

# Supporting Information

## Repeated Growth–Etching–Regrowth for Large-Area Defect-Free Single-Crystal Graphene by Chemical Vapor Deposition

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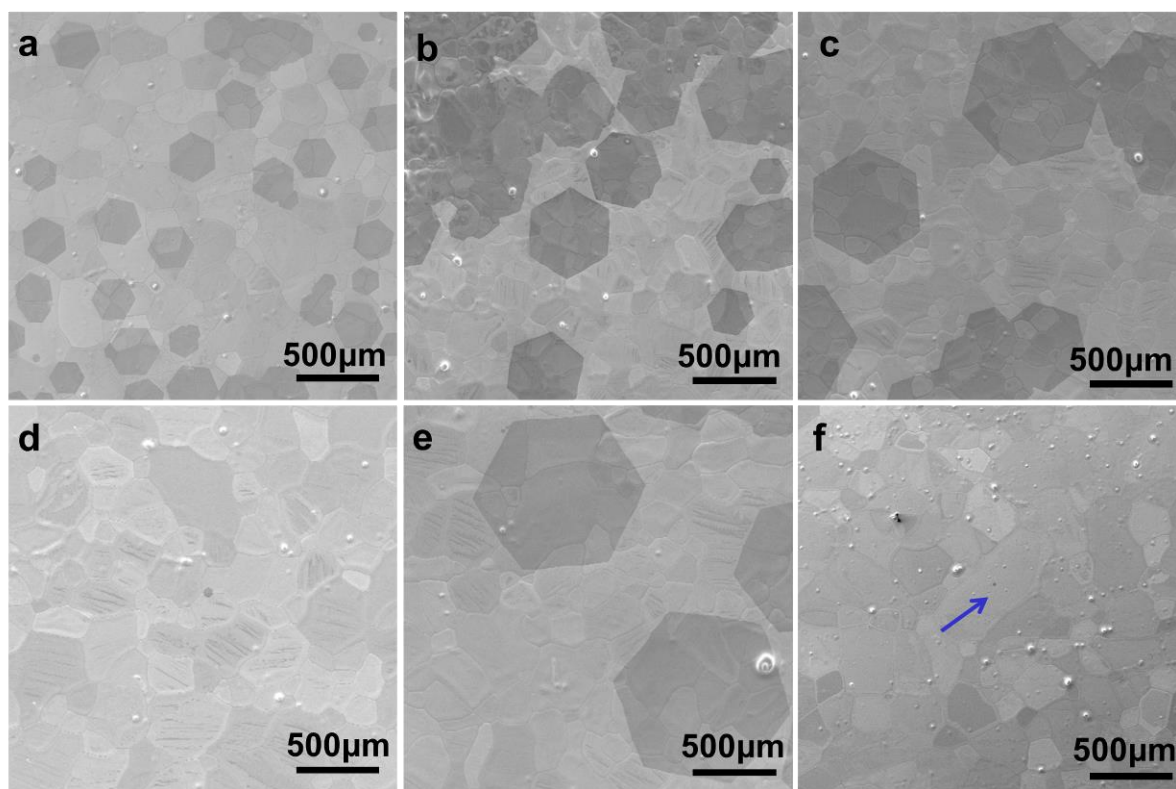
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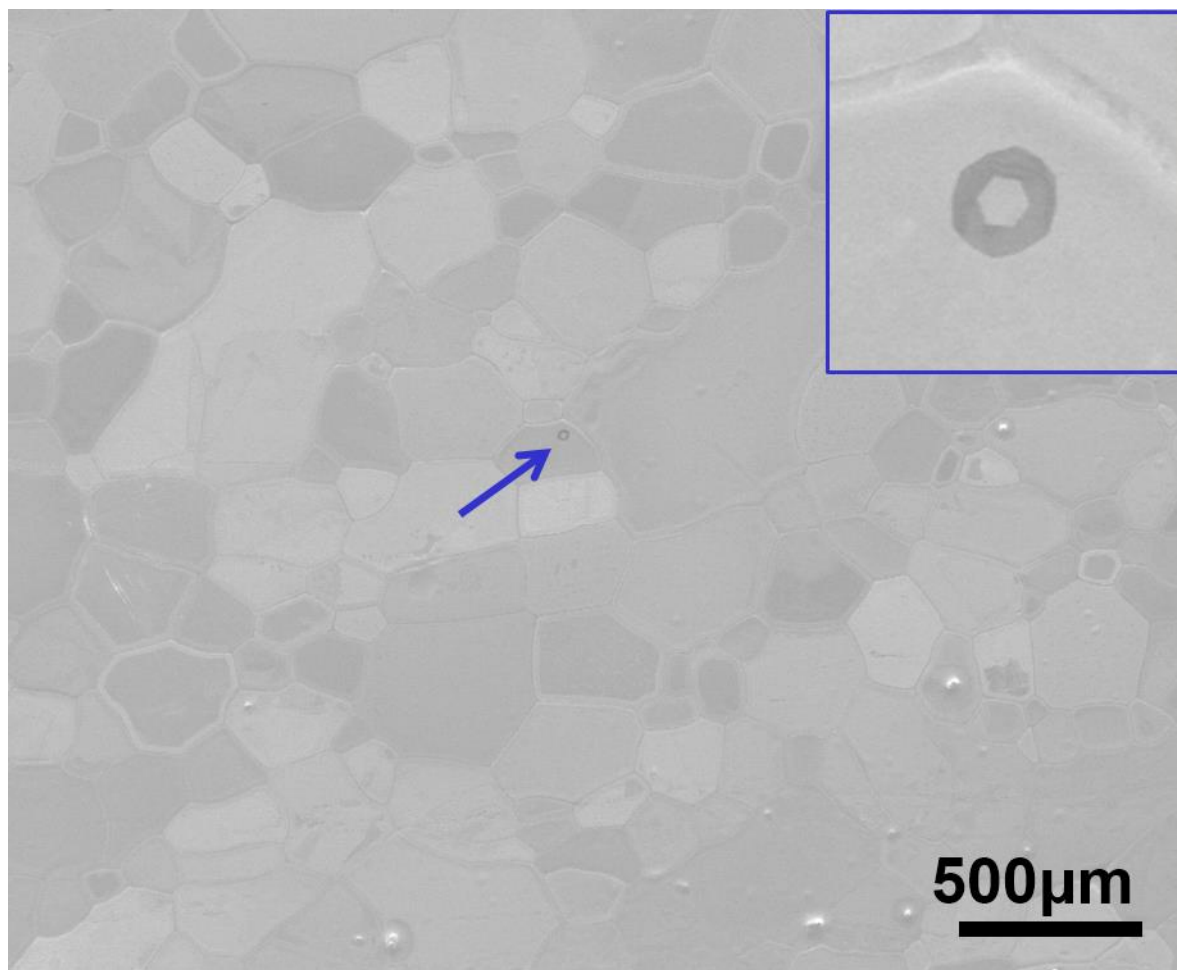
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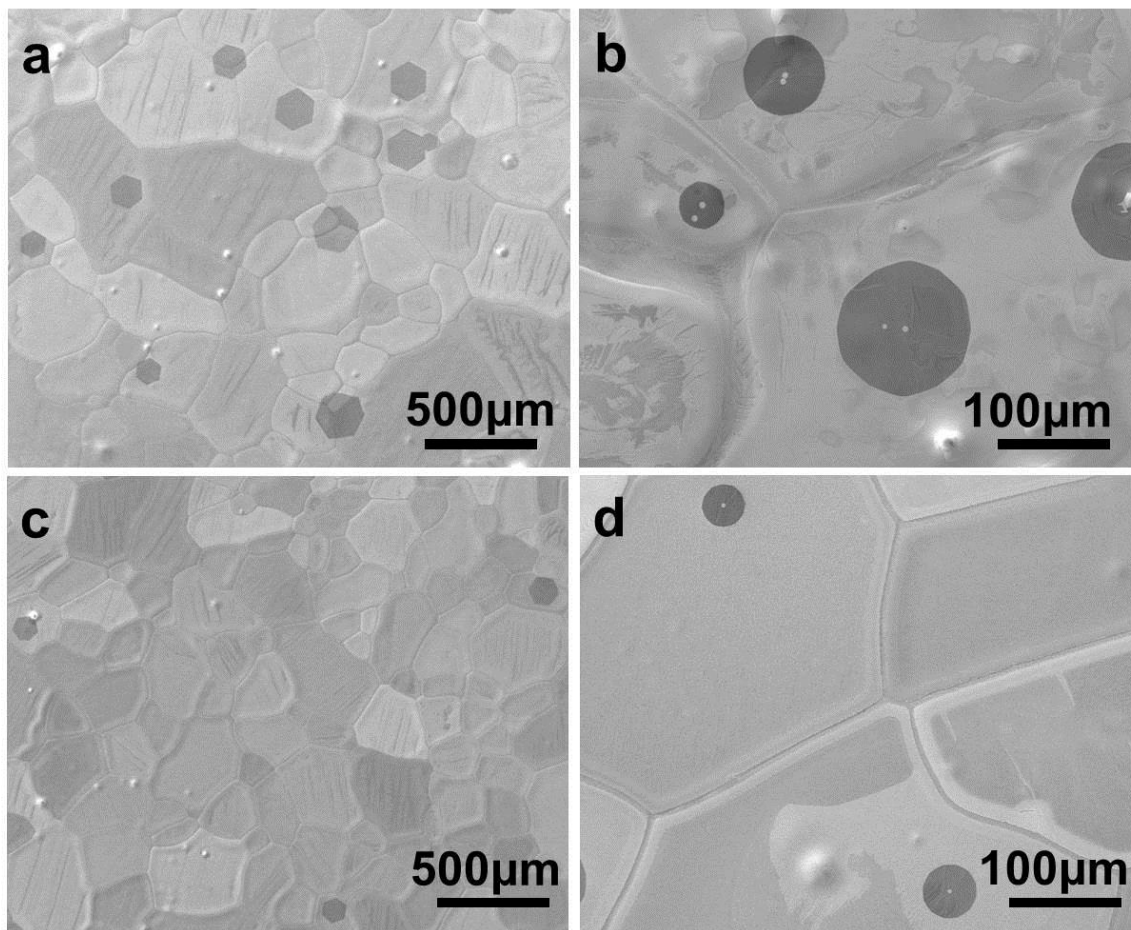
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**Figure S1.** The influence of methane flow rate on the growth of single-crystal graphene domains. SEM images of single-crystal graphene domains grown in a gas flow of 700 sccm hydrogen and (a) 3.7 sccm methane for 20 min, (b) 3.6 sccm methane for 50 min, (c) 3.5 sccm methane for 2 h, (d) 3.4 sccm methane for 5 h, (e) 3.4 sccm methane for 7 h, and (f) 3.3 sccm methane for 8 h.



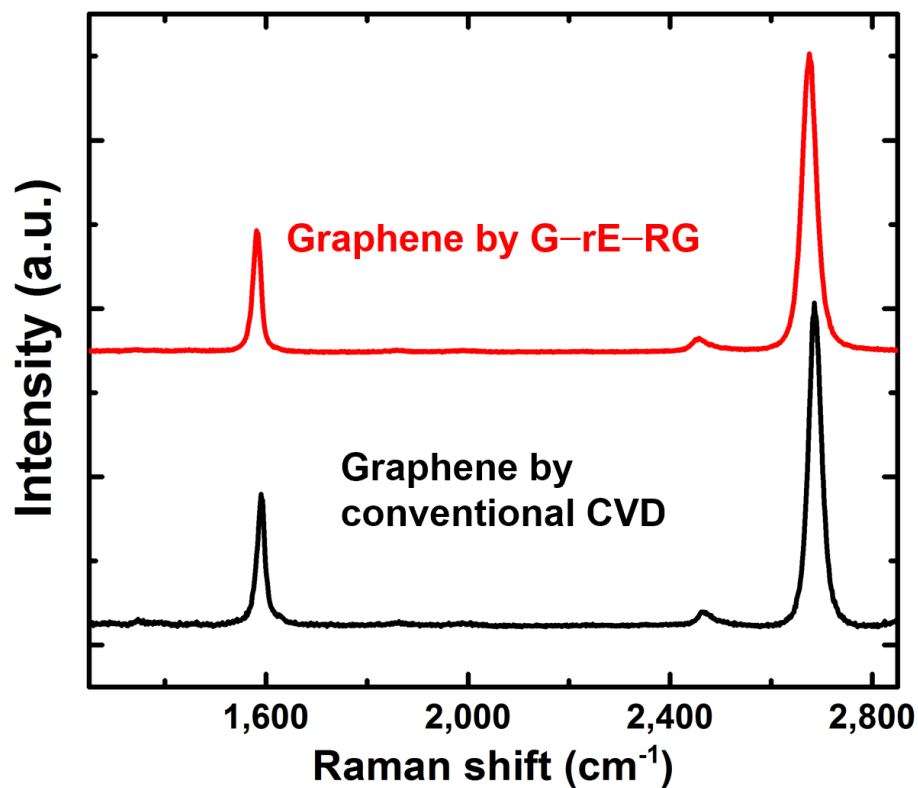
**Figure S2.** SEM image of a single-crystal graphene domain in a region of  $\sim 3 \times 3 \text{ mm}^2$ , which was obtained by  $\text{H}_2$  etching after initial CVD growth. The inset shows the high-magnification SEM image of the graphene domain indicated by blue arrow.



**Figure S3.** The influence of the methane flow rate on the quality of single-crystal graphene domains. SEM images of single-crystal graphene domains grown in a gas flow of 700 sccm hydrogen and (a) 4.0 sccm methane for 5 min and (c) 3.5 sccm methane for 80 min. (b,d) The graphene domains obtained after etching for 30 s from (a) and from (c), respectively. Note that after etching, more holes appeared in the domains grown with a high methane flow rate than in those grown with a low methane flow rate, indicating more defects are present in the former sample.

The etching of a hexagonal single-crystal graphene domain starts from its six vertexes, and it experiences a series of edge structure and shape evolution during the etching process.<sup>31</sup> Under

the same etching conditions, the etching rates of the graphene domains with the same edge structure should be the same. Therefore, the size of the initial graphene domains have an important influence on the shape of the graphene domains etched for a certain time. Generally, the shape change is much smaller for the large domain although almost the same areas are etched away after the same etching time. For instance, the graphene domain in Figure 2g still keeps nearly hexagonal shape but the domains in Figure S3b and d are changed to round shape (dodecagon) after etching because of the difference size of the initial domains. However, with further extending the etching time, all the graphene domains will become the same shape, as shown in ref 31.



**Figure S4.** Typical Raman spectra of the single-crystal graphene domains obtained by G-rE-RG (red) and conventional CVD (black). It is worth noting that the domains produced by G-rE-RG show a much weaker D band than those produced by conventional CVD, suggesting fewer defects are present in the former sample.

**Table S1.** Comparison of the synthesis method, structure and transport properties of single-crystal graphene domains obtained by CVD.

	Substrate	Temperature (°C)	Pressure	Synthesis method	Size (μm)	Growth rate <sup>a</sup> (μm/min)	Shape	Edge type	Mobility on SiO <sub>2</sub> /Si (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	Reference
1	Cu	1000	Ambient	Reduce the flow rate ratio of CH <sub>4</sub> to H <sub>2</sub>	3	0.1~0.2	Hexagon	/	1200~1971 FET, RT, AC	Adv. Mater., 2011 <sup>21</sup>
2	Cu	1000	Ambient or low	Reduce the flow rate ratio of CH <sub>4</sub> to H <sub>2</sub>	20	0.4	Hexagon	ZZ	Not discussed	ACS Nano, 2011 <sup>22</sup>
3	Cu	1035	Low	Grow inside a copper-foil enclosure	500	6	Star shape	Random	4000 FET, RT	J. Am. Chem. Soc., 2011 <sup>52</sup>
4	Cu	1050	Ambient	Reduce the flow rate ratio of CH <sub>4</sub> to H <sub>2</sub>	20	2	Hexagon	ZZ	10000 Hall, LT, VC	Nat. Mater., 2011 <sup>7</sup>
5	Cu	1050	Ambient	Polish substrate and reduce the flow rate ratio of CH <sub>4</sub> to H <sub>2</sub>	70	2	Hexagon	ZZ	Not discussed	ACS Nano, 2011 <sup>55</sup>
6	Cu	1160	Ambient	Use liquid Cu	120	10~50	Hexagon	ZZ	1000~2500 FET, RT, AC	PNAS, 2012 <sup>51</sup>
7	Cu	1000	Low	Vapor trapping growth: put Cu foil into a reaction tube with only one end opened	100	3	Flower shape	Random	4200 FET, RT	Nano Lett., 2012 <sup>50</sup>
8	Cu	1077	Low	Polish and anneal substrate, and reduce the flow rate ratio of CH <sub>4</sub>	2300	18	Hexagon	ZZ	11000 Hall, RT, VC	ACS Nano, 2012 <sup>17</sup>

				to H <sub>2</sub>						
9	Cu	1090	Ambient	Use melted copper	200	2	Hexagon	ZZ	Not discussed	ACS Nano, 2012 <sup>56</sup>
10	Cu	1045	Ambient	Anneal the substrate	450	28	Square	Rough	Not discussed	J. Am. Chem. Soc., 2012 <sup>19</sup>
11	Cu	1000	Low	Growth inside a copper-foil enclosure	250	2	Star shape	Random	27000 Hall, LT, VC	Nano Lett., 2012 <sup>57</sup>
12	Cu	1035	Low	Suppress evaporative loss of Cu: use Cu tubes formed out of Cu foil as the growth substrate	2000	5	Hexagon	Rough	5200 FET, RT	Adv. Mater., 2013 <sup>18</sup>
13	Cu	1050	Ambient	Oxidize the Cu surface to obtain oxide nanoparticle as the growth seeds	5900	/	Hexagon	/	Not discussed	ACS Nano, 2013 <sup>25</sup>
14	Cu	1075	Ambient	Use resolidified copper	1000	3	Hexagon	ZZ	Not discussed	ACS Nano, 2013 <sup>58</sup>
15	Cu	1050	Ambient	Use polystyrene as the carbon source and pulse heating	1200	13	Hexagon	/	5000~8000 FET, RT	Adv. Funct. Mater., 2013 <sup>53</sup>
16	Cu	1070	Low	Maintain a catalytic inactive Cu <sub>2</sub> O layer on Cu substrate to reduce the nucleation density	5000	2	Hexagon	ZZ	8117 FET, RT, AC	Nat. Commun., 2013 <sup>24</sup>
17	Cu	1035	Low	Control oxygen on the Cu surface to reduce the nucleation density and	10000	14	Irregular shape	Random	8400 Hall, RT	Science, 2013 <sup>23</sup>



				accelerate graphene growth						
18	Cu	1050	Ambient	Regrowth from an existing graphene seed	1000	1	Hexagon	Not discussed	Not discussed	Chem. Mater., 2014 <sup>27</sup>
19	Cu	1045	Low	Regrowth from an existing graphene seed	500	21	Square or hexagonal	Not discussed	Not discussed	CrystEngComm, 2014 <sup>28</sup>
20	Cu	1040	Low	Use a Ar pulse to deactivate the active carbon growth species to reduce nucleation density	1500	12	Hexagon	Rough	Not discussed	ACS Nano, 2014 <sup>59</sup>
21	Cu	1050	Low	Insert a Cu foil into a tube with one end closed	1900	6	Hexagon	Rough	2400 FET, RT, VC	Sci. Rep., 2014 <sup>54</sup>
22	Ge	900~930	Low	Epitaxial growth on a hydrogen-terminated germanium substrate	50800	/	/	/	10620 Hall, RT, VC	Science, 2014 <sup>26</sup>
23	Pt	1040	Ambient	Reduce the flow rate ratio of CH <sub>4</sub> to H <sub>2</sub>	1000	6	Hexagon	ZZ	7100 FET, RT, AC	Nat. Commun., 2012 <sup>20</sup>
24	Pt	1060	Ambient	G-rE-RG	3000	6	Hexagon	ZZ	13000 FET, RT, AC	This manuscript

<sup>a</sup>. Growth rate = domain size/total reaction time

RT = Room temperature LT = Low temperature AC= Ambient condition VC= Vacuum condition

**Table S2.** Growth characteristics of graphene domains grown at different flow rate ratios of H<sub>2</sub>/CH<sub>4</sub>

Temperature (°C)	H <sub>2</sub> (sccm)	CH <sub>4</sub> (sccm)	Nucleation density (nuclei/cm <sup>2</sup> )	Possible largest domain size (μm)	Total reaction time	Incubation time	Domain size (μm)	Mean growth rate <sup>a</sup> (μm/h)	Mean growth rate <sup>b</sup> (μm/h)
1060	700	3.7	300	500	20 min	5 min	300	1200	900
1060	700	3.6	200	700	50 min	12 min	600	947	720
1060	700	3.5	100	1200	2 h	1 h 5 min	800	873	400
1060	700	3.4	3	3000	5 h	4 h 47 min	90	415	18
1060	700	3.3	1	10000	8 h	7 h 57 min	18	360	2.25

<sup>a</sup>. mean growth rate = domain size/(total reaction time – incubation time)

<sup>b</sup>. mean growth rate = domain size/total reaction time

To determine the incubation time for each growth condition, we have done lots of CVD growth experiments with different reaction time, the time from the introduction of methane to the stop of the reaction, for each growth condition, and used SEM to survey the whole growth substrate to identify whether the graphene domains were formed after a certain reaction time. To ensure a rapid quenching of the reaction and avoid the possible formation of graphene in the cooling step, the Pt foil was quickly removed from the high-temperature zone by rapidly pulling out the reaction tube after reaction, and then the furnace was shut down and the CH<sub>4</sub> was stopped. The incubation time for each growth condition was determined using the following procedure: (1) we grew graphene

domains with a size of  $l$  ( $\mu\text{m}$ , normally  $\sim 50 \mu\text{m}$ ) and  $l_{\text{large}}$  ( $\mu\text{m}$ , larger than  $50 \mu\text{m}$ ) in a reaction time of  $t$  (min) and  $t + 20$  (min), respectively. The average growth rate of graphene was determined by  $r$  ( $\mu\text{m}/\text{min}$ ) =  $(l_{\text{large}} - l)/20$ . (2) We estimated the possible nucleation time  $t_n$  (min) by  $t_n = t - [l/r]$ . (3) We performed CVD growth for a reaction time of  $t_n$ . If there were still some graphene domains formed with a size of  $l_1$  ( $\mu\text{m}$ ) for a reaction time of  $t_n$ , then we used  $t = t_n$  and  $l = l_1$  in equation  $t_n = t - [l/r]$  to obtain a new  $t_n$ . We repeated this step until no graphene domains were found. (4) We performed CVD growth with a reaction time of  $t_n = t_n + n$  ( $n = 1, 2, 3, \dots$ ) until graphene domains were observed, and  $t_n - 1$  was defined as the incubation time.

## References

55. Luo, Z.; Kim, S.; Kawamoto, N.; Rappe, A. M.; Johnson, A. T. Growth Mechanism of Hexagonal-Shape Graphene Flakes with Zigzag Edges. *ACS Nano* **2011**, *5*, 9154-9160.
56. Wu, Y. A.; Fan, Y.; Speller, S.; Creeth, G. L.; Sadowski, J. T.; He, K.; Robertson, A. W.; Allen, C. S.; Warner, J. H. Large Single Crystals of Graphene on Melted Copper Using Chemical Vapor Deposition. *ACS Nano* **2012**, *6*, 5010-5017.
57. Petrone, N.; Dean, C. R.; Meric, I.; van der Zande, A. M.; Huang, P. Y.; Wang, L.; Muller, D.; Shepard, K. L.; Hone, J. Chemical Vapor Deposition-Derived Graphene with Electrical Performance of Exfoliated Graphene. *Nano Lett.* **2012**, *12*, 2751-2756.
58. Mohsin, A.; Liu, L.; Liu, P.; Deng, W.; Ivanov, I. N.; Li, G.; Dyck, O. E.; Duscher, G.; Dunlap, J. R.; Xiao, K.; *et al.* Synthesis of Millimeter-Size Hexagon-Shaped Graphene Single Crystals on Resolidified Copper. *ACS Nano* **2013**, *7*, 8924-8931.
59. Eres, G.; Regmi, M.; Rouleau, C. M.; Chen, J.; Ivanov, I. N.; Poretzky, A. A.; Geohegan, D. B. Cooperative Island Growth of Large-Area Single-Crystal Graphene on Copper Using Chemical Vapor Deposition. *ACS Nano* **2014**, *8*, 5657-5669.