SUPPLEMENTARY INFORMATION

Exploring Mechanical Properties of Nanometer-thick Elastic Film through Micro-drop Impinging on Large-area Suspended Graphene

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SI1. Single-layer graphene growth — chemical vapor deposition

Before transferring process, the continuous single-layered graphene sheet is grown on copper foil, pretreated by electro-polishing method, then placed on a SiC coated graphite boat in a cold-wall rapid thermal annealing (RTA). There are 5 stages for the growing process which is sustained at low pressure (1 Torr), first, with 500 sccm Ar flow, ramping to annealing temperature within 5 minutes, annealing at 800℃ for 10 minutes, temperature ramped to growing temperature in 2 minutes, constant temperature to grow graphene sheet at 1000℃ for 20 minutes with gas flow H_2/CH_4 ratio of 5:2 (H_2 50 sccm, CH_4 20 sccm) accompanied by 500 sccm Ar flow, and finally fast cooling to temperature by switching off the heating lamp for 15 minutes. Fig. S1a is the photo of copper foil on which graphene is grown. The images from optical microscope of single-layered graphene sheet, transferred onto SiO_2/Si substrate by standard bubble method[1], observed from optical microscope and scanning electron microscope (SEM) are shown in Fig. S1b and c, respectively, revealing that the graphene grown under the condition is continuous film. Furthermore, the measurement for thickness through atomic force microscope (AFM) for mono-layer graphene is approximately 0.58 nm, Fig. S1e, the profile along boundary of graphene on the substrate, whose image from AFM is in Fig. S1d. Theoretical calculated thickness of graphene is 0.33 nm[2,3], indicating that there is some contamination between graphene and the substrate.

Number of graphene layer can be indicated from Raman spectroscopy, inelastic scattering of electrons excited by laser whose energy provides electronic transition in phonon, and the characteristic Raman peaks of graphene for 532 nm excitation laser are D, G and 2D around 1350 cm^{-1}, 1580 cm^{-1} and 2680 cm^{-1} represents disordered structure, strong C-C bonding and perfection in structure. For single layer graphene, the ratio of intensity of 2D to G peak is approximately 2 and the full width at half maximum (FWHM) of symmetric 2D peak is about 33 cm^{-1} [4–6]. In Fig. S1f, the intensity of 2D peak divided by G peak is 2.33, with symmetric 2D peak of FWHM 33 cm^{-1}. Combination of the experimental results measured above, it can be indicated that the graphene grown under specific parameters for the standard CVD procedure is continuously-distributed single-layered graphene.

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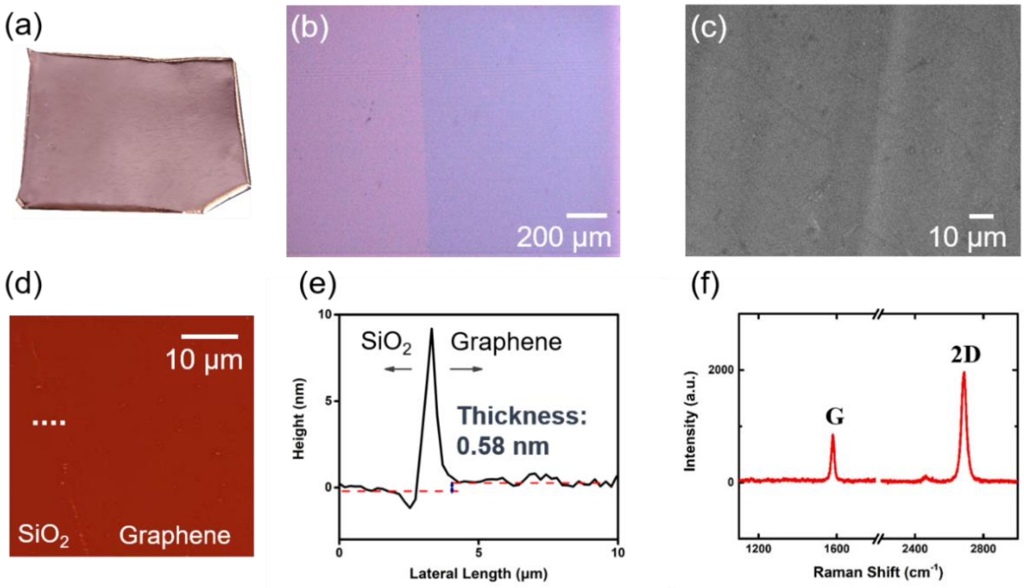

Fig. S1 (a) The photo of graphene-grown copper foil. (b) The image from optical microscope of CVD grown graphene transferred on SiO_2/Si substrate, indicating that the graphene is single layer and fully covered. The image presented the boundary of graphene sheet transferred onto the substrate; on the left and right is the substrate, SiO_2/Si, and graphene respectively. (c) The image of scanning electron microscope (SEM) of graphene grown on copper, and graphene layer is a continuous sheet. (d) The image measured by atomic force microscope (AFM), indicating the morphology of the graphene surface. (e) The profile along white line in (d), which is the boundary between graphene and the substrate, and the thickness of single layer graphene is 0.58 nm. (f) Raman spectrum of single layer graphene, the ratio of intensity of 2D to G peak is 2.33 and FWHM of 2D peak is 33 cm^{-1}, consisting to the characteristics of single layer graphene.

Preparation of LSG on holey substrate

A hole with 400 μm in diameter is drilled, by laser, through the 100 μm thick copper substrate whose schematic diagram along with dimensions is illustrated in Fig. S2a, and the photo taken by camera of holely copper substrate before and after transferring graphene is in Fig. S2b and c. The graphene sheet on the copper substrate is black, and the insight of Fig. S2c is the image of LSG from optical microscope with magnification 10X. There is a hole on each substrate, and thus it is more effortless to align micro-drop on the suspended graphene.

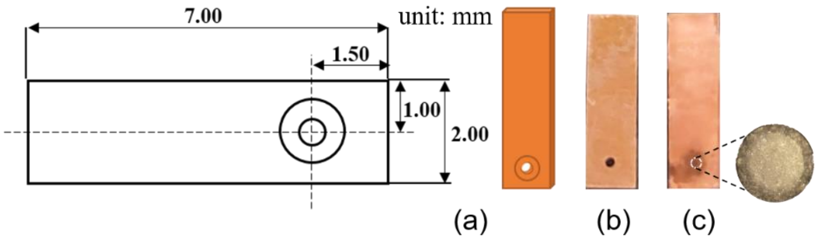

Fig. S2 (a) The dimensions, and schematic diagram of holely substrate made of copper (b) Picture taken by camera of the holely substrate, and after transferring graphene onto the holely substrate, the graphene would be suspended whose photo is in (c) with insight to be the OM image of LSG with magnification 10X.

LSG fabrication method

Fig. S3 illustrates transferring method of LSG. The graphene/Cu, Fig. S3a, cut into $0.5\ cm \times 0.5\ cm$, is then placed into the copper etchant (Sigma-Aldrich, 667528) to etch copper foil for about 10 minutes, Fig. S3a, so the graphene sheet is floating on the copper etchant, scooping up the graphene sheet from the copper etchant by a glass slide, then plunging it into deionized water (DI water) vertically and gradually for several rounds to confirm the cleanness of graphene sheet, and then whole graphene sheet would float on the DI water to dilute copper etchant on graphene sheet, then to another bulk of DI water in order to clean graphene, asFig. S3b-d illustrates. The graphene on either copper etchant or DI water can be recognized by eyes owing to 2.3% optical absorption of graphene.

Since single-layer graphene cannot be suspended over the hole with diameter 400 μm without any supporting layer, the graphene layers are stacked at least 4 layer to transfer onto the substrate. The method to stack graphene layers is illustrated in Fig. S3e, scooping up the graphene, floating on DI water, with the copper foil graphene grown on to stack bi-layer graphene, and then placed above the heater to dry, Fig. S3f. Next, redo Fig. S3a to Fig. S3f to stack multi-layer graphene; after the copper foil is etched away, multi-layer graphene was floating on the copper etchant, scooping up multi-layer graphene by slide glass, and moved downward into the DI water several rounds, Fig. S3h-k, and multi-layer graphene floats on the surface of DI water. Finally, scoop multi-layer graphene onto the holey substrate. By moving substrate upward gently and steeply, Fig. S3l, and placed the LSG target, above the heater to dry the graphene layer, illustrated in Fig. S3m. Whether graphene can still be suspended over the hole relies on the evaporation rate and surface tension of liquid; the free-standing graphene would be deformed downward since the force rising from the water evaporation and thus, resulted in rupture of free-standing graphene[7]. For the targets of PMMA coated graphene, the fabrication process is identical except that graphene/Cu would be substituted into graphene/Cu after coating progression whose thickness can be precisely controlled.

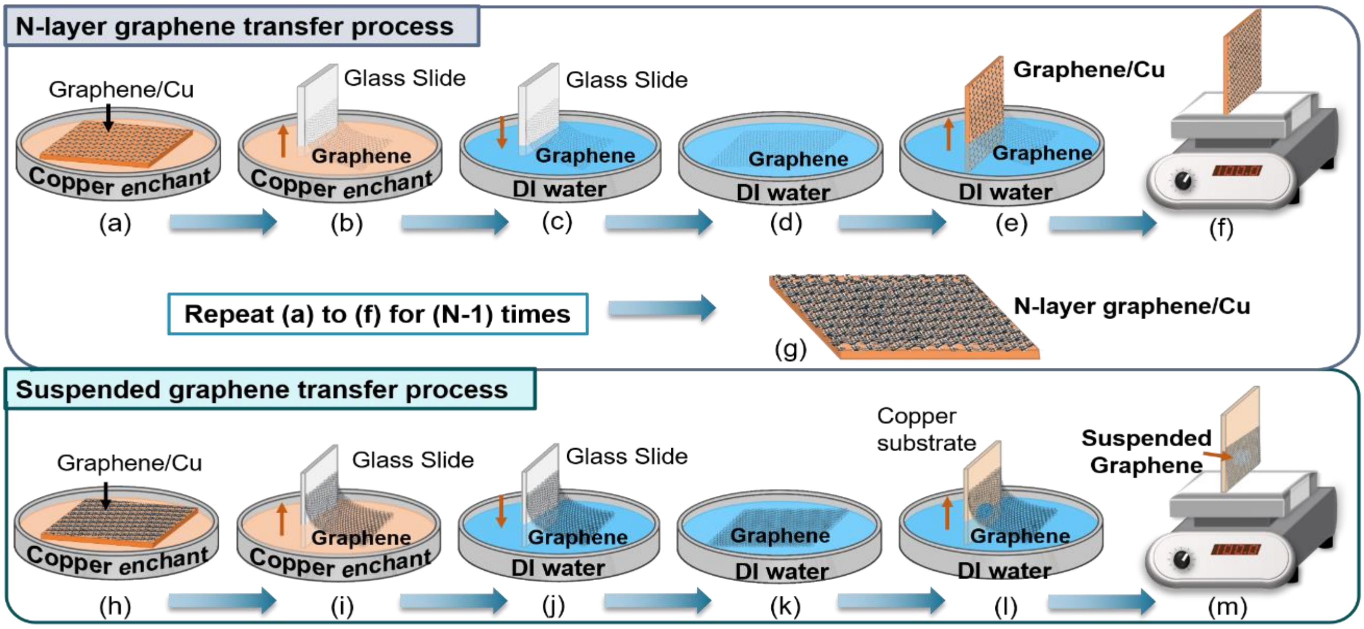

Fig. S3 Transferring method of LSG. (a) Place the mono-layer graphene/copper onto the copper etchant, so the copper foil would be etched, and the graphene layer would float on the fluid. (b- d) Scoop up single-layer graphene with glass slide from the copper etchant to DI water, graphene floating on the surface of DI water, then to another bulk of DI water, to clean graphene. (e) To stack multi-layer graphene, single-layer graphene floating on DI water is fished up by the copper foil on which the graphene is grown. (f) Keep the graphene/copper vertical on the heater to bake the graphene on the copper to remove moisture from graphene. Repeat process (a) to (f) for several times to precisely control the number of layers of graphene on copper foil, (g). (h-k) The multi-layer graphene/copper is placed on copper etchant to etch the copper underneath the graphene and then multi-layer graphene is scoped up by glass slide from copper etchant to DI water, similar to previously mentioned process (a-d). (l) Fish up multi-layer graphene floating on DI water onto the holey substrate (m) Place the suspended graphene target above heater to dry the free-standing graphene sheet.

Liquid droplet impingement experiment

The ink-jet printing system, jetlab® 4xl & xl-A - Larger Area / Improved Accuracy Printing Platforms, is purchased from MicroFab, consisting of the ink-jet micro-dispenser, driving electronics, backpressure control & observation camera, electrically controlled stage, illustrating in Fig. S4. The inkjet piezo dispenser consisting of a glass tube with diameter 50 μm, bonded by poled radially piezoelectric element coated with metal electrode, is actuated electrically by applying voltage signal waveform to control pressure wave within the nozzle to dispense the liquid at stable speed. The stability and properties of the droplet is observed by strobing LED lit by a pulse synchronized with the drop generation in the opposite of the observing camera focusing of the dispensed drop. An adjustable delay between the actuation pulse for the drop generation and the LED pulse freezes the drop along its path for observation, and the diameter of the drop can be measured.

The dynamic of impinging process is observed by the high-speed camera of fps to be 10000, with serial number SN23990 E310L purchased from PHANTOM, AMETEK's, and the high-speed camera is anchored on the alignment stage with inclination angle 15° for easier observation of the suspended graphene. The motor controls the stage of the micro-dispenser motion vertically and the stage of the suspended graphene target moves in planar direction. The desired position of the drop to dispense is first aligned by the infrared microscope at fixed distance from the dispenser, and then the calibration is conducted through the difference of the desired position and the actual position of dispensed droplet.

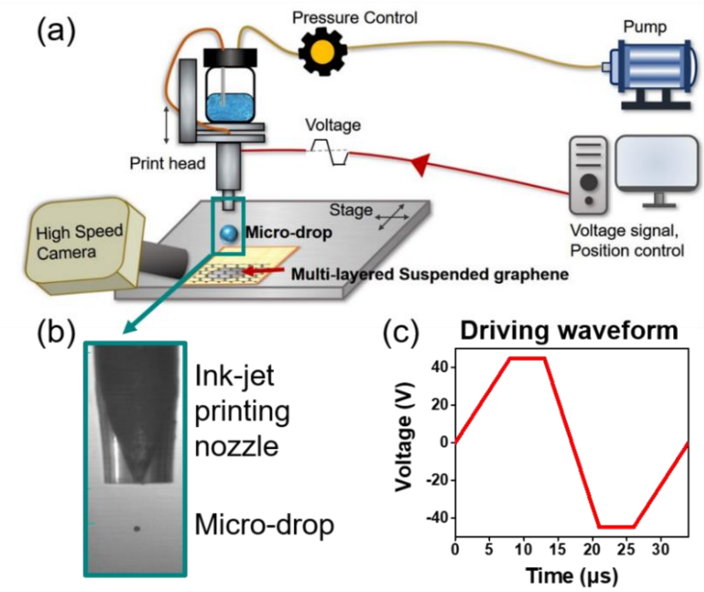

Fig. S4 (a) Schematic diagram of the drop impingement experiments. (b) Photo of the droplet dispensed from the nozzle captured by the camera of the inkjet system. (c) Driving waveform output to the nozzle.

Fracture of suspended graphene

The fracturing process of thin film is described by the multi-layered suspended graphene penetrated by μ-bullet at ultrasonic speed, resulting in localized and very–high–strain-rate tensile deformation[8], and the illustration is presented in Fig. S5a. As the jet impacts, the elastic wave propagates radially at speed of sound in graphene, $c_{||} = 22.2\ km$, (step 1,2) and the suspended graphene deforms in cone due to radial gradient of the force with base radial speed v_c. The cracks are developed at the region of impact from the tangential tensile stress (step 3), and then propagate outward in the radial direction (step 4). The momentum transformed from the jet results in folding of petal and some of petals are dragged out by the PEG droplet because of its hydrophilicity while the elastic extension of the membrane is relaxed along the radial direction (step 5). The maximum crack distance is defined from the average of the vertex of the fractured area to the center of impact as L_{max}, the yellow line in Fig. S5b and c, and the yellow circle in the center is the area of the jet impinging. The L_{max} for 4 layer suspended graphene of diameter 400 μm and 250 μm are 110.82 μm and 76.95 μm, respectively, indicating that conic deformation of 400 μm is larger than 250 μm before fractured. Furthermore, from the insight of cracks, right images in Fig. S5; the crack at the vertex of 4 layer suspended graphene of diameter 400 μm is wider and shorter than that of 250 μm, which are fine cracks, and the graphene on the surface wouldn’t crack completely while there is dystomic beneath the surface layer. Both the evidence of the area of cracks and the fracturing area confirms that 4-layer suspended graphene of larger diameter experiences larger deformation before it breaks, that is, softer than the one with smaller diameter.

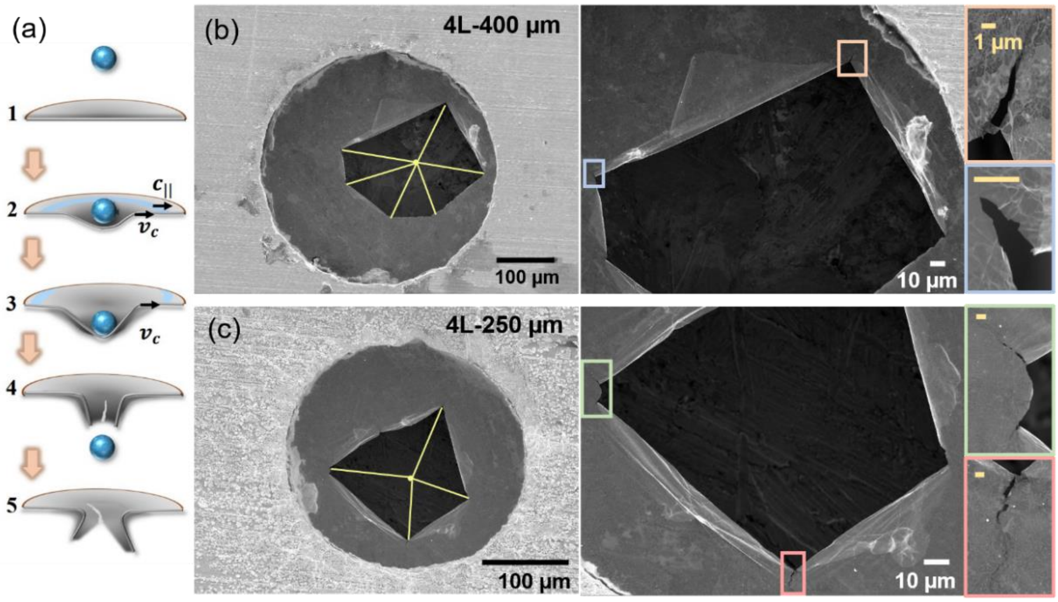

Fig. S5 (a) The fracturing process of then thin film. (b, c) The SEM images of fractured area of 4 layer suspended graphene of diameter 400 µm and 250 µm, and the images on the right is the zoom in images of the cracks and pedals, whose frames are colored as the rectangles labelling the area of insight.

Raman spectrum of LSG

To measure the Raman spectrum, the sample is placed under the optical microscope, and the laser spot of width 1.0 µm can be recognized simultaneously. By adjusting the stage of the sample, the Raman spectrum of the desired area can be measured. The internal strain and structural information of suspended graphene were analyzed from the spectral of a self-mounting micro-Raman spectroscopy (µ-RS) equipped with laser of wavelength 532 nm with spatial resolution 1.0 µm and spectral resolution 0.5 cm^{-1}.

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