# Supplementary information

# **Oxidation-assisted graphene heteroepitaxy on copper foil**

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# 1) Review on Cu foils with large grain sizes in the context of graphene growth by chemical vapor deposition

Reference	Orientation	Approximative grain size	Starting foil	Treatment
[1]	Predominantly (111)	Many millimeters	99.999%, 0.25 mm thick, Alfa-Aesar	Melted on tungsten; atmospheric pressure, hydrogen and argon flow rates were adjusted to 60 and 940 sccm; temperature was first ramped up to 1000 °C in 50 min and then to 1100 °C in 10 min. The temperature was kept constant for 30 min and then slowly ramped down (1 °C/min) to 1075 °C.
[2]	Dominantly (100)	Up to a few millimeters	Alfa Aesar, 99.8% Cu 25 µm thick	Oxidation in air + annealed at 1040 °C in a quartz tube for 3 h in a 10 sccm $H_2$ flow at 150 mTorr.
[3]	(111)	Several millimetres	Alfa Aesar, (purity 99.8%, lot no. 13382)	25 mbar, argon 1000 sccm, 10 min, at 1000 °C.
[4]	(111)	A few millimetres	25 mm in thickness, purity of 99.8%	Thermal annealing at 1000 $^{\circ}$ C under a H <sub>2</sub> atmosphere with 400 sccm flow at 500 Torr.
[5]	Predominantly (100)	From a few millimeters to as large as a centimeter	Alfa Aesar, purity of 99.8%	Annealing at 1035 °C in 40 mTorr of $H_2$ for 30 min.
[6]	(111)	At the foil scale (up to 16 cm in length, ~2 cm in width)	Nilaco corporation, #CU-113213, 99.9% purity	Annealing it for up to 12 hours at a temperature of 1030 °C in an $Ar/H_2(100 \text{ sccm})$ environment, a total pressure of 26 Torr.
[7]	(111)	At the foil scale (6 $\text{cm} \times 3 \text{ cm}$ )	A 100-µm-thick copper foil (from Nilaco, 99.96%)	Annealed at 1075 °C with 1000 sccm Ar and 500 sccm $H_2$ for 2 h, polished using chemical- mechanical polishing/repeated several times until Cu(111) orientation is achieved.

**Table S1**: Information extracted from several publications dealing with graphene growth by chemical vapor deposition on Cu foils mentioning the formation of large (more than 1 mm) grains, as quoted in the article.

#### 2) Impacts of mechanical deformations on the recrystallization

The morphology of three  $3 \times 3$  cm<sup>2</sup> foils is investigated in a systematic way ( $5 \times 4$  mm<sup>2</sup> windows every 5 mm, 36 measurement points in total for each foil). We illustrate that mechanical deformations in the Cu foil have a strong influence on the reconstruction. First, after the S#1:noH<sub>2</sub>/S#2:H<sub>2</sub> pregrowth treatment, the Cu foil often remains polycrystalline on the edges, and more specifically around the corners of the Cu foil (see Figure S1a,b), where the foil was stressed during its cutting with scissors from the larger  $30 \times 30$  cm<sup>2</sup> as-received Cu foil. Moreover, it can be seen in Figure S1c that the region around an initial crumple in the foil also remains polycrystalline even after a S#1:noH<sub>2</sub>/S#2:H<sub>2</sub> annealing, while the piece is (111)-oriented everywhere else. Figure S1d shows a closeup view on the crumple with an optical microscope, where the crumple is much better seen than by scanning electron microscopy by the presence of shadows. The same elongated grain is evidenced in both pictures by a red-edged rectangle for facile comparison. These two observations evidence that it would be preferable to receive flat foils, instead of rolled ones, to avoid any manipulation during the unfurling which very often incurs folds and crumples in the foil, notwithstanding pleats already present in the as-received foil. We also believe that the final outcome of the annealing is in a large part determined by the internal strains in Cu foil, which is beyond our control. It is also interesting to note that, due to these "edge effects", the S#1:noH<sub>2</sub>/S#2:H<sub>2</sub> annealing of 1×1 cm<sup>2</sup> Cu pieces very often results in a very erratic reconstruction, either absent or very partial.

Finally, we have investigated what happens to a Cu piece cut from a larger (111)reconstructed one, when it is once again subjected to a  $S#1:noH_2/S#2:H_2$  pregrowth annealing (see Figure S1e,f). To help the reader to compare, a few identical grains are highlighted in red-edged rectangles. It is revealed that the (111) reconstruction is reversible on the edges of the piece that where stressed due to the cutting. Indeed, in Figure S1g, the top edge that was cut with scissors returns back to a polycrystalline state while the right one (uncut) remains (111)-oriented



**Figure S1**: Low magnification scanning electron microscopy (SEM) image of (a),(b) the edge of a  $3\times3$  cm<sup>2</sup> S#1:noH<sub>2</sub>/S#2:H<sub>2</sub> Cu foil, remaining partially polycrystalline. (c) Low magnification SEM image of a crumpled area in a  $3\times3$  cm<sup>2</sup> S#1:noH<sub>2</sub>/S#2:H<sub>2</sub> Cu foil remaining polycrystalline. (d) Optical microscopy picture of the area in the rectangle with red edges in (c), better highlighting the crumple in the Cu foil. (e) Low magnification SEM image of the surface of a ~1 cm<sup>2</sup> Cu piece cut with scissors from a  $3\times3$  cm<sup>2</sup> S#1:noH<sub>2</sub>/S#2:H<sub>2</sub> Cu foil. (f) Same image taken at the same location after a second S#1:noH<sub>2</sub>/S#2:H<sub>2</sub> treatment. (g) Low magnification SEM image of one corner of the same sample.

## 3) Bulk reconstruction of the Cu foil

The *recto* and the *verso* of the same Cu foil treated by S#1:noH<sub>2</sub>/S#2:H<sub>2</sub> is examined at the exact same location in Figure S2. It clearly appears that both sides are identical even if the contrast of some grains is different due the uneven topography of the Cu foil. To help the reader, a few identical grains are highlighted in red-edged rectangles. The backside picture is flipped vertically to enable a direct comparison.



**Figure S2**: Low magnification scanning electron microscopy image of (a) the front- and (b) the backside (flipped vertically) of a Cu foil at the exact same location, evidencing the bulk reconstruction of the foil. The bend corner used to handle the Cu piece is seen to point downward in (b).

## 4) Prolonged Cu foil annealing in argon and hydrogen

Similar to the three  $3\times3$  cm<sup>2</sup> S#1:noH<sub>2</sub>/S#2:H<sub>2</sub> Cu foils mentioned in the manuscript, this Cu foil annealed in argon and hydrogen during four hours (S#1 30 min + S#2 30 min+ S#3 180 min) is also scanned in 36 positions to get a global view. The two pictures in Figure S3a,b both evidence a uniform contrast (except for the (001) grains and the pleats), testimony to the reconstruction of the foil. Figure S3c reveals that, around a crumple, the foil remains polycrystalline.



**Figure S3**: Two typical low magnification scanning electron microscopy images of a  $3 \times 3$  cm<sup>2</sup> Cu foil annealed during four hours in argon and hydrogen.



## 5) Electron-backscattering diffraction on Cu(001) grains

**Figure S4**: Electron-backscattering diffraction inverse pole figure maps of an elongated grain, (a) out-of-plane (z direction) and (b) in-plane (y direction). In inset are seen the corresponding inverse pole figures. The grain has a (001) orientation. (c) Corresponding analyzed area in the red rectangle of the scanning electron microscopy picture.

#### 6) Abnormal grain growth

As it is, a cold worked metal foil contains a large amount of dislocations introduced during plastic deformation. As pictured in Figure S5a, when exposed long enough at high temperature, the metal foil becomes fully recrystallized (primary recrystallization), meaning that new dislocation-free grains have formed. Upon further annealing, the average grain size keeps growing in a continuous manner, a process called normal grain growth (NGG, see Figure S5b). In peculiar circumstances (see Figure S5c), NGG can lead to abnormal grain growth (AGG) (also called secondary recrystallization). Contrary to NGG, AGG is a discontinuous phenomenon, resulting in a bimodal grain size distribution. More details can be found in Ref. [8]. The mechanism of AGG is clearly identified in the pictures shown in Figure S5d,e.



**Figure S5**: Schematic representation of (a) the fully recrystallized state, (b) normal grain growth, and (c) abnormal grain growth. (d) Illustration by scanning electron microscopy of the process of abnormal grain growth, where a large, elongated Cu(111) grain (near the edge of the foil) is surrounded by much smaller grains, and is on the verge of contacting another much larger Cu(111) grain. (e) Electron-backscattering diffraction is used to determine the surface orientation of both grains (same magnification as in Figure S5d). The corresponding stereographic triangle can be seen with the 001, 101, and 111 poles.

#### 7) X-ray photoelectron spectroscopy data

Depth profile X-ray photoelectron spectroscopy (XPS) is performed to compare two foils subjected to  $S#1:H_2/S#2:H_2$  and  $S#1:noH_2/S#2:H_2$ , respectively. The analyses point out that there is no difference between the two samples: at the surface, peaks related to CuO, Cu<sub>2</sub>O, Cu(OH)<sub>2</sub>, and H<sub>2</sub>O show up with practically the same relative intensities, subsequent to interaction with oxygen and water present in the air<sup>9</sup> (see Figure S6a-d); in depth, Cu is not oxidized at all. It is worth noting that the manufacturer specifies a trace oxygen concentration of 0.01% in the Cu foil, well below the detection threshold of XPS. Next, the same XPS analysis is conducted on a Cu piece after the S#1:noH<sub>2</sub> thermal treatment, evidencing that, on the investigated thickness, Cu is weakly oxidized and the atomic oxygen concentration decreases progressively (see Figure S6e). The signal is integrated over a 250-µm-diameter spot and gives thus only average concentrations.



**Figure S6**: X-ray photoelectron spectroscopy (XPS) depth profiles performed to compare two foils subjected to  $S#1:H_2/S#2:H_2$  (a) and  $S#1:noH_2/S#2:H_2$  (b), respectively. Cu is oxidized only at the surface of the samples. (c,d) Corresponding high-resolution core level spectra at the very surface of the two foils. XPS depth profiles carried out on a  $S#1:noH_2$  Cu foil showing that Cu is oxidized in depth.

# 8) Energy-dispersive X-ray spectroscopy spectra



**Figure S7**: Energy-dispersive X-ray spectroscopy spectra recorded on a Cu specimen subjected to  $S#1:noH_2$ . Spectrum of (a) a  $Cu_2O$  inclusion and (b) the background.

#### 9) Estimation of the oxygen partial pressure

First, we ensure that the flow inside the quartz tube is laminar. In that case, when argon is introduced, all the air in the tube is driven away without turbulence, gently pushed outside by argon. Therefore, argon does not mix with air, preserving its initial purity. The Reynolds number, Re, is a dimensionless number allowing to determine, given the rate and the geometry of the flow, if the regime is laminar or turbulent. For a flow in a pipe, it is given by the well-known formula:

 $\text{Re} = (\rho \times v_{\text{mov}} \times L)/\mu$ ,

where  $\rho$  is the density of the fluid [kg/m<sup>3</sup>], v<sub>moy</sub> is the average velocity of the flow [m/s], L is a characteristic linear dimension [m], and  $\mu$  is the dynamic viscosity of the fluid. In the case of a cylindrical pipe, the characteristic linear dimension is the diameter  $\phi$ , L =  $\phi$ .

The average velocity can be easily calculated:  $v_{moy} = F/S$ , with F the volumetric flow rate  $[m^3/s]$  and S the section of the pipe  $[m^2]$ . For a cylindrical pipe,  $S = \pi \times (\phi/2)^2$  and  $Re = (4/\pi) \times (\rho \times F)/(\mu \times \phi)$ .

In the specific case of an argon flow,  $\rho = 1.7832 \text{ kg/m}^3$  and  $\mu = 2.2 \times 10^{-4} \text{ kg/(m.s)}$  (at 15 °C and 1013 mbar). We take into consideration the "worst case scenario" by taking the highest F value of 2 l/min (=  $1/30 \times 10^{-3} \text{ m}^3/\text{s}$ ) used in the process. Finally, with  $\phi = 2.5 \times 10^{-2} \text{ m}$ , we find Re = 13.8. This value is well below the value of 2300 generally considered for a transition to a turbulent flow.<sup>10</sup> Here again, we consider an upper bound for Re with respect to the temperature, since we consider the room temperature values of  $\rho$  and  $\mu$ , and  $\rho$  varies as  $\sim 1/\text{T}$  while  $\mu$  increases with increasing temperatures ( $\sim T^{1/2}$ ), thus Re(1050 °C) << Re(15 °C).

In the case of a mixture of argon and hydrogen, the contribution of hydrogen can be neglected because it has a much smaller density compared with argon. In addition, the typical hydrogen flow used here (20 ml/min) is also much lower compared to the argon flow.

Based on the data provided by the argon cylinder supplier (Air liquide, purity alpha2 99.9995%), the amount of O<sub>2</sub> should be below 0.5 ppm. So we can estimate that the O<sub>2</sub> partial pressure  $p_{O_2}$  is not greater than ~10<sup>-7</sup> bar. Based on the Ellingham diagram for the Cu/O<sub>2</sub> couple and considering  $p_{O_2} = 10^{-7}$  bar, we deduce that Cu<sub>2</sub>O is stable for any temperature lower than ~1050 °C. This is all the more true for any  $p_{O_2}$  greater 10<sup>-7</sup> bar.

## 10) Cu foil annealing in argon alone

Cu foils are annealed in argon alone for 30 min, 1 h or 2 h to observe how the morphology of the sample evolves with the hydrogen-free annealing time. From Figure 3e-g of the main manuscript, it is seen that, obviously, the density in Cu<sub>2</sub>O inclusions increases with the exposure duration to residual oxygen. These crystals are preferentially formed on the rolling striations, where Cu shows more defects, or along grain boundaries. More importantly, when comparing the surface morphology of each sample, it appears clearly that the average grain size stagnates at ~50  $\mu$ m and does not increase after 30 min, even if a prolonged annealing of 2 h is performed, as though the recrystallization becomes somehow inhibited. In a second experiment, the same Cu piece is annealed twice in a row in the same conditions (S#1:noH<sub>2</sub>). The inspection of the foil at the exact same place by scanning electron microscopy discloses that, as could be anticipated based on the previous observation, the grain morphology does not evolve in the least bit (see Figure S8a,b). The only notable difference lies in the larger number of inclusions adding to the ones already present.



**Figure S8**: (a) View by scanning electron microscopy of the surface of a Cu foil annealed 30 min in argon alone and (b) the same foil at the same spot annealed a second time 30 min in argon alone.

## 11) Reverse pregrowth treatment

We evaluate the effect of a reverse pregrowth treatment (S#1:H<sub>2</sub>/S#2:noH<sub>2</sub>) on the growth of graphene. For the same methane flow as the one used in Figure 4c of the main text (0.35 sccm), the growth following that treatment exhibits a full coverage by monolayer graphene with many multilayer graphene patches underneath (see Figure S9a). Figure S9b displays a scanning electron microscopy picture for an amount of methane decreased down to 0.2 sccm in order to obtain a partial coverage (in the same methane flow conditions, no growth occurs with the standard S#1:noH<sub>2</sub>/S#2:H<sub>2</sub> treatment). Even when the methane flow is decreased in that way, the coverage is almost complete, except for a few areas where it is possible to distinguish the edges of some hexagons only partially incorporated into the graphene film, or very occasionally isolated ones. The reduced methane flow allows determining that the typical hexagon size is below 50  $\mu$ m. It is also worth noting that the Cu film is polycrystalline and the graphene flakes grow with random orientations.



**Figure S9**: Scanning electron microscopy images of the graphene growth subsequent to the reverse pregrowth sequence, with a 0.35 (a) or 0.2 (b) methane flow.

## 12) Smoothing of the Cu foil after hydrogen annealing



**Figure S10**: Scanning electron microscopy pictures of a Cu piece (a) before any thermal annealing and (b) subjected to the  $S#1:H_2/S#2:H_2$  treatment at the exact same location. One can visualize the smoothing of the cold-roll striations and of a scratch in the top right corner of the foil. In addition, the annealed sample reveals a drastic increase of the grain size.

## 13) Supplementary low-energy electron diffraction patterns

The graphene/Cu(111) specimen seen in Figure 4c of the main text is analyzed in several points randomly chosen all over its surface ( $\sim 1 \text{ cm}^2$ ). It is found out that the sample presents a unique Cu(111) orientation. Graphene shows epitaxial alignment with respect to Cu(111), as testified by the unique set of LEED spots in Figure S11a–c. A weak misorientation is occasionally observed, as attested by the very faint ring in Figure S11d (white arrow), possibly related to the fact that the foil is not polished, thereby causing little graphene misorientation with respect to Cu(111).<sup>7</sup>



**Figure S11**: Low-energy electron diffraction patterns recorded in random positions on the sample pictured in Figure 4c of the main text.

## 14) Micro-Raman spectroscopy statistics and full spectra

In the average and standard deviation values given in the main text, we also include the data recorded on the edges of the hexagonal graphene domain. These data often show a large spread relative to the average value. Indeed, by excluding the edges, the standard deviation decreases. The average and standard deviation are calculated from more than 400 data points.

	$\Gamma_{2D} \left[ cm^{-1} \right]$	$\omega_{2D} \left[ cm^{-1} \right]$	$\omega_{G} [cm^{-1}]$	$I_{2D}/I_G$
μ	25.8	2684.6	1582	2.3
μ(wo edges)	25.5	2684.4	1.1	0.5
σ	1.4	0.9	1585.3	2.3
σ(wo edges)	1.1	0.8	1	0.2

**Table S2**: Summary of the average and standard deviation of the 2D-band full width at half maximum ( $\Gamma_{2D}$ ), 2D-band shift ( $\omega_{2D}$ ), G-band shift ( $\omega_G$ ), and 2D-band over G-band intensity ratio ( $I_{2D}/I_G$ ) extracted from the micro-Raman mappings in Figure 5 of the main manuscript.



**Figure S12**: 10 micro-Raman spectroscopy full spectra recorded at random positions on the sample (note that the spectra are shifted vertically relatively to each other for clarity).

## 15) Nanobeam electron diffraction patterns

Figure S12 shows all the electron diffraction (ED) patterns recorded in nanobeam mode on the graphene flake shown in Figure 6a of the main text. All the ED patterns correspond to a graphene single crystal oriented along the [0001] zone axis. Between all the ED patterns, the rotation of the  $\delta$  angle (defined in Figure 6b of the main text) is small, thus highlighting the single crystalline nature of the graphene flake.

1 δ=63.3°	<b>2</b> δ=63.2 °	<b>3</b> δ=63.5 °	4 δ=62.7 °	5 δ=64.1°	6 7 δ=62.8 °
<b>7</b> δ=63. 5°	<b>8</b> δ=59.3°	δ=66.2° <b>9</b>	δ=63.2° 10	<b>11</b> δ=66.1°	<b>12</b> δ=66.2°
<b>13</b>	14	<b>15</b> δ=65 δ=65	<b>16</b>	17	<b>18</b>
δ=64.5°	δ=63.0°		δ=62.0°	δ=61.8°	δ=63.5°
<b>19</b>	<b>20</b>	<b>21</b>	<b>22</b>	<b>23</b>	<b>24</b>
δ=62.9°	δ=63.4°	δ=63.7°	δ=62.4°	δ=62.0°	δ=62.3°

**Figure S13**: The 25 electron diffraction (ED) patterns recorded in nanobeam mode and through the holes of the TEM grid. Each ED pattern is labelled according to the location indicated in Figure 6a of the main text. In addition, the value of the  $\delta$  angle (defined in Figure 6b of the main text) is given for each ED pattern.

### 16) Cleaning of the Cu foils

It is of great importance to properly prepare the Cu foils before growing graphene on top of it in order to achieve graphene films of the best quality. In the scientific literature, many different pretreatment techniques can be found: (1) chemical treatment in various liquids such as acetic acid,<sup>11,12,13,14,15,16,17</sup> solvents,<sup>18</sup> water, <sup>19,20</sup> inorganic acids (dilute HNO<sub>3</sub>,<sup>11,19,21</sup> dilute HCl,<sup>21,22,23</sup>), FeCl<sub>3</sub>,<sup>11,24</sup> Cr or Ni etchants;<sup>21</sup> (2) electropolishing;<sup>11,12,13,19,25</sup> (3) chemical mechanical polishing. <sup>26</sup> More particularly, the removal of Cu oxide with acetic acid was shown to be very effective.<sup>27</sup> In the perspective of large-scale production, it also presents the distinctive asset not to involve complicated treatments or hazardous chemicals. On the other hand, many works reported in the literature deal with graphene growth on Alfa Aesar Cu foils (25-um-thick: 99.8% reference number 13382; purity; explicitly mentioned in<sup>11,12,14,15,18,19,20,23,24,25, 28,29</sup>). However, it is rarely reported that these foils are in fact coated with a thin metallic oxide anticorrosion film.<sup>16,25,29</sup> It goes without saying that this coating must be entirely removed, without degrading the underlying Cu foil, prior to graphene synthesis.

Here, we consider the widely used Cu foils mentioned above (Alfa Aesar #13382). X-ray photoelectron spectroscopy was first used to assess the presence of contaminants on the foil's surface before any treatment (so-called "as-received" foil). Two different as-received samples  $(1 \times 1 \text{ cm}^2)$  are analyzed in two and three distinct spots randomly chosen, respectively. The concentration of the detected elements is determined from the survey scan (see Figure S14). The main detected elements are oxygen (O 1s) and carbon (C 1s), corresponding to organic contamination. The presence of chromium (Cr 2p) is also unambiguously identified, corresponding to a layer of chromium oxide (the anticorrosion coating mentioned above). In addition, peaks that can be attributed to calcium (Ca 2p; between 8 and 10%) and phosphorus (P 2p; around 6%) appear. Other contaminants such as nitrogen (N 1s) or chlorine (Cl 2p) are also found, albeit in very weak amounts (less than 1.5%). The concentrations in the different elements can be found in Table S3.



Figure S14: X-ray photoelectron spectroscopy survey scan of an as-received Cu sample.

In order to remove the observed contaminants, we have next tested simple recipes involving harmless chemicals such as glacial acetic acid (GAA; Acros Organics; >99.8% purity), distilled water (DW) or isopropyl alcohol (IPA): (1) GAA alone for 15 min; (2) DW alone for 15 min; (3) mixture of GAA and DW in a 1:1 ratio for 15 min; (4) GAA alone for 15 min followed by rinsing in IPA. All the treatments are performed at room temperature. Finally, the Cu pieces are gently blown dry with nitrogen. All the recipes leave the chromium oxide layer intact, as one would expect (see Figure S15a). The only technique being efficient in

removing calcium is the third one (GAA+DW) (see Figure S15b). Phosphorus is still present in all cases. The concentrations in the different elements are summarized in Table S3.



**Figure S15**: (a) Cr 2*p* core level spectrum for the as-received, the GAA+DW cleaned, and the annealed Cu pieces, respectively. (b) X-ray photoelectron spectroscopy survey scan of a Cu sample cleaned in a mixture of glacial acetic acid and distilled water.

		Composition							
Sample type	Point	O 1 <i>s</i>	Cu 2 <i>p</i>	C 1 <i>s</i>	Ca 2 <i>p</i>	P 2p	Cr 2 <i>p</i>	N 1 <i>s</i>	Cl 2 <i>p</i>
As- received #1	1	40	5	38.5	8	5.6	1.4	1.5	Х
	2	41.8	5	35.9	8	6.1	1.5	1.7	Х
As- received #2	1	46.9	5.9	28.9	9.4	6.4	2	X	0.5
	2	46.7	5.8	29	9.7	6.4	1.8	X	0.6
	3	45.3	5.8	30.3	9.5	6.5	1.8	X	0.8
Cleaned in	1	51.1	13.7	16.5	6.6	9	3.1	X	Х
GAA	2	51.8	13.2	16.3	6.4	9	3.3	X	Х
	3	51.3	14.2	14.1	7.2	9.8	3.4	Х	Х
Cleaned in	1	47	10.8	24.8	6	8.8	2.6	X	Х
DW	2	46.2	9.4	28.6	5.2	7.9	2.7	X	Х
	3	45.2	9.5	28.8	5.5	8.4	2.6	X	Х
Cleaned in	1	48.7	17.6	22.3	Х	8.2	2.6	X	0.6
GAA+DW	2	49.2	17.9	21.4	Х	8.1	2.8	X	0.6
	3	49.6	22.2	14.8	X	9.8	2.9	X	0.7
Cleaned in	1	52.1	12.6	17.6	6.3	8.5	2.9	X	Х
GAA, rinsed	2	52.3	12.1	17.2	6.8	8.5	3	X	Х
in IPA	3	50.9	12.2	18.2	6.7	9.1	2.9	X	Х

**Table S3**: Superficial composition of the as-received samples and of the samples cleaned by the four different methods, obtained from the survey scan.

We have next investigated the superficial composition after annealing (i.e. growth without methane, in the standard conditions, see Figure 1a of the main text) or after growth (in the standard conditions as well), for each type of treatment, in three distinct points. Table S4 summarizes the composition of the surface of the diverse Cu pieces. The conclusions are essentially the same in both cases: the chromium oxide layer evaporates during the thermal treatment (also confirmed by the high-resolution core level spectrum of Cr 2p in Figure S15a), as well as phosphorus, chlorine, and nitrogen, for all four treatments. The only remaining impurity is calcium, in small amounts (around 1%), except for the GAA+DW recipe, as already observed before. In addition, the only treatment leading to the successful growth of graphene is GAA+DW, as testified by the much higher carbon concentration of the sample cleaned with GAA+DW (~48% versus less than 15% for the other three methods) and careful scanning electron microscopy (SEM) inspection of each kind of samples (not shown). This is further illustrated by the SEM picture displayed in Figure S16, corresponding to a growth performed on a sample half-dipped in the GAA+DW mixture. It clearly shows that graphene grows on the half dipped in GAA+DW while it does not on the untreated one. It is even possible to perceive a difference in color between both parts, evidencing the effect of the GAA+DW cleaning.

In conclusion, it appears (1) that the inhibited growth of graphene is related to the imperfect removal of calcium from the surface and (2) that the chromium oxide layer is removed by the thermal treatment (and in fact even before the beginning of the growth process, since otherwise, the growth would not occur), as well as the other minor contaminants. This study also illustrates that some cleaning recipes presented in the literature are not universal and the cleaning of the Cu foil must be adapted to the foil's manufacturer (coating, contaminations).

		Composition							
Sample type	Point	O 1 <i>s</i>	Cu 2 <i>p</i>	C 1 <i>s</i>	Ca 2p	P 2p	Cr 2 <i>p</i>	N 1 <i>s</i>	Cl 2 <i>p</i>
Cleaned in	1	37.2	46.3	15.1	1.4	X	X	X	Х
GAA/after	2	35	51.8	11.8	1.4	X	Х	X	Х
annealing	3	36.2	48.2	14.5	1.1	X	Х	X	Х
Cleaned in	1	37.5	45.6	16.1	0.8	X	Х	X	Х
DW/after	2	34.7	51.8	12.8	0.7	Х	Х	Х	Х
annealing	3	36.8	48.1	14	1.1	X	Х	Х	Х
Cleaned in	1	37.7	46.1	16.2	Х	Х	Х	Х	Х
GAA+DW/after	2	35.8	52.5	11.7	Х	Х	Х	Х	Х
annealing	3	36.5	50.9	12.6	Х	X	Х	Х	Х
Cleaned in GAA,	1	37.4	44.5	17.1	1	X	Х	X	Х
rinsed in IPA/after	2	37.2	47.8	13.9	1.1	X	Х	Х	Х
annealing	3	35.9	48.2	14.7	1.2	X	Х	Х	Х
Cleaned in	1	36.7	45.2	15.8	2.3	X	Х	X	Х
GAA/after	2	29.8	61.2	7	2	X	X	X	Х
growth	3	25.7	68.3	3.7	2.3	X	Х	Х	Х
Cleaned in	1	35	50.6	13.7	0.7	X	X	X	X
DW/after	2	27.5	65.5	6.6	0.4	X	Х	X	Х
growth	3	29.1	61	9.4	0.5	X	Х	X	Х
Cleaned in	1	5.7	46.2	48.1	X	X	X	X	Х
GAA+DW/after	2	6	45.9	48.1	X	X	X	X	Х
growth	3	6	45.7	48.3	X	X	X	X	Х
Cleaned in GAA,	1	38.8	43.2	16	2	X	X	X	X
rinsed in IPA/after	2	37.8	48.6	7	1.9	X	X	X	X
growth	3	34.6	54.1	8.7	2.6	X	X	X	X

**Table S4**: Superficial composition of the samples cleaned by the four different methods after annealing or after growth, obtained from the survey scan.



**Figure S16**: Scanning electron microscopy picture corresponding to a growth performed on a Cu piece half-dipped in the GAA+DW mixture.

## 17) Additional experimental details

## Scanning electron microscopy (SEM)/Energy-dispersive X-ray spectroscopy (EDX):

The morphology and the size of the Cu grains and graphene domains are monitored with two different microscopes: a Jeol JSM-6010LV InTouchScope at low magnification (operated at an accelerating voltage of 5 kV and a spot size between 30 and 50, with a working distance of 25 mm to increase the field of view, in secondary electron mode) and a Jeol JSM-7500F at high resolution (operated at an accelerating voltage of 1 kV and an emission current of 5  $\mu$ A, with a working distance of 3 mm, in secondary electron mode with a low gentle beam of 0.2 kV applied to the specimen). EDX mapping is performed with the Jeol JSM-7500F at 15 kV with a probe current of 1 nA and a resolution of 512×384 pixels.

## **Electron-backscattering diffraction (EBSD)**:

The analysis of the Cu foil crystal orientation is performed using a SEM ZeissSupra55 fitted with a HKL-Oxford Instruments EBSD system featuring the Nordlys II camera. Data analysis is realized using the associated Channel 5 software suit. EBSD data collection is operated at an accelerating voltage of 15 kV, a working distance of 11 mm, and a sample tilt of 70°. The out-of-plane inverse pole figure maps are in the z direction, perpendicular to the Cu foil surface, while the in-plane inverse pole figure maps are in the y direction, parallel to the plane of the Cu foil (instead, the in-plane inverse pole figure maps could also be given in the x direction, the information being the same). The zero solutions (electron-backscattered diffraction patterns that cannot be indexed due to very poor quality) are replaced by an extrapolation based on the neighboring points.

Figure	Pixel size [µm <sup>2</sup> ]	Raster size	% of correct indexation
2a	4×4	100×100	84
2c,f	10×10	194×148	97.45
2d,g	13×13	100×100	95.64
2e,h	10×10	197×143	86.86
S4	2×2	150×114	96.78
S5	12×12	261×194	95.68

**Table S5**: More details about the different inverse pole figure maps presented in this work.

## Low-energy electron diffraction (LEED):

The LEED patterns are acquired in a ultrahigh-vacuum setup after outgassing the samples at 300 °C for one hour. The energy of the incident electrons is set to 70 eV, with an analysis spotsize of  $\sim$ 1 mm.

## X-ray photoelectron spectroscopy (XPS):

A ThermoFisher Scientific K-alpha spectrometer is utilized. It is fitted with a monochromatized Al  $K\alpha 1,2$  x-ray source and a hemispherical deflector analyzer. The spectra are recorded at constant pass energy (150 eV for depth profiling and survey; 30 eV for high resolution spectra). A flood gun (low energy electrons and Ar<sup>+</sup> ions) is used during all the measurements. During the sputtering, the Ar<sup>+</sup> ion gun is operated at an accelerating voltage of 2 kV, with an erosion time of 5 s per cycle, and the analysis is done in snapshot mode. The XPS data are treated with the Avantage software. High resolution spectra are fitted by Gaussian-Lorentzian lineshapes with an Avantage "smart" background (*i.e.* a Shirley

background in most cases, or a linear background in case the lineshape decreases with increasing binding energy). The diameter of the analyzed surface is  $250 \ \mu m$ .

## Micro-Raman spectroscopy (µRS):

A LabRam HR 800 confocal laser system from Horiba Jobin Yvon is used for the acquisition of the Raman spectra. The measurements are performed at room temperature with a laser wavelength of 514 nm in backscattering geometry. The spectra are acquired on a 950  $\mu$ m by 1100  $\mu$ m grid with a spacing of 30  $\mu$ m between each measurement spot (totalizing 32×37 spectra). A 100× objective (NA = 0.95) is used to collect the signal. The incident power is kept below 1 mW to avoid any heating effect. High resolution (1800 lines/mm) gratings are used for the measurements (with a corresponding spectral resolution < 1 cm<sup>-1</sup>). For the data analysis, the spectra are first fitted with Lorentzian functions. Then, the full width at half maximum, the position, and the integrated intensities of the 2D and G bands are extracted from the resulting fits.

## Transmission electron microscopy (TEM)/electron diffraction (ED):

The TEM experiments are performed by using a FEI Titan Cube operating at 80 kV and equipped with a  $C_S$  image corrector. The analyses are performed at liquid-nitrogen temperature to hinder carbon contamination and electron-beam damages. The effective diameter of the area probed on the specimen during nanobeam electron diffraction is around 150 nm.

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