution to transfer GP sheet on Cu foil is ammonium thiosulfate  $((\text{NH}_4)_2\text{S}_2\text{O}_3)$ . Therefore the remain metal ions on the transferred GP sheet would be only Cu. As the condition to grow CNTs was optimized based on Fe catalyst, there are few HACNTs grown out of GP sheets.



**Fig. S8.** The controlled experiment to grow HACNTs without carbon gas feeding. It is obvious that there is no HACNTs grown out of GP sheet. The CNTs grown on the GP sheets are shown in the Figure 4d.