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Scrolled Production of Large-Scale Continuous Graphene on Copper Foils

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We report an efficient and economical way for mass production of large-scale graphene films with high quality and uniformity. By using the designed scrolled copper-graphite structure, a continuous graphene film with typical area of $200 \times 39\,\mathrm{cm}^2$ could be obtained in 15 min, and the production rate of the graphene film and space utilization rate of the CVD reactor can reach $520\,\mathrm{cm}^2\cdot\mathrm{min}^{-1}$ and $0.38\,\mathrm{cm}^{-1}\cdot\mathrm{min}^{-1}$, respectively. Our method provides a guidance for the industrial production of graphene films, and may also accelerate its large-scale applications.

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Graphene has been widely investigated in the fields of materials, physics and chemistry due to its novel properties and various potential applications.[1–5] However, up to date, the industrial applications of graphene were limited to a small range, leaving most of its excellent mechanical, thermal and electrical properties underutilized. To fully utilize those properties, scalable production of high-quality graphene films in an economical and efficient way is in great demand.[6] At present, the most prevailing strategies for massive production of graphene flakes/films can be roughly divided into two groups: (i) chemical/electrochemical exfoliation of graphite in aqueous solution, which is cost-effective but of inferior quality;[7–11] (ii) chemical vapor deposition (CVD) growth of graphene on epitaxial substrates of metals or dielectrics,[8] which leads to growth of graphene with high quality and proves to be optimal in electronic and optoelectronic devices.[12–15]

Since the realization of uniform growth of monolayer graphene on copper (Cu) foils,[13] the research interests of CVD-grown graphene have been focused on two points: large size and high quality.[16–20] Among all the techniques developed so far, the roll-to-roll growth method shows the best potential for industrialization.[21–23] In most cases of this method, a winder roll is applied to deliver Cu stripes at a typical transport velocity of 10–50 $\mathrm{cm}\cdot\mathrm{min}^{-1}$ to achieve a full coverage of graphene on Cu surface.[24–26] In principle, the productivity is proportional to the exposed catalytic Cu surface area under the optimal growth condition.[27–31] Therefore, a larger equipment seems to be the final choice to further improve the yield, which in turn will also increase costs and space. Besides the roll-to-roll growth technique, a different synthesis method of graphene on rolled Cu has been recently reported, which has high efficiency in a much smaller reactor due to the increased exposed surface

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area of Cu.[32,33] However, the rolling construction of Cu foil as well as the growth temperature in these works should be precisely controlled to prevent the collapse and fusion of the adjacent Cu layers. Therefore, an efficient method that can balance the productivity and quality of large-scale graphene films is in great demand.

In this work, we develop a scrolled production technique to realize the industrial-scale growth of graphene film with high quality in a commonly used laboratory CVD furnace. By adding a graphite paper as the separating layer, our method achieved high stacking density of Cu layers in a small CVD system. Meanwhile, with the excellent thermal stability, the graphite paper could also prevent the adjacent Cu from adhesion. In our experiments, the production rate of the graphene film and space utilization rate of the CVD reactor can reach $520\,\mathrm{cm^2{\cdot}min^{-1}}$ and $0.38\,\mathrm{cm^{-1}{\cdot}min^{-1}}$, respectively. Structural characterizations and transmittance tests of our large-scale graphene film revealed its high quality and uniformity. With such high productivity and quality, industrialization and commercialization of continuous graphene films will be highly accelerated.

The scrolled production of a graphene film was performed in a commonly used CVD furnace as shown in Fig. 1(a), where a stacked Cu foil and a graphite paper were rolled coaxially onto a small inner quartz tube. Here, this inner quartz tube was used for three benefits: (i) to assist the rolling process of the Cu foil and the graphite paper and to facilitate the loading process of the scrolled sample; (ii) to improve the gas utilization rate by avoiding gas leakage from the inside cavity of the scrolled structure; (iii) to maintain this scrolled structure during the graphene growth at low temperatures. A pair of quartz holders on both ends of the inner quartz tube was used to avoid compaction of the bottom scrolled Cu [Fig. 1(b), upper panel]. With this design, the stacked structure is dense enough to fully utilize the small space, meanwhile loose enough for the flow of gas to form a uniform graphene film [Fig. 1(b), lower panel, the measurement of the gap size is shown in Fig. S1 in the Supplementary Materials]. Most importantly, with the assistance of the graphite paper, the shape of the Cu foil can remain intact after the high-temperature annealing (up to 1065 ℃ as shown in Fig. S2) and graphene growth in such a small CVD furnace (otherwise it will collapse and stick together as shown in Fig. S3). This simple design ensures the massive production of graphene without excessively relying on enlarging the CVD equipment.

In our experiment, a $200 \times 39\,\mathrm{cm^2}$ Cu foil was scrolled with a graphite paper and loaded into the CVD system. After growth at the high temperature of 1050 °C for 15 min with the flow rate of CH_4/H_2 at 10 sccm/10 sccm, a full coverage of graphene on the Cu foil was realized [Fig. 1(d)]. The production rate of the graphene film is $520\,\mathrm{cm^2{\cdot}min^{-1}}$, and the space utilization rate of the CVD reactor is as high as $0.38\,\mathrm{cm^{-1}{\cdot}min^{-1}}$ (the volume of the reactor is $\sim 1373\,\mathrm{cm^3}$). Compared with the previous works[27–33] using roll-to-roll growth, batch-to-batch growth and rolled Cu growth techniques, both the rates are superior [Fig. 1(c)]. This significantly increased productivity benefits from the designed scrolled Cu-graphite structure, which leads to the best utilization of space and feedstock simultaneously. In addition, to exclude the influence of the graphite paper on the synthesis of graphene, we conducted a controlled experiment without introducing CH_4, and no graphene film was found on Cu (Fig. S4), indicating that the graphite paper was the excellent separator and would not bring additional factors.

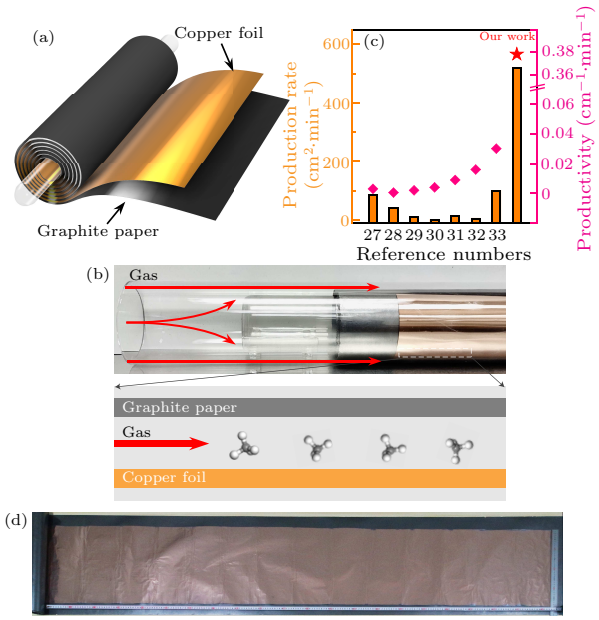

Fig. 1. CVD growth of large-scale graphene with the scrolled growth technique. (a) Schematic of the scrolled Cu-graphite structure, the graphite paper is used as the separator and a small inner quartz tube is used as the core of the structure. (b) Upper panel: photograph of the apparatus, lower panel: schematic of the gas flow in the confined space between Cu and the graphite paper, the model shown here is for CH_4 molecules. (c) Comparison of the production rate (orange column) and productivity (pink rhombus) in the previous works[27–33] with this work. (d) Photograph of the continuous graphene film on Cu with an area of $200 \times 39\,\mathrm{cm^2}$.

In addition to the coverage of graphene, the quality of graphene is another general concern about this close-packed configuration. To find the most appropriate condition for the high-quality growth of graphene, the flow ratio of CH_4/H_2 was fixed at 1,[23] while the flow rate of CH_4/H_2 varied from 80 sccm/80 sccm, 40 sccm/40 sccm to 10 sccm/10 sccm. With the CH_4 concentration decreasing, the graphene films tend to be more uniform as shown in optical images [Fig. 2(a)

and Fig. S5]. Raman spectra (with excitation laser wavelength of 633 nm) were conducted in randomly chosen regions on three typical samples correspondingly. As the concentration of CH_4 decreases, the intensity ratio of the 2D peak and G peak (I_{2D}/I_G) increases, and the full width at half maximum (FWHM) of the 2D peak decreases, indicating that the multilayer area of the sample is greatly reduced. The graphene film with best quality is acquired under the CH_4 flow rate of 10 sccm, with Raman spectra showing the intensity ratio of D peak and G peak (I_D/I_G) less than 0.02 [Fig. 2(b)]. This phenomenon can be understood qualitatively as follows: with the flow rate of CH_4 and H_2 increasing (40 sccm and 80 sccm) in the atmospheric pressure CVD (APCVD) system, the thermal dissociation and collision become much more intense, and the nucleation of graphene will take place more easily on high energy sites, thus multilayer graphene with high density of defects will emerge;[34,35] while in the lower CH_4 concentration case, the nucleation and adlayer growth are effectively suppressed, leading to the formation of the high-quality graphene film [Fig. 2(c)].[36]

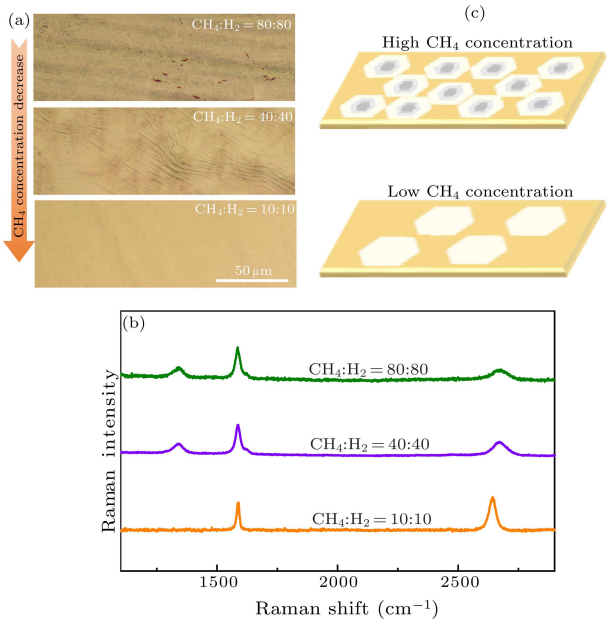

Fig. 2. The dependence of the graphene quality on CH_4 and H_2 concentration. (a) Optical images of the as-grown graphene films with different CH_4 concentrations. These images are of the same size. (b) Raman spectra of the corresponding samples in (a). (c) Schematic of the graphene growth under different CH_4 concentrations.

To further evaluate the quality and uniformity of the as-grown graphene in an extended region of the 2-m-long Cu, we selected 5 positions on the Cu foil with intervals of ∼0.5 m, and transferred them onto the 300 nm SiO_2/Si substrates. Raman spectra (with excitation laser wavelength of 532 nm) of these 5 different samples all show typical monolayer characteristics without D peaks [Fig. 3(a)]. In addition, Raman mappings were also carried out on the 5 samples correspondingly: the FWHM of the 2D peak, I_{2D}/I_G and I_D/I_G are all of high uniformity at a 100-μm-scale area [Figs. 3(b)–3(d) and Figs. S6–S8]. These results demonstrate that even the Cu foil is stacked in such a scrolled regime, the obtained graphene film is still of high quality and uniformity at large scale.[33]

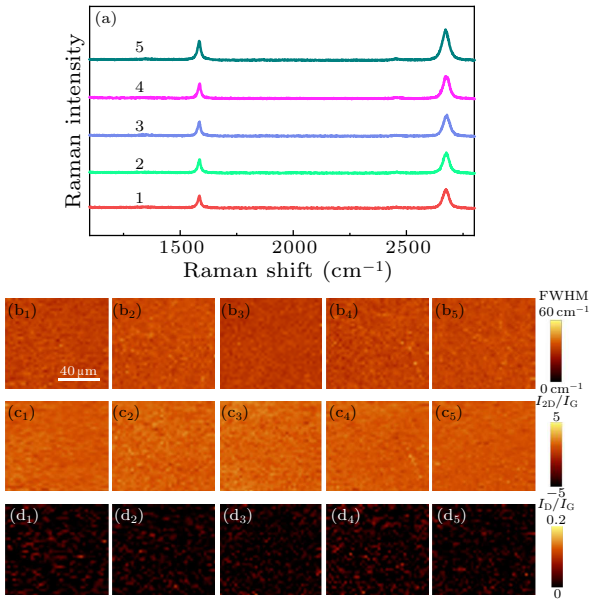

Fig. 3. Raman characterization of the transferred graphene. (a) Raman spectra of the 5 transferred samples on 300 nm SiO_2/Si. (b)–(d) Raman mappings of 2D peaks' FWHMs (b), I_{2D}/I_G (c) and I_D/I_G (d), respectively. The subscripts 1–5 represent the samples shown in (a). These maps are of the same size.

To investigate the origin of the excellent performance of this scrolled growth technique, we examined the crystal structure of the Cu foil since it can significantly affect the epitaxial quality of graphene. In our experiments, the as-received commercial Cu foil was polycrystalline and the XRD 2θ scan results indicated that they were (200) oriented (Fig. S9). After the annealing process, it showed a single pronounced Cu(111) peak [Fig. 4(a)]. Furthermore, the EBSD mapping proved that the single crystal was of large-scale uniformity [Fig. 4(b)]. These results demonstrated that the Cu foil was transformed into Cu(111) single crystals during the high-temperature annealing process,[37] and each single crystal region was at least of centimeter scale. This phenomenon can be understood as follows: during annealing at a reduced atmosphere, the main driving force for the abnormal grain growth is surface energy minimization.[38] Thus the Cu(111) facet which has the lowest surface energy is obtained (Table S1). For graphene growth on such the Cu(111) substrates, typical high-resolved TEM (HRTEM) images revealed the single-crystal nature of graphene without detectable defects [Fig. 4(c)]. With further decreasing the growth time,

aligned graphene domains on Cu foil can be found, and the alignment level reaches > 98% [Figs. 4(d)–4(f)]. As is widely accepted, Cu(111) is the most ideal substrate for the growth of single-crystal graphene due to their same rotation symmetry and the small lattice mismatch (4%).[31] Thus, we can attribute the high-quality growth of the graphene film to the seamless stitching of separated graphene domains on Cu(111) single crystals (details are shown in Fig. S10).

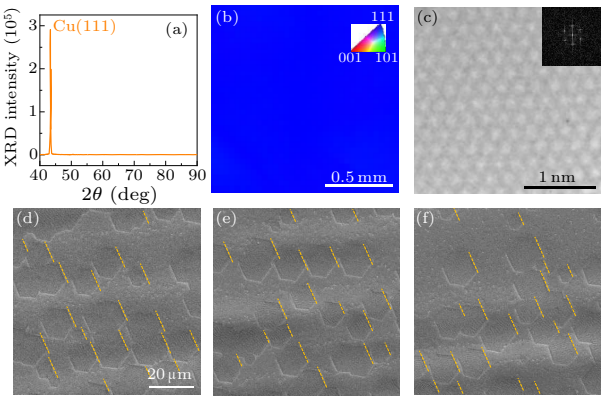

Fig. 4. Characterizations of single-crystal Cu foils. [(a),(b)] XRD 2θ-scan spectrum (a) and EBSD IPF map (b) of the annealed Cu, proving a large-scale single-crystal Cu(111) formed in the scrolled structure. (c) Representative HRTEM image of monolayer graphene showing a uniform crystal lattice structure. Inset: corresponding fast Fourier transform (FFT) pattern. (d)–(f) SEM images of unidirectionally aligned graphene domains obtained at different areas on one single-crystal Cu(111) grain. These images are of the same size.

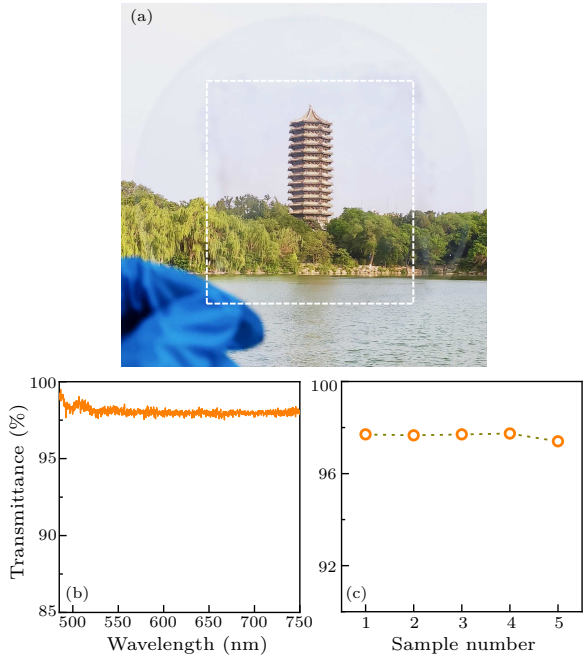

Fig. 5. Transmittance characterization of graphene transferred onto fused silica. (a) Photograph of the graphene featuring a good transparency to the underneath BoYa Tower in Peking University. The size of the fused silica is 4 inch. (b) Visible spectrum of the representative transferred graphene film. (c) The transmittance at 550 nm of the transferred graphene films at different areas.

Using this scrolled production technique, we are able to obtain uniform large-scale graphene films efficiently, and various applications of this film are already expected. Here, we transferred a transparent graphene film onto a 4-inch fused silica for examination [Fig. 5(a)], and the BoYa Tower in Peking University is clearly seen through this transparent film. The optical transmittance at 550 nm is reduced by ∼2.3% at different positions [Figs. 5(b) and 5(c)], which implies a single layer property of the transferred sample.[39] Sheet resistance of the graphene film was also measured, and an average value of ∼450 Ω/sq was obtained (Fig. S11). The measured field-effect transistor mobility of the graphene film was ∼2600 $cm^2 \cdot V^{-1} \cdot s^{-1}$ at 1.5 K (Fig. S12). The excellent optical transparency and good electrical property of the as-grown graphene demonstrate its capability as transparent electrodes in electronic and optoelectronic devices.

In summary, a scrolled Cu-graphite structure has been designed to successfully synthesize a $200 \times 39\ cm^2$ uniform graphene film. The use of graphite separator is a crucial strategy to increase the stacking density of the Cu substrate, which leads to the fast growth of graphene in a limited space. The production rate of the graphene film reaches 520 $cm^2 \cdot min^{-1}$, and the space utilization rate of the CVD reactor is as high as 0.38 $cm^{-1} \cdot min^{-1}$, which are several times or even magnitude higher than those in the literature available. Large single crystals of the Cu substrate formed in our scrolled structure through high temperature annealing treatment are proved to ensure the quality of the epitaxial-grown films. Our method thus implies a suitable balance between productivity and quality of the massive production of graphene films. We believe that this scrolled growth technique will be a significant promotion to the large-scale industrialization and commercialization of graphene films.

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Supplementary Materials: Scrolled Production of Large-Scale Continuous Graphene on Copper Foil

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Experimental section

Scrolled growth of graphene film

Before the first use of the graphite paper (100 μm-thick, 99%, Beijing Jinglong Special Carbon Technology Co. Ltd.), it was pre-annealed at 1050 ℃ for 72 h to release the impurities that may adsorb on its surface. Then the Cu foil (25 μm-thick, 99.8%, Sichuan Oriental Stars Trading Co. Ltd., #Cu-1031) and the graphite paper were scrolled together with the assistance of an inner quartz tube (outer diameter: 4 cm), and then the samples were loaded into the quartz tube (outer diameter: 6 cm) of a high-temperature CVD furnace (Tianjin Kaiheng Co. Ltd.). The system was heated to 1050 ℃ under a reduced atmosphere with Ar = 100 standard cubic centimetre per minute (sccm)

and H_2 = 50 sccm. After annealing of the Cu substrate at this temperature, different flow of CH_4/H_2 (80 sccm/80 sccm, 40 sccm/40 sccm and 10 sccm/10 sccm) were introduced to facilitate the graphene growth at atmospheric pressure.

To avoid the influence of oxygen on the synthesis of graphene, the system was evacuated by a vacuum pump for 2 min after the loading of the samples, then the vacuum pump was turned off and the system was purged with pure Ar to atmospheric pressure. This procedure was repeated for 3 times to minimize the amount of the trapped oxygen in the quartz tube. What's more, during the annealing and growth procedure, the H_2 was always switched on to reduce the native oxide layer of Cu caused by the mild-oxidation at room temperature and oxygen leakage from environment.

Sample transfer

The sample was transferred by the typical wet transfer method. First, the graphene was spin-coated with polymethyl methacrylate (PMMA) and baked at 120 ℃ for 2 min. Then the sample was immersed into ammonium persulphate solution to etch the Cu away. After washing the PMMA/graphene by deionized water, it was placed onto the substrate of SiO_2/Si or fused silica. Finally, the PMMA was dissolved by acetone.

Characterization

Raman characterization was conducted using an Alpha300R system (WITec, Germany) with excitation laser wavelengths of 532 or 633 nm. X-ray diffraction (XRD) 2θ-scan measurements were conducted using a Bruker D8 Advance system with Cu target. Electron backscattered diffraction (EBSD) characterizations were carried out using PHI 710 Scanning Auger Nanoprobe. Transmission electron microscopy (TEM) experiments were performed with a FEI Titan Themis G2 300 operated at 80 kV. Scanning electron microscopic (SEM) images were obtained using Thermal Fisher, Quattro S. The room temperature sheet resistance of the graphene films was measured by using a four-probe resistance measuring metre (CDE RESMAP 178).

Transmission Spectra

We applied a home-built confocal transmission system to collect the optical contrast signal of graphene. A supercontinuum laser (Fianium SC-400-4) was used as the light source. An objective (Mitutuyo M Plan 50 X, NA=0.42) was placed to focus the light onto the sample and another objective (Mitutuyo M Plan 50 X, NA=0.42) was placed to collect the transmitted light. Two sets of transmission spectra were collected, one with the as-grown graphene in the beam focus (I_{in}) and another out of the beam focus (I_{out}), and the final contrast spectra was obtained ($\Delta T/T = (I_{in}-I_{out})/I_{out}$).

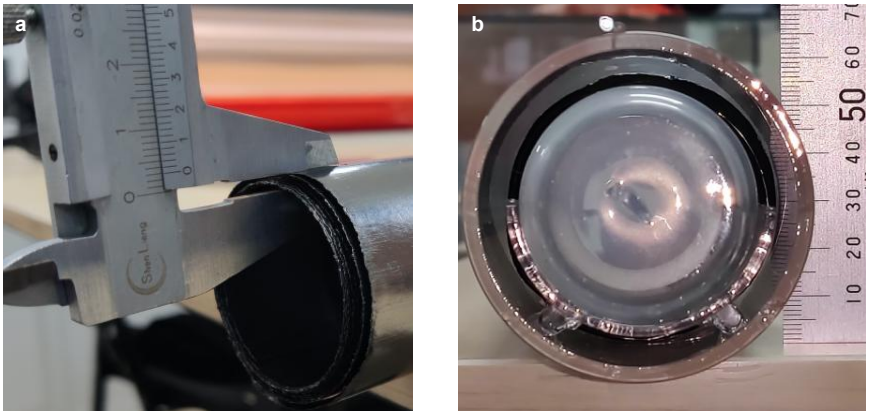

Figure S1 | a, Measurement of the gap size between Cu foil and graphite paper. **b**, Side view of the sample loaded into the quartz tube. 14 rolls of Cu foil (25 μm) and graphite paper (100 μm) in our "scrolled" structure had a space of 3 mm, thus the average gap size under the influence of gravity was estimated to be ~75 μm (**a**). This size is loose enough for the gas passing. And thanks to the quartz holder, the space for the whole scrolled structure is approximately the same (**b**).

Figure S2 | Photograph of Cu foil on graphite paper after annealing at 1065 ℃ for 1 hour under a reduced atmosphere. The scrolled Cu-graphite structure we developed won't fuse and adhere together at the growth temperature as high as 1065 ℃.

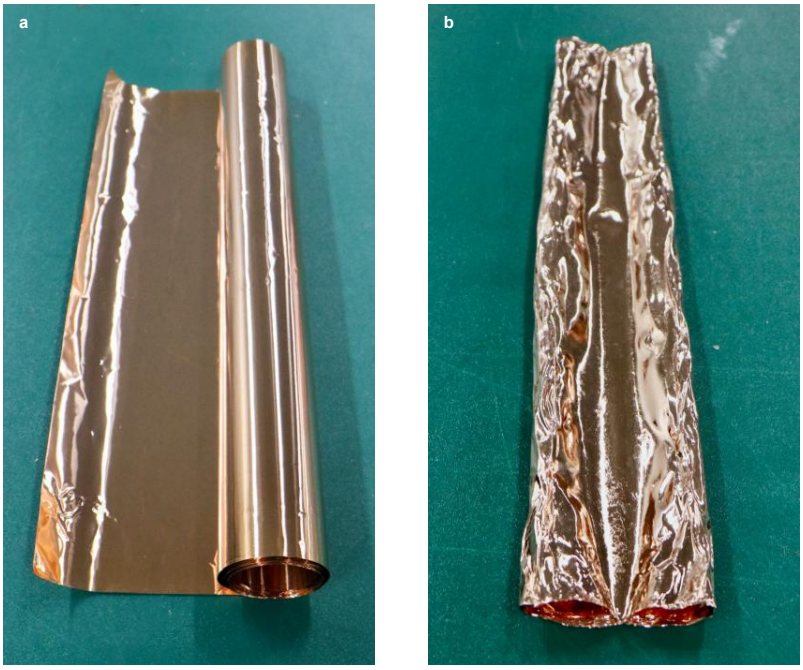

Figure S3 | The Cu scrolled structure without the graphite separator and inner quartz tube. a-b, Optical images of the scrolled Cu (200×39 cm^2) structure before (**a**) and after (**b**) high temperature annealing. After the same growth procedure as we used in the main text, the scrolled structure collapsed without the support of the inner quartz tube, and the Cu foil stuck together without the assistance of the graphite separator. These results clearly demonstrate that the design of our scrolled Cu-graphite structure is the key to ensuring the continuous graphene film growth.

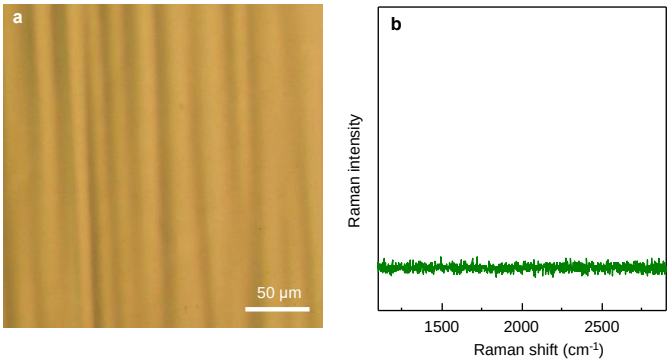

Figure S4 | Optical image (**a**) and Raman spectrum (**b**) of the Cu surface after the same graphene growth procedure without methane flow. The surface of the obtained Cu foil was clean and no graphene film was formed on it.

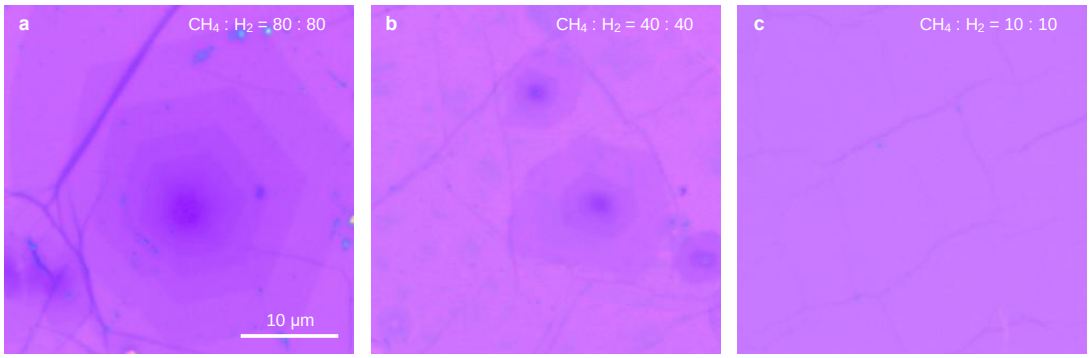

Figure S5 | a-c, Optical images of the transferred graphene films under different CH_4 concentration.

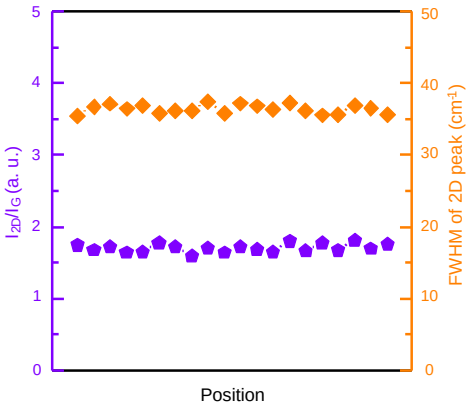

Figure S6 | Raman spectra of the graphene film at different positions in a large area. The small fluctuations in both the I_{2D}/I_G and the FWHM of 2D peak demonstrate that the graphene film has good homogeneity over a large area.

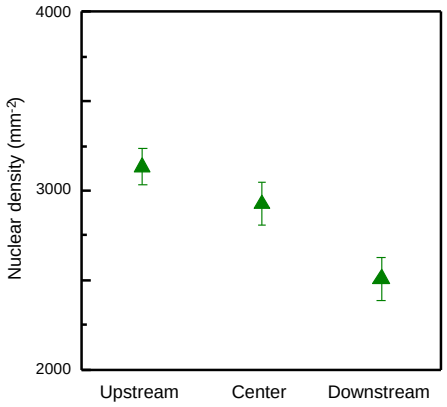

Figure S7 | The nucleation density of the graphene film after 5 minutes' growth at different positions. Due to the sufficient carbon supply, the nucleation density of graphene islands in the upstream region are higher than those in the center or downstream locations at the beginning of growth.

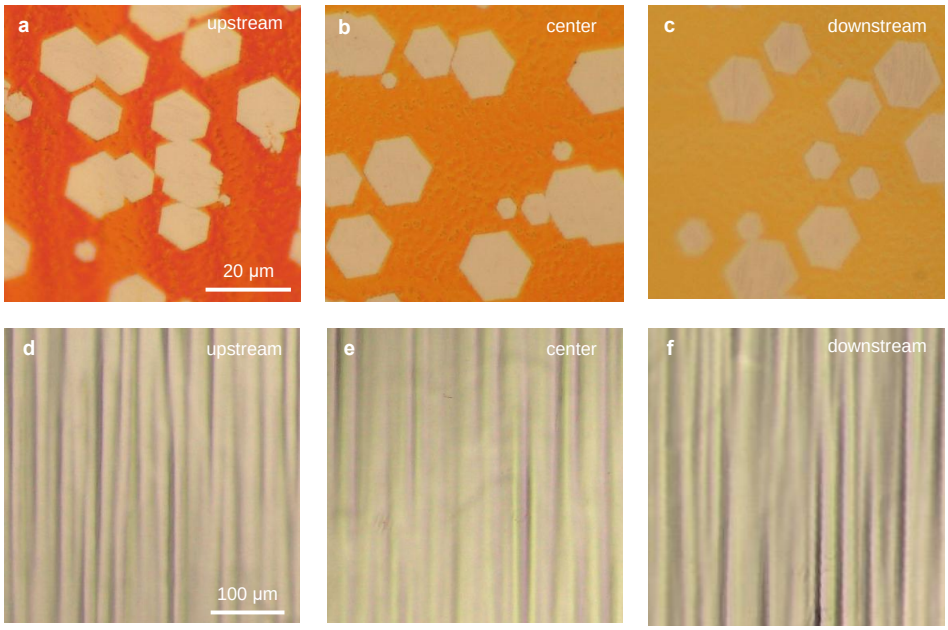

Figure S8 | Optical images of the graphene film grown at different position for 5 minutes (**a-c**) and 15 minutes (**d-f**) respectively. After 15 minutes' growth, a full coverage of monolayer graphene film at all positions can be formed due to the self-limited growth mechanism on copper foils.

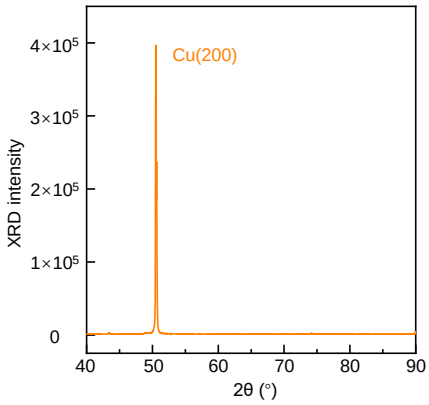

Figure S9 | XRD 2θ spectrum of the original Cu foil before thermal treatment.

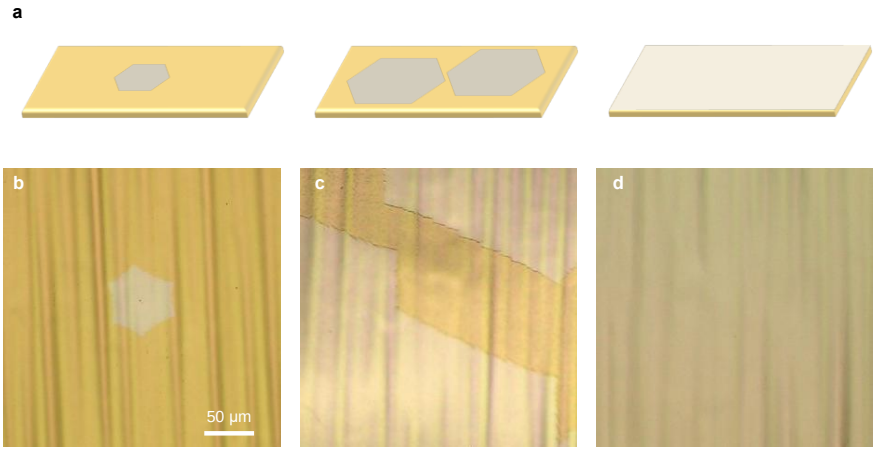

Figure S10. a, Illustration of the growth process of graphene film. **b-d**, Optical images of graphene grown on Cu(111) at 1 min (**b**), 10 min (**c**) and 15 min (**d**) respectively. Epitaxial growth of graphene can be strongly modulated by the lattice structure of substrates. Due to the symmetry matching between Cu(111) and graphene (C_3 rotation symmetry) and their small lattice mismatch (4%), graphene domains tend to be unidirectionally aligned on Cu(111) surface, and will finally seamlessly stitch to a uniform graphene film (**b-d**).

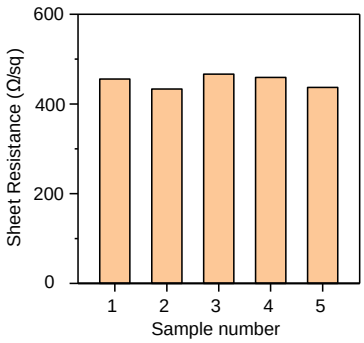

Figure S11 | Room temperature sheet resistance of the graphene films. The average sheet resistance of the graphene film is ~450 Ω/sq.

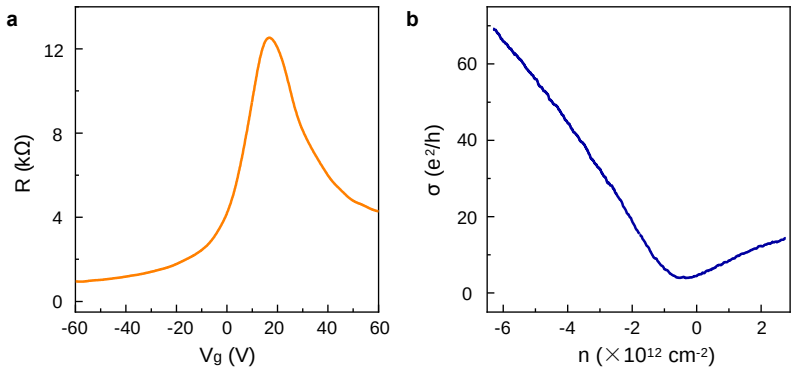

Figure S12 | Transport measurement of the transferred monolayer graphene film. a, Resistance as a function of back-gate voltage at 1.5 K. **b**, Conductance as a function of charge carrier density derived from (**a**).

Surface index	Surface energy (eV/nm²)	Surface index	Surface energy (eV/nm²)
111	8.1	211	9.4
100	8.9	221	9.2
110	9.9	311	9.6
210	9.91	322	9.0
310	9.92	332	8.9

Table S1 | Surface energy for 10 facets of Cu.