Electronic Supplementary Information (ESI)

3-D Conformal Graphene for Stretchable and Bendable Transparent Conductive Film

Xuefen Song1,2†, Jun Yang1†, Qincui Ran1, Dapeng Wei 1†, Liang Fang2, Haofei Shi2, and Chunlei Du2

1 Chongqing Key Laboratory of Multi-scale Manufacturing Technology, Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, PR China.
2 State Key Laboratory of Mechanical Transmission, College of Physics, Chongqing University, Chongqing, 400044, PR China.
†† These authors contributed equally to this work and should be considered co-first authors.

1. Experimental section

1.1 Preparation of Graphene Samples.

First of all, the copper foils with periodic micro structures were prepared by lithography and wet etching, keeping the depth of the structure for ~2μm and the period of the structure for ~20μm, then cleaned for use. We selected a tube-style chemical vapor deposition(CVD) system to deposit graphene(Gr) films on cleanly structured copper foils (S-Cu) substrates (Gr/S-Cu) using mixture gas of hydrogen (purity:99.999%) and methane (purity:99.999%). Under atmospheric pressure, mixture gas of 25% methane in hydrogen was introduced into the chamber after substrate temperature (T) increased up to 1000 °C. The graphene growth maintained for 10-30 minutes, and then the samples were cooled to room temperature rapidly.

1.2 Preparation of Conformal Graphene.

The PDMS polymer was prepared by mixing a silicone elastomer base with a curing agent with a ratio of 10:1. Then the as-prepared PDMS was coated onto the surface of Gr/S-Cu, and was dried on the hot plate at 80 °C for 180min. A aqueous solution of ferric nitrate solution (Fe(NO₃)₃) was used to sufficiently dissolve S-Cu without leaving any residue overnight at room temperature. After cleaning, the perfect graphical surface structure was copied from micro-structured copper wafers, and presented in the inverted PDMS/Gr, which was named as conformal graphene (CGs/PDMS).

1.3 Characterization.

The as-grown samples were directly characterized by a Renishaw in Via Manual WiRE3.4 Microscopes Raman Spectrometer with the laser excitation energy of 532nm. Atomic Force Microscopy (AFM) characterization of structured copper foils and CGs were conducted under a Dimension Icon equipment of Bruker Corporation. Transmittance of CGs, PDMS and CG/PDMS were measured by Ultraviolet spectrophotometer. The sheet resistance of CGs was tested under a self-assemble electrochemical workstation system at ambient temperature. The micro-photographs were got by an electron microscope.
2. Figures

Fig. S1 The optical microscope images of large-scale graphene. (a) Conformal graphene film grown on structured copper wafers, (b) Conformal graphene film transferred on transparent and flexible PDMS. The both images are the magnifying LOGO in Fig. 1b and 1c.

Fig. S1 shows completely inverted LOGO patterns on Fig. S1a and Fig. S1b. The distinct patterns on Fig. S1b shown on the surface of CGs/PDMS suggest the integrality and advisability of this conformal transfer method.

Fig. S2 The SEM images of large-scale graphene (a) grown on structured copper wafers and (b) transferred on transparent flexible PDMS.

The consistent micro-patterns on Fig. S2a and Fig. S2b mean that it is a perfect and practical transfer method for the production of CGs.
Fig. S3 Transparency of large-area CGr layers transferred on PDMS, the blue, red and black lines represent the transmittance of CGr/PDMS, structural PDMS substrate and relative CGr, respectively.

Fig. S4 Electrochemical workstation electrical measurement on conformal graphene films shows the line function relationship of current and potential (I-V).

The typical I-V characteristics plots are shown in Fig. S4. It is found that the current increases linearly with voltage from 0 V to +5 V, which could be used to estimate the conductivity of graphene films.
Fig. S5: Resistance (black line) and Gauge Factor (blue line) of a 1×1 cm² CGr film on PDMS substrate stretched along the x direction. (a) monolayer CGr, (b) 2 layers CGr, (c) 3 layers CGr and (d) few-layer CGr correspond to growth times of 2, 5, 10, and 20 min, respectively.

Fig. S5 shows the strain tension and strain sensitivity of the CGr/PDMS with different numbers of stacked layers (1, 2, 3 and few) on longitudinal condition, using the instant resistance and Gauge factor, respectively. For the stretching test on longitudinal condition, with the increasing numbers of stacked layers, CGr/PDMS show clearly increased strain tension on the black lines. The instant resistance shows a straight line-like type on the front half part of the strain tension for 0-10%, 0-20%, 0-20% and 0-40% of 1, 2, 3, and few layers CGr/PDMS, respectively. And the remaining instant resistances of four samples on the latter part of their corresponding strain tension show zooming trends with increscent resistance interval. However, strain sensitivity (blue lines) of the thickening of CGr express inverse rules. The opposite trend of resistance and Gauge factor on Fig. S5 reveal that these stacked layers of graphene films were another crucial factor for the stretching capabilities of 3D conformal samples. The reason for this case: compared with monolayer sample, on the same tensile tests, the thicker graphene films exhibit greater extensibility but weaker contact response on tensile direction.