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 ($\Delta T/T = (I_{in}-I_{out})/I_{out}$).

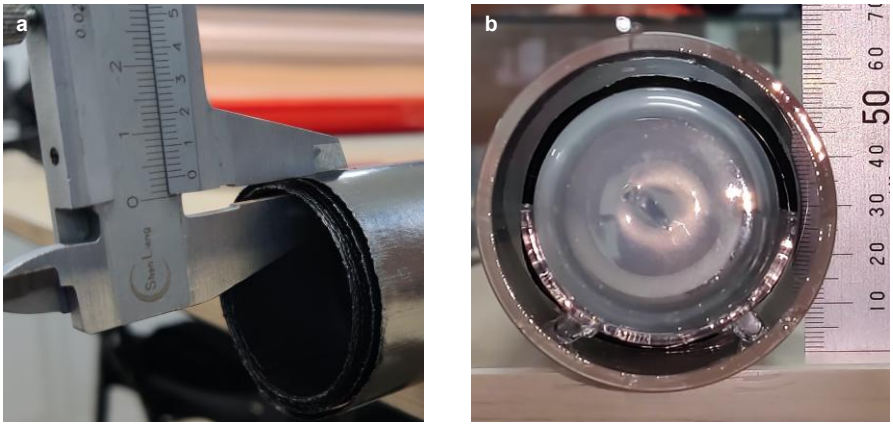

Figure S1 | a, Measurement of the gap size between Cu foil and graphite paper. **b**, Side view of the sample loaded into the quartz tube. 14 rolls of Cu foil (25 μm) and graphite paper (100 μm) in our "scrolled" structure had a space of 3 mm, thus the average gap size under the influence of gravity 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**).

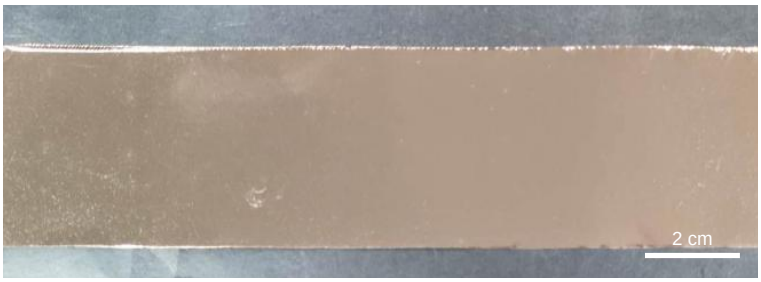

Figure S2 | Photograph of Cu foil on graphite paper after annealing at 1065 ℃ for 1 hour under a reduced atmosphere. The scrolled Cu-graphite structure we developed won't fuse and adhere together at the growth temperature as high as 1065 ℃.

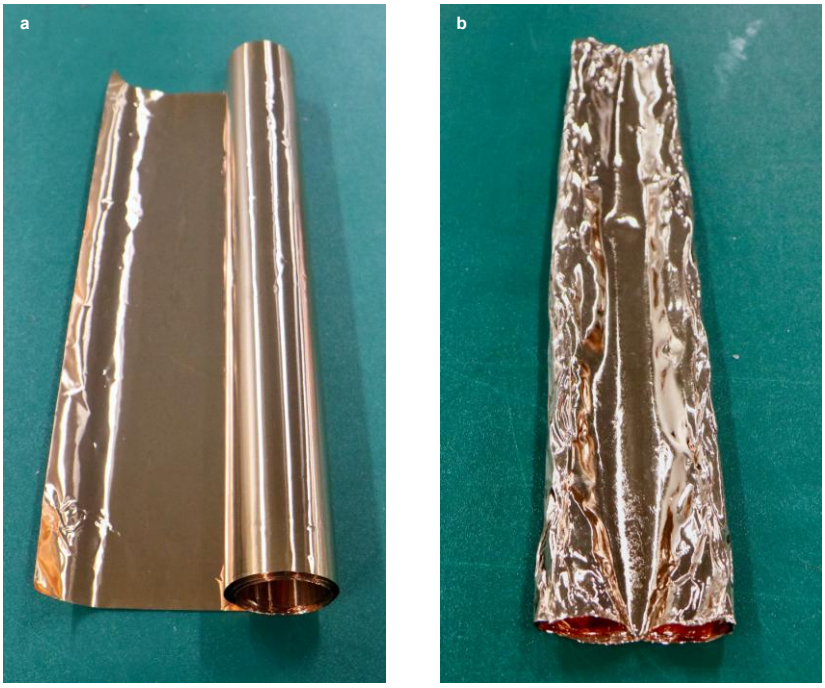

Figure S3 | The Cu scrolled structure without the graphite separator and inner quartz tube. a-b, Optical images of the scrolled Cu (200×39 cm^2) structure before (**a**) and after (**b**) high temperature annealing. After the same growth procedure as we used in the main text, the scrolled structure collapsed 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.

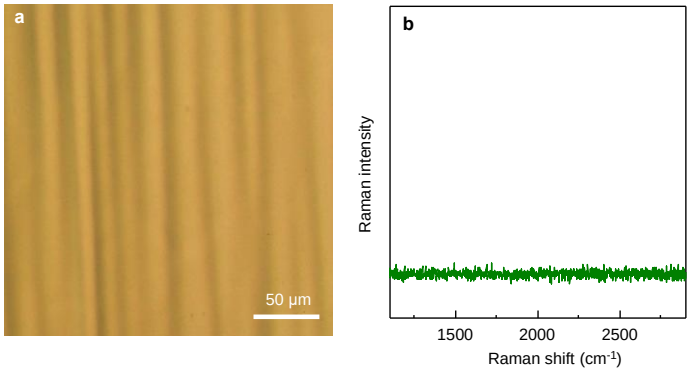

Figure S4 | Optical image (**a**) and Raman spectrum (**b**) of the Cu surface after the same graphene growth procedure without methane flow. The surface of the obtained Cu foil was clean and no graphene film was formed on it.

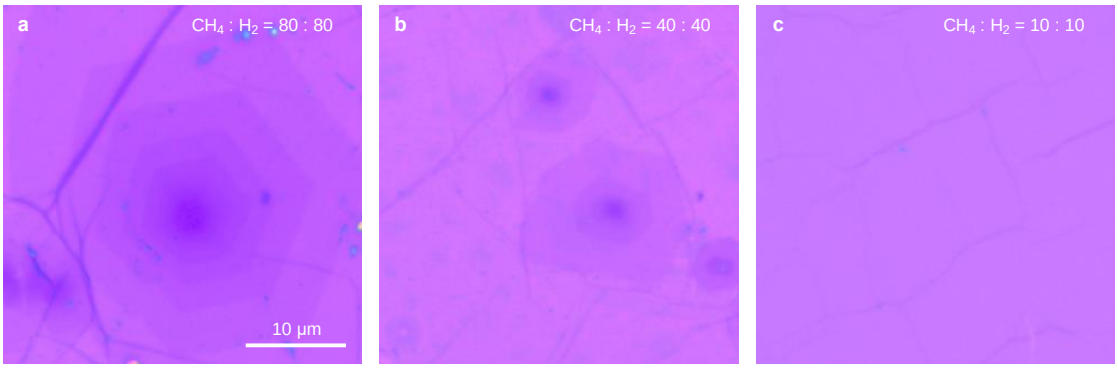

Figure S5 | a-c, Optical images of the transferred graphene films under different CH_4 concentration.

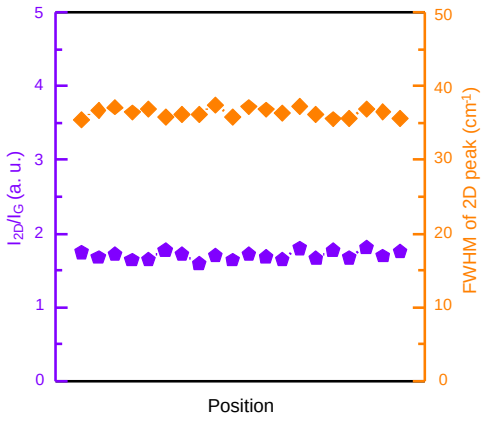

Figure S6 | Raman spectra of the graphene film at different positions in a large area. The small fluctuations in both the I_{2D}/I_G and the FWHM of 2D peak demonstrate that the graphene film has good homogeneity over a large area.

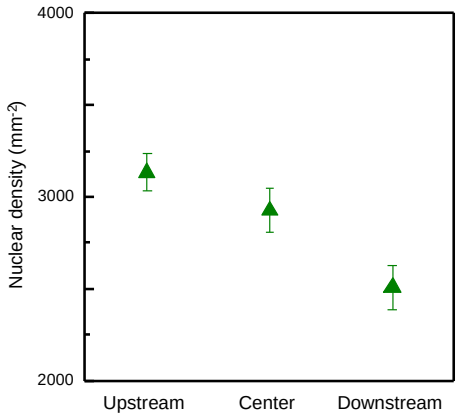

Figure S7 | The nucleation density of the graphene film after 5 minutes' growth at different positions. Due to the sufficient carbon supply, the nucleation density of graphene islands in the upstream region are higher than those in the center or downstream locations at the beginning of growth.

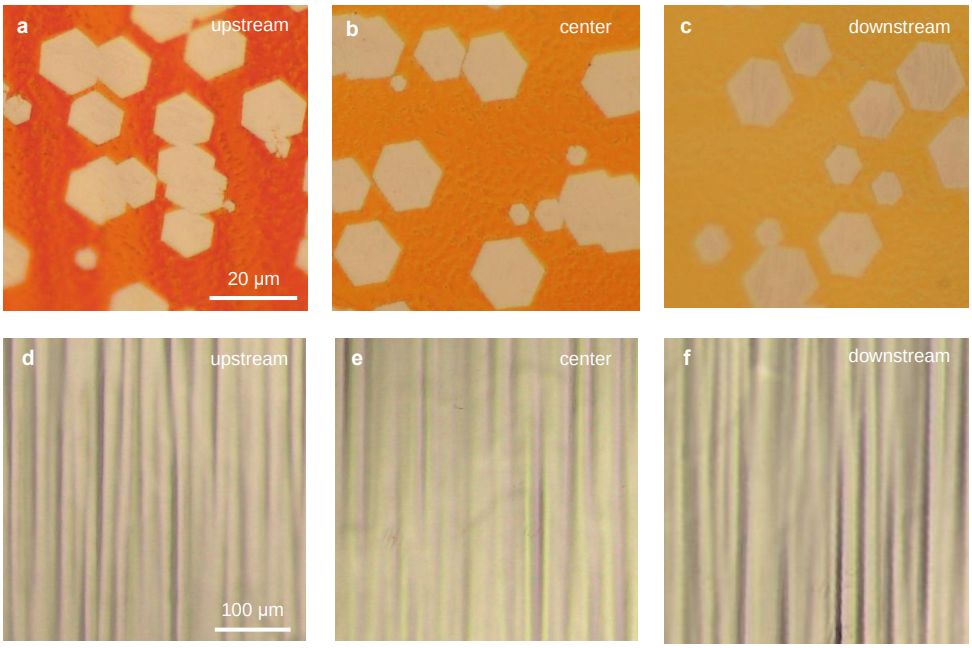

Figure S8 | Optical images of the graphene film grown at different position for 5 minutes (**a-c**) and 15 minutes (**d-f**) respectively. After 15 minutes' growth, a full coverage of monolayer graphene film at all positions can be formed due to the self-limited growth mechanism on copper foils.

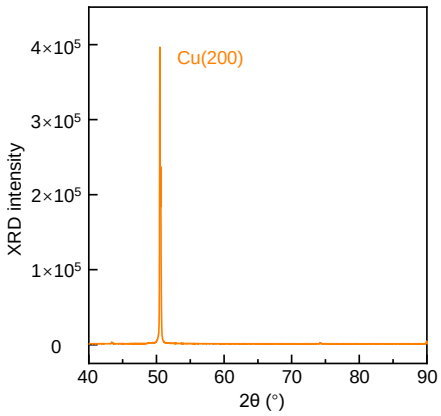

Figure S9 | XRD 2θ spectrum of the original Cu foil before thermal treatment.

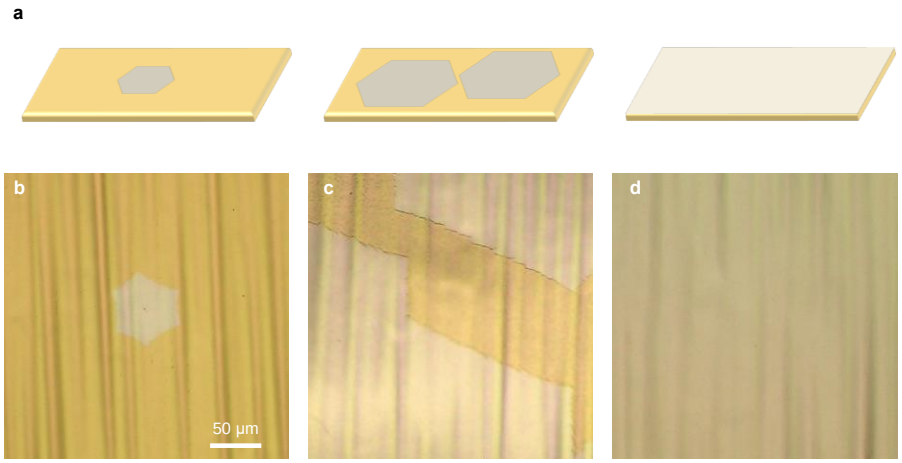

Figure S10. a, Illustration of the growth process of graphene film. **b-d**, Optical images of graphene grown on Cu(111) at 1 min (**b**), 10 min (**c**) and 15 min (**d**) respectively. Epitaxial growth of graphene can be strongly modulated by the lattice structure of substrates. Due to the symmetry 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**).

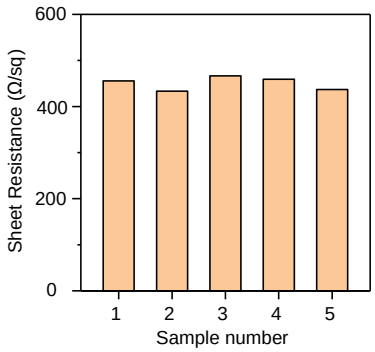

Figure S11 | Room temperature sheet resistance of the graphene films. The average sheet resistance of the graphene film is ~450 Ω/sq.

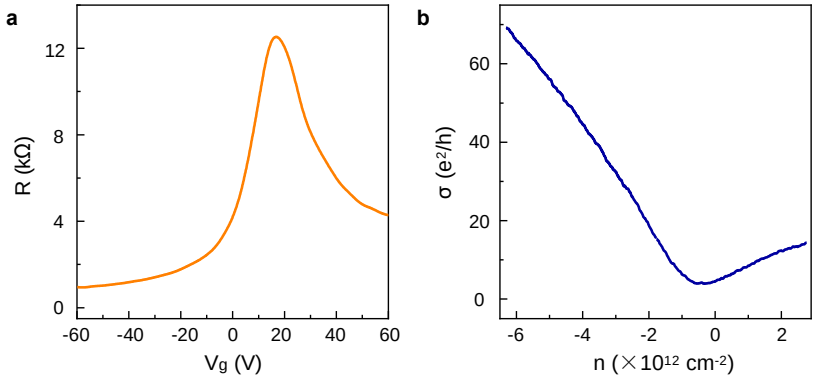

Figure S12 | Transport measurement of the transferred monolayer graphene film. a, Resistance as a function of back-gate voltage at 1.5 K. **b**, Conductance as a function of charge carrier density derived from (**a**).

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.